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Metallurgical Analysis and High Temperature Degradation
of the Black Chrome Solar Selective Absorber

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ABSTRACT

The characteristics of black chrome, a solar selective absorber, have been the object of much interest by solar materials scientists. For this study, a well known coating, Harshaw Chemical Company's "Chromonyx" was selected for detailed scrutiny of its properties and degradation modes when exposed to high temperatures. Both as-plated and annealed microstructural models were presented. Technical means used in this microstructural characterization were: scanning and transmission electron microscopy, Auger depth profiling hemispherical reflectance and energy dispersive X-ray analysis. From these results a physical metallurgical model for wavelength selective properties of the coating was developed. Thus, it was observed that black chrome degraded as Cr_2O_3 oxide particles grew and chromium depleted. This effect was pronounced in air and to a lesser degree in medium vacuum. Oxidation by preferential diffusion and outgassing which causes structural changes, may take place.

1. INTRODUCTION

Manufacturers and users have been interested recently in black chrome because of its temperature stability below 400°C and high solar selectivity. Scientists have been intrigued at the promise of

understanding this complex of this metal/metal oxide microstructure. Earlier work had revealed some of the morphology and chemistry of the coating¹⁻⁵ and it had also been determined that the coating would become unstable at temperatures above 500°C for very short exposure times,⁶ although it can be stabilized up to 400°C for very long times.^{5,7}

Some theoretical implications have been proposed but there is still a gap between the actual morphology and the theoretical.⁸⁻¹¹ One question raised here is whether different black chrome coatings have a related common morphology which exhibits characteristic optical selectivity or if there is a range of composition and microstructure which accounts for similar properties. Yet to be thoroughly understood are the effects of humidity both in air and evacuated tube (medium vacuum) environment (which model simplified operating conditions) upon the optical selectivity and stability of the coating. Also, the effects of thermal aging and stagnation events upon the stability of black chrome are very important. The work which follows concentrates upon these effects of high temperature upon the microstructure and reflectance properties for short times (100 hrs.), and includes a broad range of experiments performed which correlate as-plated and annealed microstructure to reflectance measurements.

2. EXPERIMENTAL TECHNIQUES

"Chromonyx" black chrome was electrodeposited on copper sheet samples, plated with dull "Nusat" nickel, by Harshaw Chemical Company (according to a specific procedure).¹² Black chrome plating was done at 216 mA/cm², 24°C for 2 minutes at 24 volts cathode potential. Identical samples were used in all cases with approximately 0.25 - 0.5 microns of black

chrome on 12 microns of nickel. Transmission electron microscopy (TEM) and Auger electron spectroscopic (AES) depth profiling techniques revealed the internal structure. Surface morphology and elemental chemistry were analyzed with the aid of scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). Hemispherical, near normal (20°) reflectance and an ambient emissometer determined changes in optical selectivity. Solar absorptance was determined by integration with respect to the Air Mass 1 solar spectrum. Calculations regarding infrared reflectance were determined also by integration in relation to 100°C black body spectra.

Annealing experiments were performed using two different procedures. Some of the samples were heat treated in dry air, annealed at 1 atmosphere in a calibrated tube furnace. An identical set of samples were vacuum annealed by heat treating quartz encapsulated specimens. The encapsulation process was done by pumping quartz ampules below 1.3×10^{-4} Pa (10^{-6} Torr), then backfilling with argon and resuming pumping. After this had been done twice, the ampules were sealed off under vacuum.

3. AS-PLATED MICROSTRUCTURE

Before detailing the annealing results, a discussion of the as-prepared microstructure is in order. The micro-rough surface usually associated with black chrome, Fig. 1a, arises from the underlying columnar nickel layer, Fig. 2a. The composition and internal microstructure have been shown in prior work.^{1,4,11} These results, including current work, are concluded in Figs. 3a, b, which show a model for the microstructure based on microscopic and chemical analysis. This microstructure is composed of agglomerated 0.05-0.3 micron size particles

with largely an oxide surface. Within these particles are 100Å (or less) metallic chromium grains. Use of AES⁴ and X-ray photoelectron spectroscopy¹¹ revealed that the volume ratio of metallic chromium to oxide increased with depth into the coating, becoming metal rich at or near the substrate interface. An intermediate region in the coating probably was responsible for high solar absorption. The metal rich and substrate region accounted for the desired infrared property reflectance.

4. SPECTRAL REFLECTANCE

Spectral reflectance for annealed black chrome is depicted in Fig. 4. Both integrated absorptance, a_j , and emittance, e_j , and total normal emittance are shown in Table I.

