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Investigation of solar selective and microstructural properties of molybdenum black immersion coatings on cobalt substrates

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Molybdenum black solar selective coatings have been produced on cobalt by immersion in a solution of ammonium paramolybdate and nickel sulphate. The cobalt was electroplated on nickel-plated copper prior to immersion in the paramolybdate solution. The maximum solar absorptance of the resulting molybdenum black coating was about 0.91. The minimum emittance was about 0.1 for coatings on cobalt deposited with an addition agent and about 0.23 for coatings on cobalt deposited without addition agent in the 60 °C plating solution. These differences have been related to the coating morphology determined by scanning electron microscopy. The emittance of coatings on cobalt deposited without addition agent decreases (or remains unchanged) during short-term heat treatment while that of coatings deposited on cobalt plated with addition agent increases somewhat. Reduction of the cobalt plating bath temperature to 45 °C can also lead to good initial coating properties but without the requirement for an addition agent in the cobalt plating bath. XPS studies show that the oxidation state of molybdenum in the coatings is approximately + 5 corresponding to Mo_4O_{11}. This reduces to + 4 after argon ion bombardment. Some cobalt may be present in the coatings in the form of CoO.

1. Introduction

Solar selective absorber surfaces are characterized by high solar absorptance, α, and low infrared (thermal) emittance, ε. Their principal application is in the coating of solar energy absorber plates in order to increase solar collector thermal efficiency. Coating of the substrate by immersion in an appropriate solution is in principle a relatively simple method of producing solar selective absorbers. The properties of Mo-black coatings prepared by chemical conversion were investigated by Hosseini [1] with reference to solar selectivity (i.e. the ratio α/ε). Such coatings had moderate selectivity [2]. Later it was shown that the selectivity and durability of Mo-black coatings on zinc substrates could be significantly improved by using substrate pretreatment [3]. It has been shown that the related electrodeposited Mo-black coatings are semiconductors [4]. They exhibit weak solar selectivity and this has been related to their semiconducting nature [2]. The electrodeposited coatings are relatively thick which probably accounts for their high emittance. It seems likely that dip coatings are also semiconductors but it has not been possible to investigate this.

The investigation of Mo-black immersion coatings on cobalt substrates which have been electroplated on nickel-plated copper sheets is described below. The role of the substrate in the structure and the radiative properties of the absorber coatings is quite important. Solar selectivity as well as durability of selective coatings does vary with the substrate structure, morphology and surface condition [5].

Mo-black coatings prepared by a conversion method on galvanized steel and zinc-plated mild steel were investigated by Agnihotri *et al.* [6]. The best values of solar absorptance and thermal emittance obtained from such coatings were 0.88 and 0.20, respectively.

Smith and Teytz [7] prepared a Mo–Co coating by the immersion method on plated cobalt on nickel-plated copper sheets by using a solution of sodium molybdate and cobalt sulphate. These coatings exhibited high absorptance ($\alpha = 0.89$) with moderately low thermal emittance ($\varepsilon = 0.16$ to 0.20). In the present work the Mo-black coatings on cobalt substrates exhibit rather better initial selectivity. Preliminary results of thermal stability testing are also promising.

We have prepared a range of coatings to optimize the radiative properties by varying the deposition parameters of Mo-black and also the initial cobalt

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layer. The morphology and composition of the coatings were studied by scanning electron microscopy and X-ray photoelectron spectroscopy, respectively.

2. Experimental procedure

2.1. Sample preparation

In this study the substrates were prepared by electroplating of a cobalt film on to dull nickel which had been plated on to copper sheet. The following procedures were used:

(a) Commercially available copper sheets were cleaned mechanically and chemically in a solution of ammonium persulphate. They were then immersed in dilute H_2SO_4 and finally washed with distilled water and alcohol and dried.

(b) Dull nickel was electroplated on the cleaned copper sheets from a solution of nickel sulphate, nickel chloride and boric acid in the respective amounts of about 200, 40 and 20 $\mathrm{g\,dm^{-3}}$. The deposition parameters used were: bath temperature, 35 to 40 °C solution pH, 3.5 to 3.8; cathode current density 20 to 25 $\mathrm{mA\,cm^{-2}}$; plating time 15 min; nickel sheet was used for the anode.

