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# Morphological investigations of a textured black copper selective coating

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The microstructural investigations of a textured black copper selective coating are reported. These surfaces possess remarkably high initial absorptance $\alpha \simeq 0.97$ to 0.98 and emittance $\varepsilon_{100} \simeq 0.2 \pm 0.02$. These surfaces reveal a new sponge-like, porous, layered microstructure. They are made of loosely packed long and fine grains which appear randomly distributed. The copper grains are dispersed in a semiconductor oxide matrix. The spacing between these grains is of the order of solar wavelength. Also, these surfaces possess opulent solar selectivity and structural stability up to 250° C in air and under vacuum conditions.

## 1. Introduction

Spectrally selective coatings possess low reflectance in the solar region (0.3 to 2.5 $\mu$m) and a high reflectance in the infrared region (2.5 to 50.0 $\mu$m) [1, 2]. Black copper selective absorbers are one of the oldest selective surfaces known [1, 3–11]. An account of such surfaces developed by various oxidation processes has been discussed at length by Roos *et al.* [5], Sherer *et al,* [10] and Milgram [11]. The stability of these surfaces reported are < 200° C. In this paper morphological investigations of a chemically converted black copper selective surface which possesses good stability up to 250° C in air and vacuum are reported.

## 2. Experimental details

Black copper selective surface was prepared by chemical oxidation of a copper substrate in an alkaline bath (laboratory grade) of potassium persulphate ($K_2S_2O_8$) [12, 13]. The conversion was carried out in the temperature range 40 to 85° C for 5 to 12 min.

Microstructural studies of this coating were carried out using a Cambridge Stereo-10 scanning electron microscope operating at an accelerating voltage of 20 keV while transmission electron microscopy was performed using (JEM-200CX) model operating at 200 keV.

## 3. Results and discussion

Textured black copper selective surfaces were prepared using the chemical conversion technique, by oxidizing the chemically cleaned copper substrate in an alkaline bath of potassium persulphate. These surfaces possess excellent solar selectivity and are highly reproducible [13, 14].

Fig. 1 shows a scanning electron microscope of the textured black copper selective surface in question. These surfaces possess solar absorptance ($\alpha$) $\simeq$ 0.97 to 0.98 and emittance $\varepsilon_{100} \simeq 0.2 \pm 0.02$ [13, 14]. On inspection, it may be observed that the copper grains are randomly distributed in the oxide matrix. These are made of long and fine grains. The longer grains are $\sim$0.1 to 0.5 $\mu$m long and 0.04 to 0.1 $\mu$m diameter, while the finer grains are $\sim$0.08 to 0.1 $\mu$m. The separation between these grains is of the order of solar wavelength. It may be noticed that the predominant morphology consists of small-scale roughness. The loose packing of the grains in the top region is due to large void fractions causing a high degree of texturing.

Fig. 2 shows transmission electron micrographs of the intermediate regions: (a) bright-field image and (b) dark-field image. The two regions are seen in (a) as needle-like long grains, and in (b) as fine grains; the longer grains are $\simeq$0.09 to 0.5 $\mu$m long and diameter $\simeq$0.01 to 0.06 $\mu$m which are of the same order as mentioned above. These grains are oriented along the substrate and appear randomly distributed.

Typical optimized thickness, as depicted by the SEM cross-sectional viewgraph presented in Fig. 3, is