Table I
Integrated Absorptance, Emittance and Total Normal Emittance
(27°C) for Heat Treated Black Chrome

Treatment	Air			Vacuum		
	a_j	e_j	e_{tn}	a_j	e_j	e_{tn}
None as-plated	0.94	-	0.11	0.94	-	0.11
300°C, 100 hrs.	0.89	0.08	0.08	0.90	0.08	0.09
400°C, 100 hrs.	0.86	0.09	0.10	0.87	0.08	0.08
500°C, 100 hrs.	0.74	0.09	0.09	0.80	0.07	0.08

From this data, it was noted that with higher temperatures, solar absorptance exhibited instability and declined with aging. The coating degraded radically at 500°C in air and to a lesser degree in medium vacuum. A similar effect is noted and discussed elsewhere.⁶ The reflectance for 500°C vacuum annealed samples is characteristic of a two layer interference film. It was obvious that the presence of air enhanced degradation, which is to be expected. For the medium vacuum annealed samples, it was assumed that enough trapped oxygen in the coating was left to sustain oxidation. At 400°C in vacuum the reflectance results were very close to 300°C air data, so they can be plotted as one in Fig.4. Emittance increased initially, and then fell. This anomaly was noted elsewhere, too,⁶ where specimens were heat treated at higher temperatures. Vacuum annealed samples showed a slight decrease of emittance for increasing temperatures.

5. ELECTRON MICROSCOPY

The growth of particles on the surface coating was studied by means of the scanning electron microscope. There was an increase in particle size and surface roughness, including formation of crystalline Cr_2O_3 particles as verified by TEM, appearing at temperatures over 300°C, as shown in Fig. 1. In all cases, a porous network of particles, coarsening with longer times and higher temperatures, made up the surface structure. Then, at higher temperatures, erupted regions appeared, indicating mechanical weakness and probable outgassing. Although the average size of the oxide particles was 0.10-0.2 microns, oxide particles in excess of 1 micron can be seen at 400°C.

Transmission electron microscopy revealed continuous Cr_2O_3 grain growth as the higher temperature treatments progressed. In Fig. 5 may be seen a sequence of diffraction patterns for the corresponding temperatures. Diffraction patterns become more intense and spotty with higher heat treatments and in air annealed samples.

The primary phase identified in all of the experiments was Cr_2O_3 . According to diffraction pattern analysis and in situ heat treatments, there is an interesting sequence of events before the formation of crystalline Cr_2O_3 . Initially, amorphous halos and chromium rings are present; then lines of $\text{Cr}_2\text{O}_3(104)$ and $\text{Cr}_2\text{O}_3(110)$ at 2.666Å and 2.480Å appear for the long times and temperatures above 300°C. At higher temperatures of at least 400°C, all of the Cr_2O_3 rings appear, become spotty (Cr_2O_3 coarsening) and follow the sequence seen in Fig. 5. A spinel phase, NiCr_2O_4 , can be expected to form at higher temperatures. Representative Cr_2O_3 particle sizes (250Å average, 190Å mean) are shown in Fig. 6 for the most vacuum degraded sample, 500°C. Particle size is smaller for the vacuum annealed samples when compared to specimens treated in air. Crystallites of 450Å average size, are noted for 500°C, 100 hour air annealed specimens.

6. AUGER DEPTH PROFILING

More extensive information was needed about chemical composition variation with depth in order to formulate a model for black chrome degradation. Auger spectroscopy was performed simultaneously with Argon sputtering at 3kV. Figure 7 shows a representative profile. Two cases were seen here, 300°C and 400°C for 100 hours in air. There was marked change in the 300-400°C temperature interval in the

oxygen and chromium curves. The atomic ratio of 60:40 chromium to oxygen signified that the coating was principally Cr_2O_3 at 400°C , with some metallic chromium near the nickel interface. That is, assuming Cr_2O_3 is the only phase present. A similar result was noted for 500°C for 100 hours. With higher temperature heat treatment, the general trend was for the nickel/chromium interface region to move closer to the surface. The apparent movement of this interface may be caused from interdiffusion, outgassing products leaving the surface, and densification. Sputtering artifacts and slight sample variations are responsible probably for the variations in the interface location in Fig. 7.

7. DEGRADED MICROSTRUCTURAL MODEL

A schematic model was developed for the degraded black chrome structure from the combined information. Basically, the structure shown in Fig. 8 is for black chrome heated either in air at 400°C or in medium vacuum at 500°C for 100 hours. The microstructure consisted of large Cr_2O_3 crystalline particles and residual chromium.

CONCLUSIONS

The 100 hour treatments of black chrome showed minor changes below 300°C in air and 400°C in vacuum and pronounced degradation at 400°C and above in air or 500°C in vacuum. The chief mode of degradation appeared to be diffusion controlled oxidation of metallic chromium particles with the subsequent growth of Cr_2O_3 crystallites, for both medium vacuum and air samples. At high temperatures, diffusion of both chromium and oxygen may be enhanced by outgassing products, possibly

CO, CO₂ (as carbon is commonly found in nickel and chromium deposits¹³), or metallic hydrides. Their emanation acts to break up the coating, providing pathways for preferential diffusion. The process of nucleation and growth of Cr₂O₃ crystals depleted the metallic chromium. The absorber became more oxidized after long times at high temperatures.