(c) Electroplating of cobalt on to the nickel-plated copper was the next step. The composition of the cobalt plating bath used was as follows:

$CoSO_4\ 7H_2O$	100 $\mathrm{g\,dm^{-3}}$
$CoCl_2$	20 $\mathrm{g\,dm^{-3}}$
H_3BO_3	40 $\mathrm{g\,dm^{-3}}$

Plating was done under various conditions in order to obtain optimum results which will be discussed in the following sections.

The final step was deposition of Mo-black on the electroplated cobalt on nickel-plated copper substrates. This was done by immersion in a solution of ammonium paramolybdate and nickel sulphate [2]. The required solution temperature was in the range 60 to 80 °C. At lower temperatures, the chemical reaction was very slow and the coating was nonuniform. To obtain an optimized coating the solution pH was in the range 2 to 3.5. If the pH was below or above this critical range a blue film formed. To obtain a uniform coating, the solution was stirred continuously during deposition. After deposition, the coatings were washed with distilled water and dried with compressed air. A range of Mo-black coatings was prepared by varying the plating parameters for cobalt and preparation of Mo-black coatings to yield an absorber with suitable radiative properties. The parameters were: cobalt bath temperature; cobalt layer deposition time; current density during cobalt deposition; deposition time of Mo-black, and temperature of the molybdate solution. The effect of an addition agent in the molybdate solution was also studied.

2.2. Radiative property measurements

The radiative characterization of the surfaces relates to the values of the solar absorptance, α, and thermal emittance, ε. Both of these quantities were determined from reflectance measurements by applying Kirchoff's law [8] for an opaque material. Total hemispherical reflectance measurements in the range 0.3 to 2.5 μm were made by using a Beckman 5240 integrating sphere spectrophotometer. α was determined by using selected ordinates for air mass 2 calculated by Wiebelt and Henderson [9]. ε was determined from specular reflectance measurements in the infrared region for the wavelength range from 2.5 to 50 μm using a Perkin-Elmer (model 683) double-beam recording spectrophotometer with reflectance attachment. The reflectance of the coating was weighted with the black body spectrum at a notional solar collector operating temperature of 35 °C.

2.3. Characterization of the Mo-black coating

The coatings were characterized microstructurally using a Cambridge stereoscan 250 MK-2 scanning electron microscope (SEM) equipped with a solid state detector. The identification of the elements present in the coatings was performed using an energy dispersive X-ray analyser (EDX) attached to the SEM. Analysis of the elemental composition of the Mo-black coatings and the oxidation state of molybdenum in the coatings was done using X-ray photoelectron spectroscopy (XPS). The spectrometer (Kratos Analytical Instruments Ltd., Model ES300) employed monochromatized $\mathrm{AlK_{\alpha}}$ radiation and had a resolution of 0.95 eV. The composition depth profile of the coatings was determined by using Ar^+ ions bombardment. The etching rate was roughly 0.1 $\mathrm{nm\,min^{-1}}$ with a 5 keV Ar^+ ion gun having a beam current of 5 mA. The atomic percentage of the chemical elements of the coatings was calculated by measuring the individual peak areas and modification by their corresponding sensitivity factors [10].

3. Results

3.1. Radiative properties

Both the plating conditions of the cobalt and Mo-black layers influence the radiative properties of the coatings. Table I shows some plating conditions of cobalt substrates as well as Mo-black coatings. The values of solar absorptance α and thermal emittance ε are also listed in Table I. These coatings have high solar absorptance (0.90–0.94) but due to high emittances (0.22–0.30), the selectivity factor α/ε is in the range 2.5 to 4. ε increased with the cobalt plating time and Mo-black deposition time. Attempts were made to reduce ε by modifying the bath composition of cobalt. It was observed that use of an addition agent (sodium laurel sulphate) in the cobalt plating solution gave a significantly reduced value of ε. Table II gives the results obtained from the coatings prepared on cobalt plated with addition agent. They indicate that a high selectivity factor can be obtained from these coatings with an absorptance of 0.91. The spectral reflectance spectra in the range (0.3 to 2.5 μm) for coatings on both types of cobalt are shown in Fig. 1. Throughout the solar region no interference peaks are observed except for a broad hump in the 1.1 to 1.5 μm