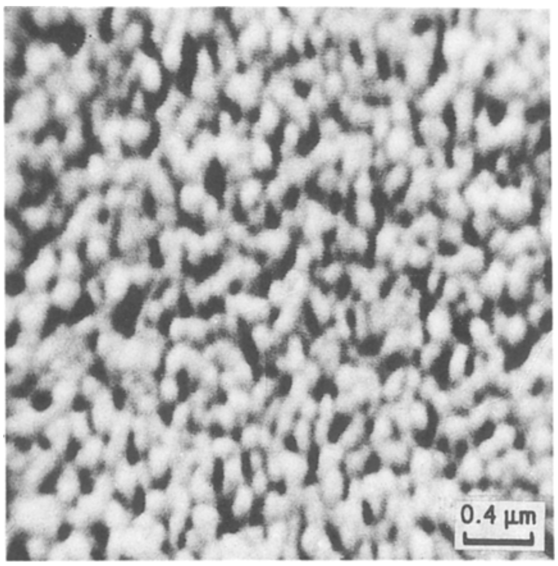


*Figure 1* Scanning electron micrograph of the as-deposited textured black copper selective surface.

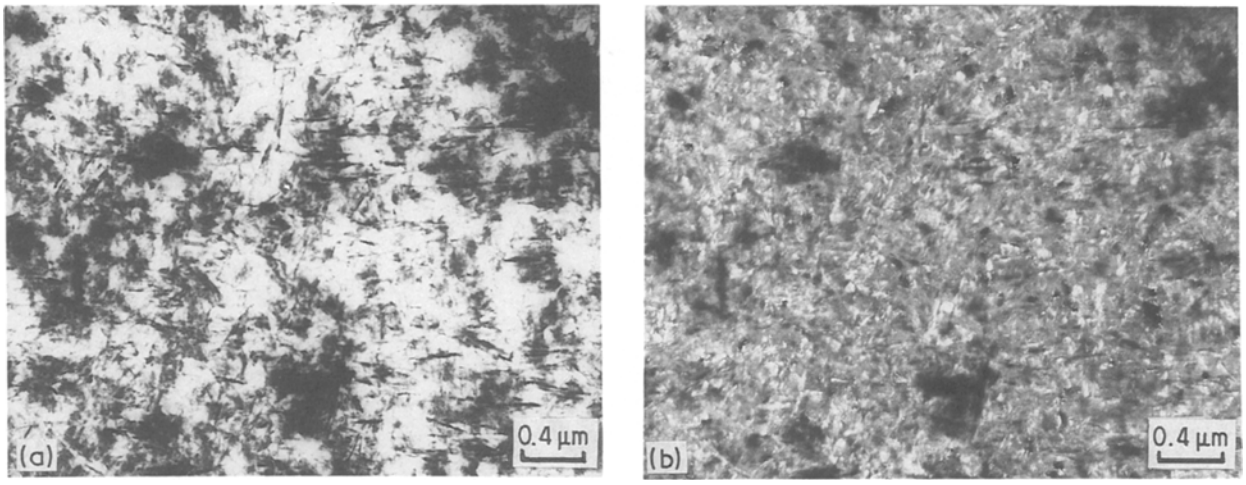


*Figure 2* Transmission electron micrographs of the black copper selective surface: (a) bright-field image, (b) dark-field image.

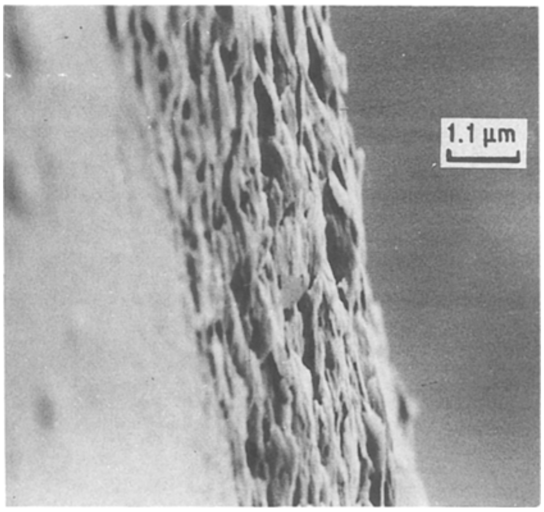


*Figure 3* A typical SEM cross-sectional viewgraph of the as-deposited selective surface.

approximately $\simeq 2.6$ to $3.0\,\mu$m. The micrograph shows a layered structure with porous cavities which can trap the solar radiation by a geometric maze effect. The viewgraph depicts a sponge-like appearance. However, no large differences between the various parts of the film have been noticed. The metal–oxide and oxide–air interfaces appear rough. The presence of this rough morphology may be due to the presence of voids resulting in an inhomogeneous, porous, layered structure.