More studies could be made. They include oxidation rate determination, outgassing analysis, finer mechanistic studies, humidity effects and thermal cycling research. Also, better control and understanding of black chrome deposition chemistry is of high priority to finishers and researchers.

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FIGURES

Fig. 1. Black Chrome examined by SEM at 20 kV after 1 hour annealing

(a) Typical surface structure for 27⁰-200⁰C annealing

(b) Structure for 400⁰C heat treated specimens

(c) Structure after 600⁰C anneal, showing oxide growth.

Fig. 2. SEM cross section of black chrome on nickel plated copper

(a) Etched nickel copper interface

(b) Highly etched region showing this black chrome layer

(c) Detail of black chrome layer and top surface.

Fig. 3. Schematic cross section of black chrome. Not shown is the presence of trapped water in the form of hydrated Cr₂O₃ on chromium hydride.

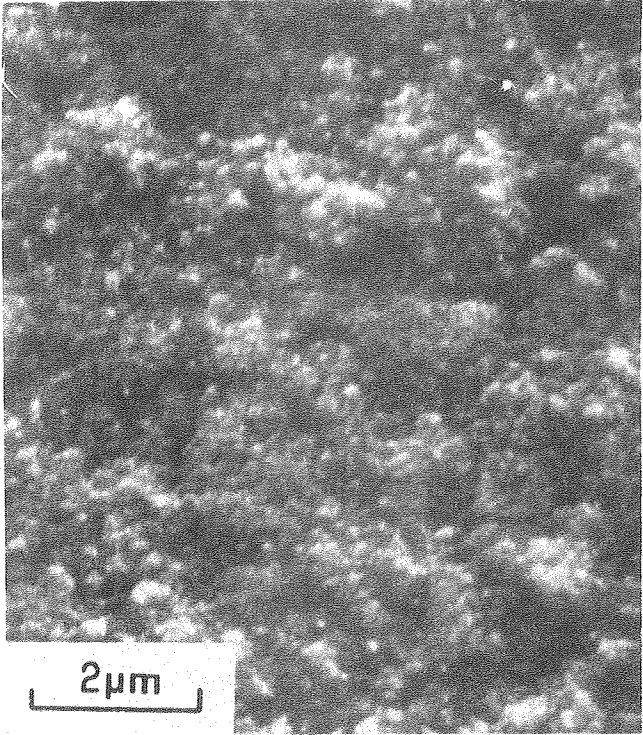
Fig. 4. Hemispherical spectral reflectance of black chrome annealed for 100 hours at various temperatures in air or medium vacuum (1.3 x 10⁻⁴ Pa).

Fig. 5. Electron diffraction pattern sequence for heat treated specimens. Increasing temperatures follow micrograph sequence a through d.

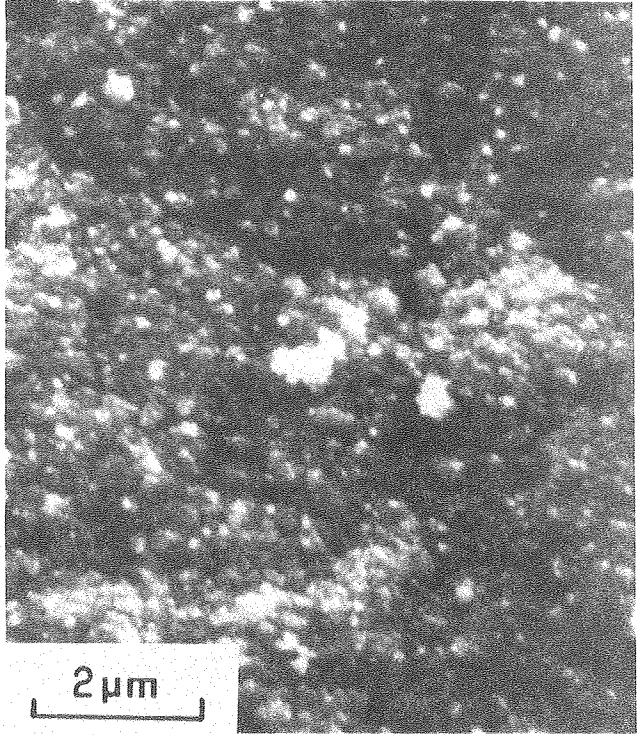
Fig. 6. TEM dark field electron micrograph with corresponding diffraction pattern for 500⁰C, 100 hour heat treated black chrome in medium vacuum. Growing chromium oxide particles are depicted as white spots.

Fig. 7. Auger depth profile for black chrome annealed at 300⁰C and 400⁰C in air. Argon sputtering rate was approximately 420 Å/min.