TABLE I Absorptance α, emittance ε and selectivity factor (α/ε) of Mo-black coatings on cobalt substrates for various plating conditions (without addition agent)

Cobalt plating			Mo-black plating		Thermal radiative properties		
Solution temperature (°C)	Current density (mA cm^{-2})	Plating time (min)	Solution temperature (°C)	Deposition time (min)	α_s	ε_{th}	$\alpha_s/\varepsilon_{th}$
60	36.8	5	60	5	0.90	0.22	4.09
56	32.1	5	60	5	0.91	0.25	3.64
60	35.0	5	60	10	0.92	0.30	3.06
56	30.6	5	60	15	0.90	0.29	3.60
56	31.7	5	80	5	0.90	0.25	3.60
56	25.0	10	60	10	0.94	0.28	3.36
56	25.0	8	60	10	0.94	0.33	2.85
60	34.1	12	60	10	0.92	0.37	2.49

TABLE II Absorptance α, emittance ε and selectivity factor (α/ε) of Mo-black coatings on cobalt substrates for various plating conditions (with addition agent)

Cobalt plating			Mo-black plating		Thermal radiative properties		
Solution temperature (°C)	Current density (mA cm^{-2})	Plating time (min)	Solution temperature (°C)	Deposition time (min)	α_s	ε_{th}	$\alpha_s/\varepsilon_{th}$
58	35.7	4	60	3	0.88	0.08	11.0
58	40.0	5	60	5	0.91	0.10	9.1
60	49.0	5	60	10	0.90	0.13	6.9
60	44.0	5	60	15	0.89	0.17	5.24
60	47.8	5	75	8	0.89	0.13	6.85
58	42.6	5	80	5	0.89	0.13	6.85
58	42.6	5	80	10	0.87	0.21	4.14

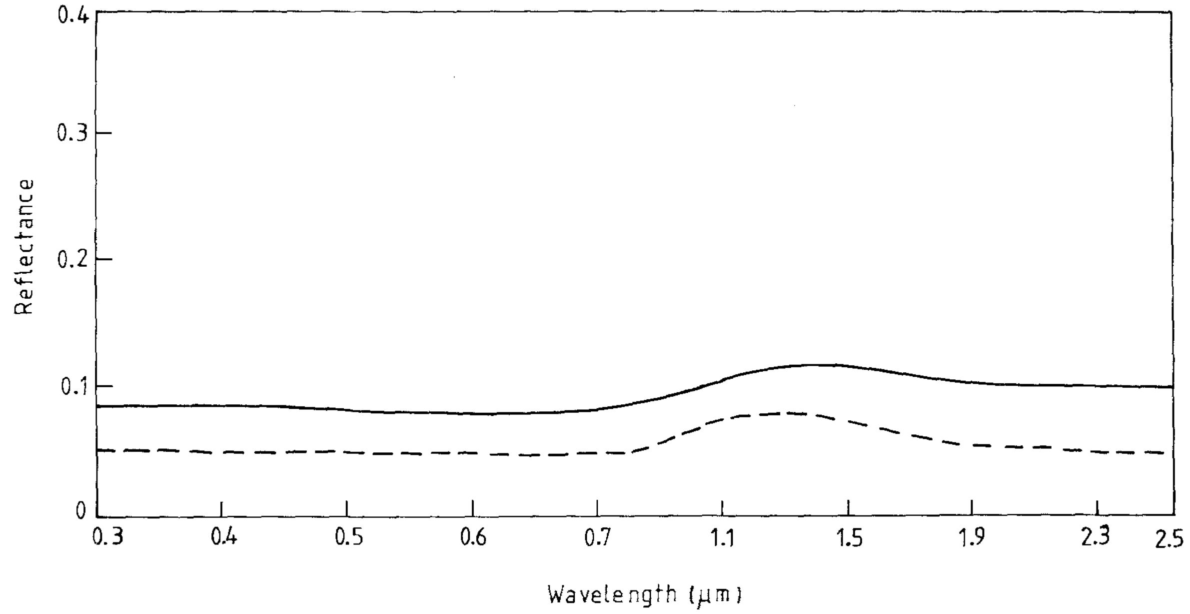


Figure 1 Spectral reflectance spectra for Mo-black dip coatings on cobalt-plated substrates. Cobalt electrodeposited without use of addition agent (– – – –) (α = 0.94, ε = 0.28). Cobalt electrodeposited using addition agent (——) (α = 0.91, ε = 0.10).