Fig. 4a shows the surface of this coating after air annealing at $\sim 250°$C for 100 h possessing $\alpha \simeq 0.95$ and $\varepsilon_{100} \simeq 0.17$, while Fig. 4b shows the surface vacuum ($10^{-3}$ torr) annealed at 250° C for 10 h with $\alpha \simeq 0.95$ and $\varepsilon_{100} \simeq 0.19$. No significant change in the surface morphology of these annealed samples has been observed, indicating the validity of the stability of these films up to 250° C.

The picture emerging from these investigations suggests that these surfaces possess a new porous, layered, sponge-like structure which is built of long needle-like and fine grains piled up in the form of layers. The spacing between these grains is approximately that of solar wavelength. The longer grains are $\sim 0.08$ to $0.5\,\mu$m long and $\sim 0.05$ to $0.09\,\mu$m diameter while the finer grains are $\sim 0.08$ to $0.1\,\mu$m diameter. These surfaces possess remarkably high initial solar absorptance ($\alpha$) $\simeq 0.97$ to $0.98$ and $\varepsilon_{100} \simeq 0.2 \pm 0.02$. Further, these surfaces also possess good solar selectivity up to 250° C in air and vacuum. No significant morphological changes have been noticed on annealed surfaces. This indicates their structural stability.

## 4. Conclusions

A new microstructure of a textured black copper

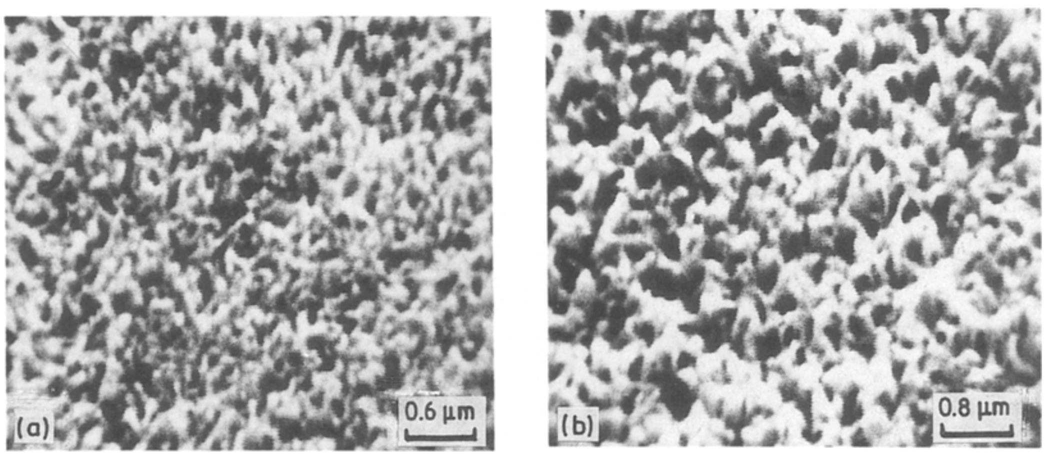


*Figure 4* Scanning electron micrograph of the air and vacuum annealed black copper selective surface: (a) air-annealed surface, annealed at $\sim 250°$C for 100 h; (b) vacuum-annealed ($10^{-3}$ torr) at 250° C for 10 h.

selective coating has been established. These surfaces are made of long and fine grains placed parallel to the substrate in a layered form. These layers consist of porous cavities and the cross-sections appear sponge-like. They possess remarkably good initial solar selectivity. Good structural stability has been depicted on annealing up to 250° C in both air and under vacuum conditions.


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