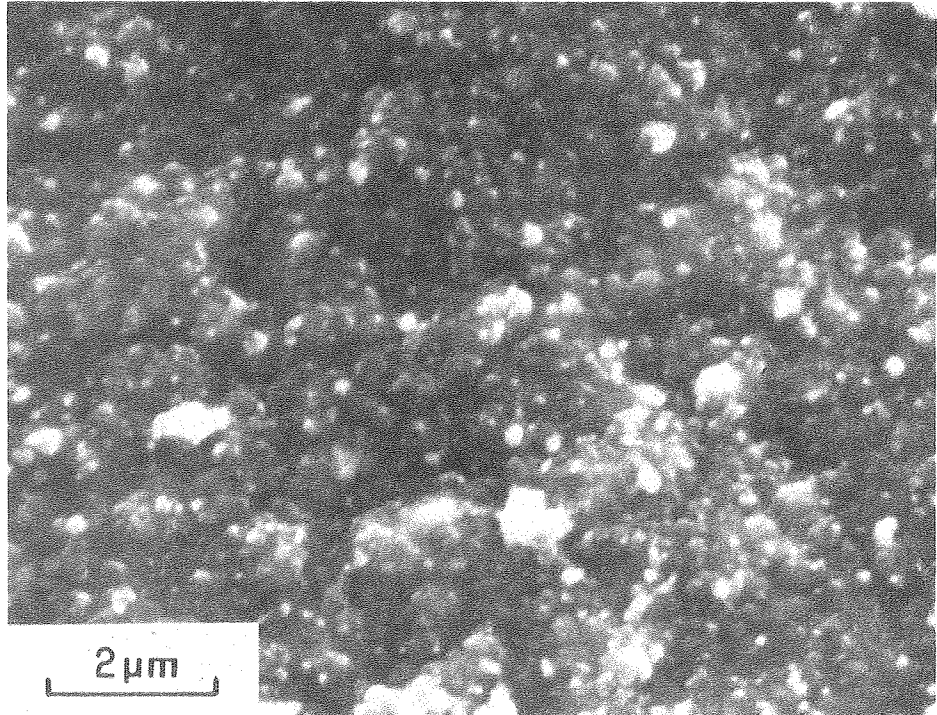
Fig. 8. Schematic microstructure of degraded black chrome after annealing at approximately 400⁰C in air or 500⁰C in medium vacuum for 100 hours.



a

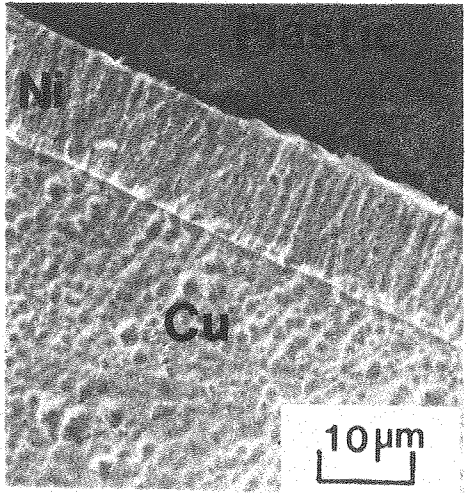


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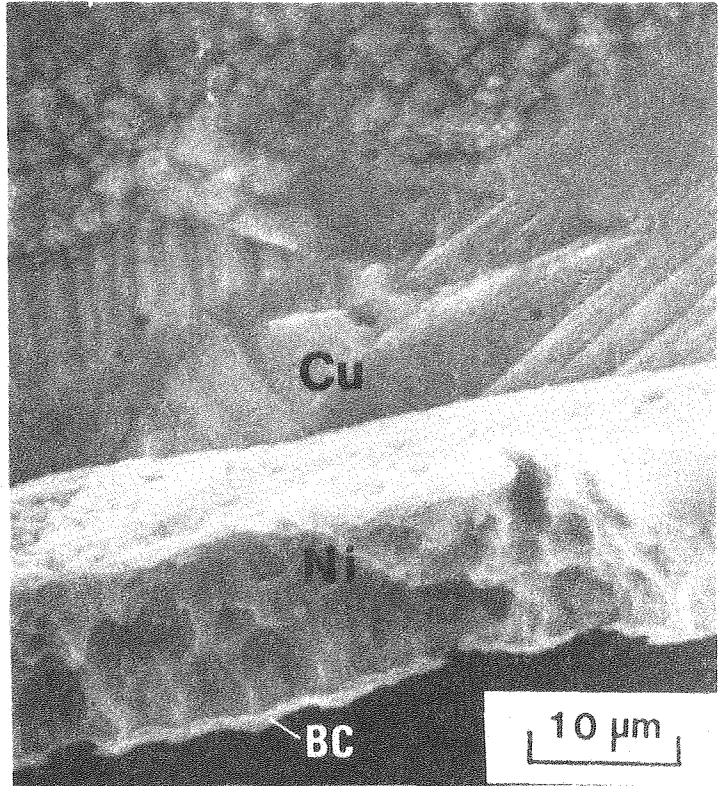


c

Fig. 1



a



b

c

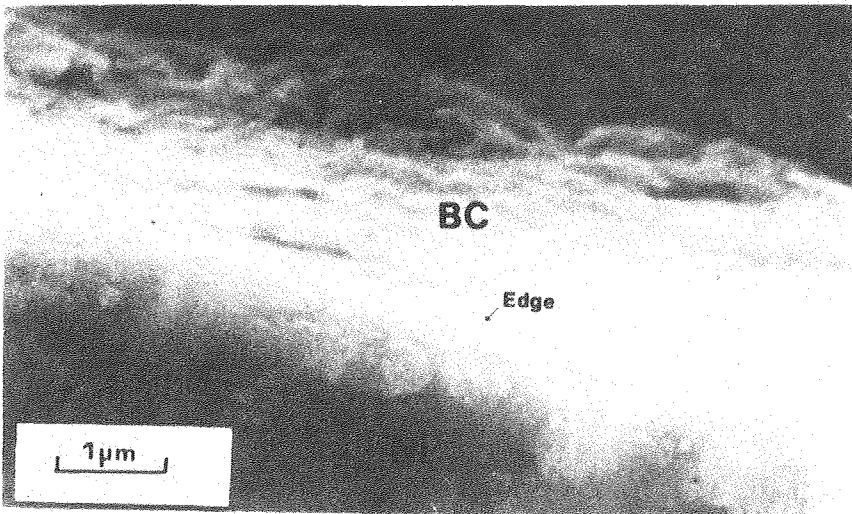


Fig. 2

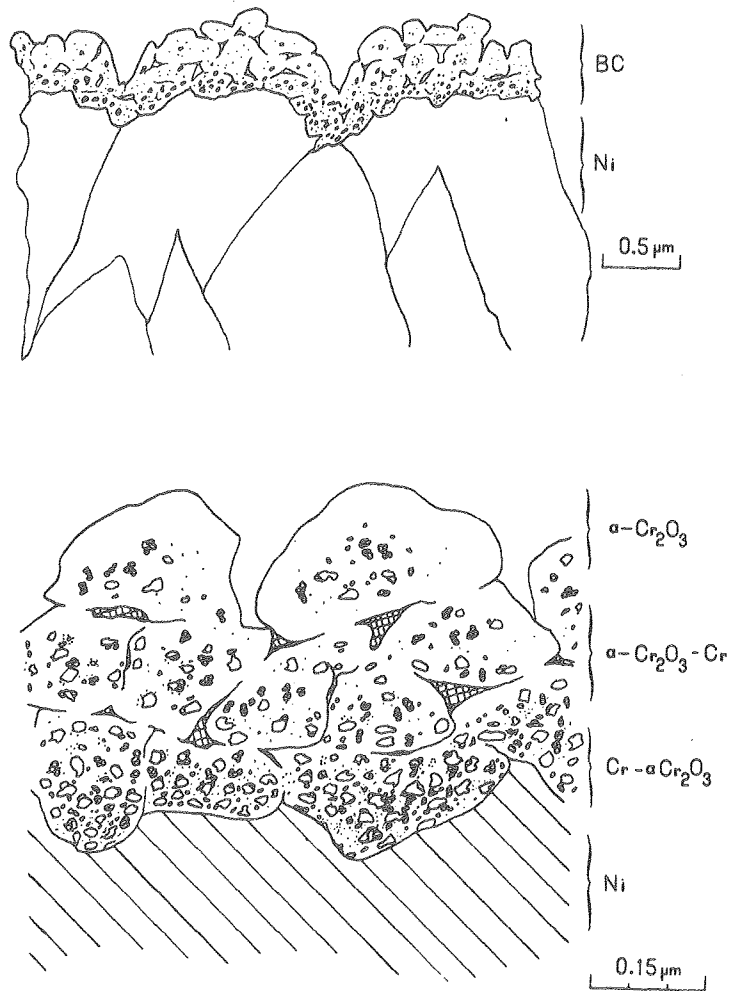
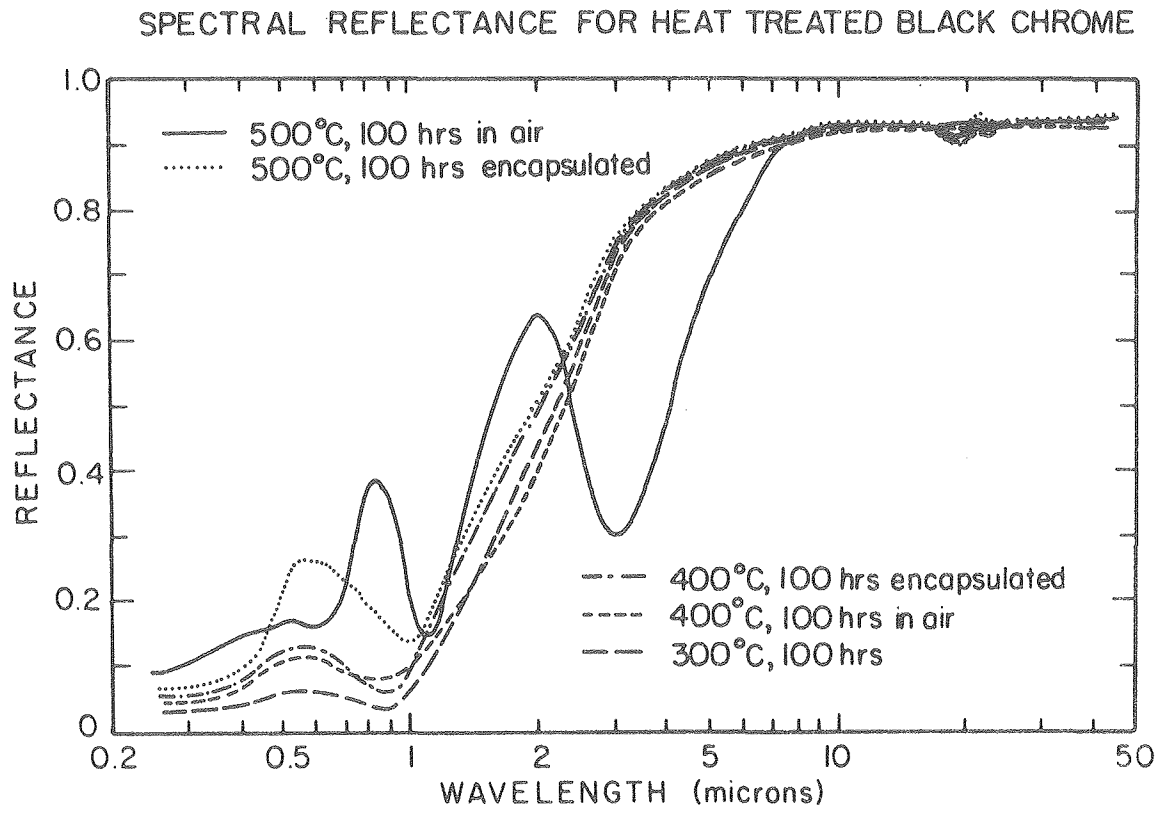


Fig.3



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Fig.4

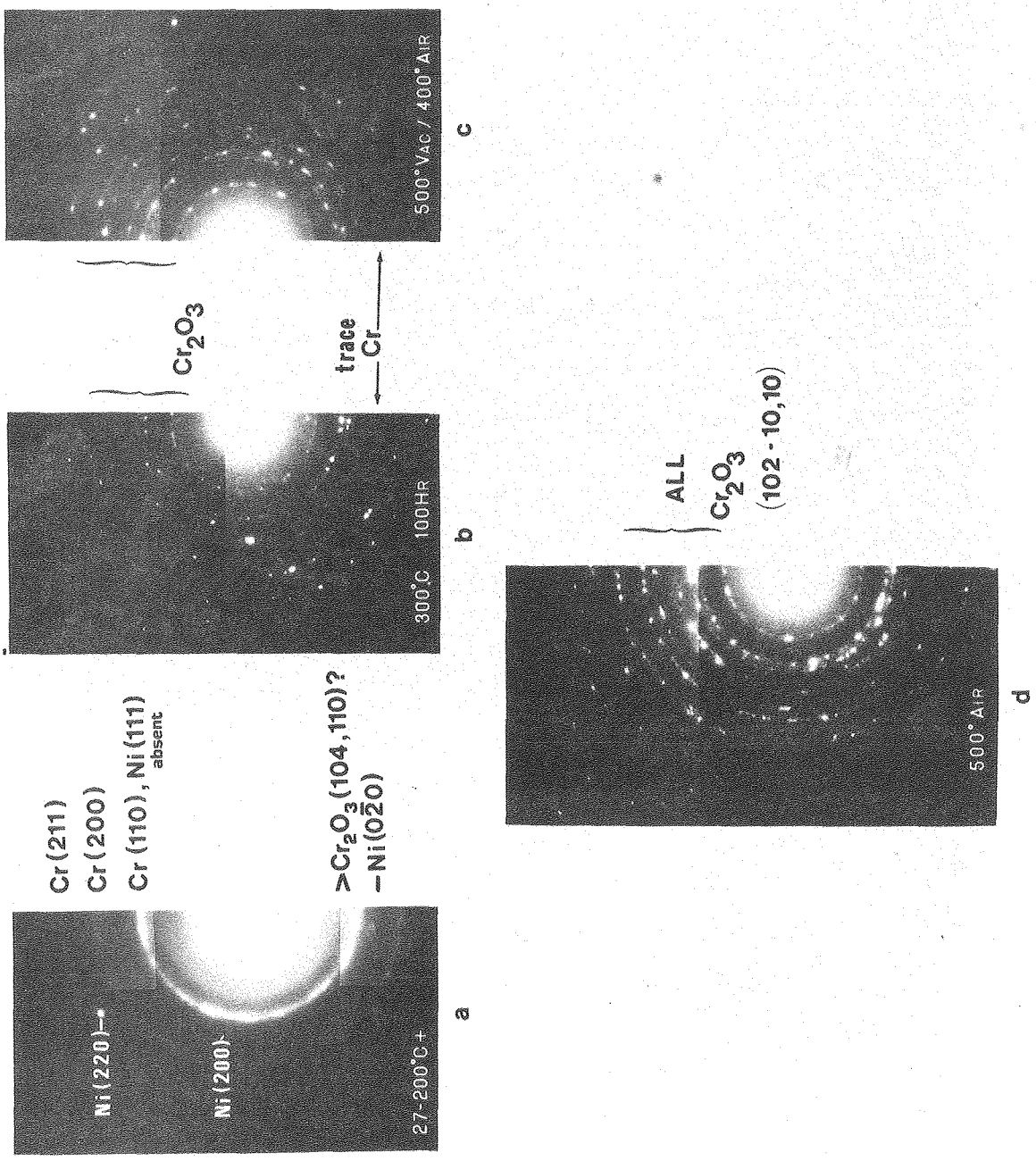
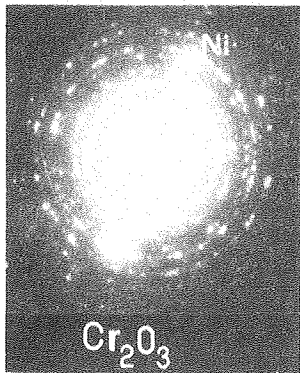
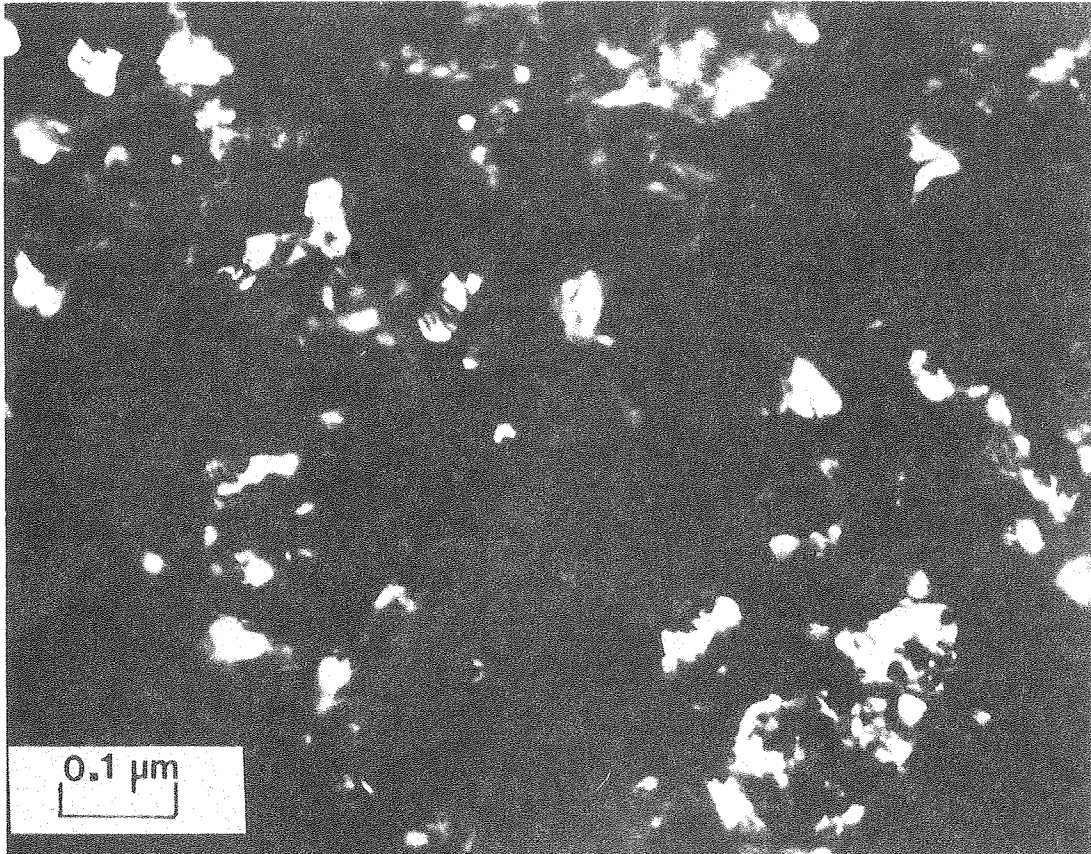
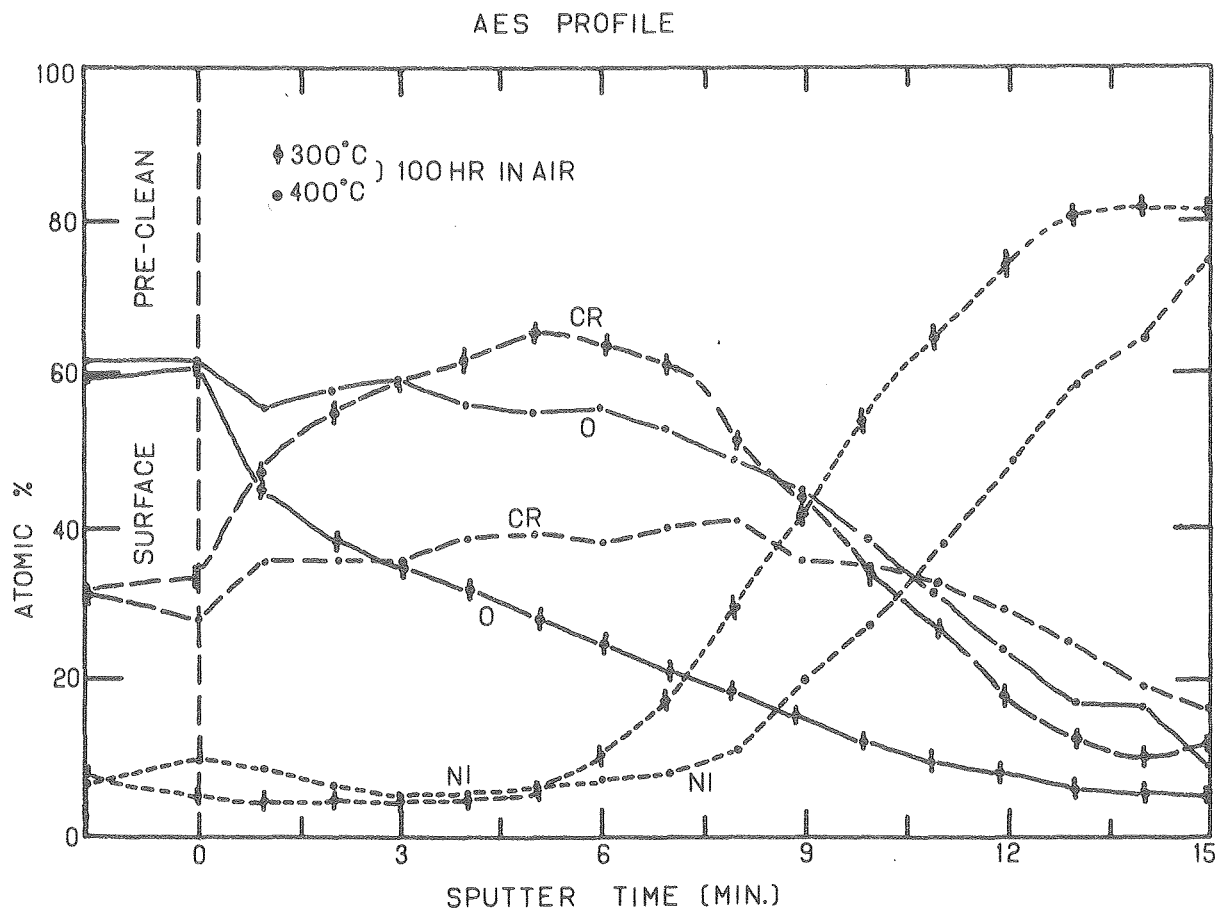


Fig. 5



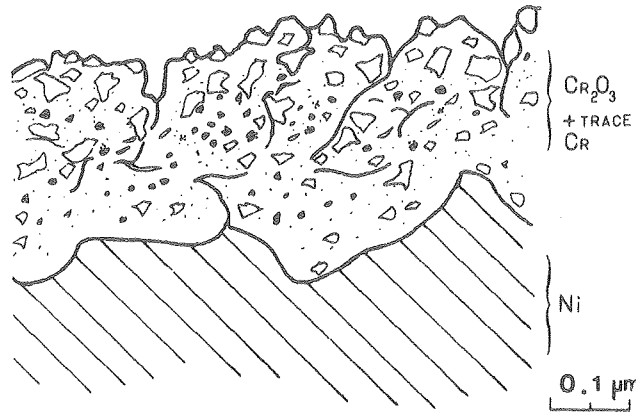
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Fig. 6



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Fig.7



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Fig.8