region. The figure also shows that the coatings on cobalt plated without addition agent have lower reflectances than those prepared with an addition agent. The coating morphology is responsible for this difference in reflectance and is discussed in the following section. The IR specular reflectance spectra in the range 2.5 to 50 μm for the coatings of Fig. 1 are displayed in Fig. 2. The coating on cobalt, plated without use of an addition agent, has a comparatively low reflectance in the IR region resulting in a high emittance.

The effects of dipping time and solution temperature on α and ε were investigated for coatings on cobalt substrates plated using an addition agent. The

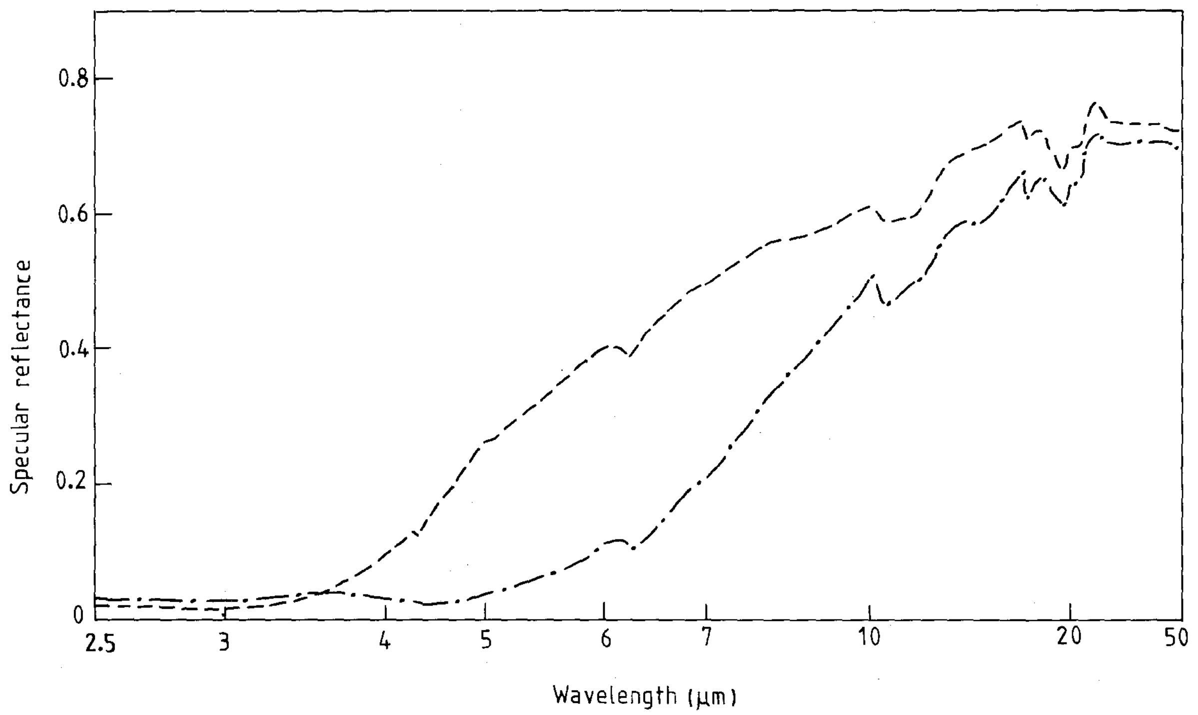


Figure 2 Specular reflectance spectra in the IR region of Mo-black dip coatings on cobalt-plated substrates. Cobalt electrodeposited without use of addition agent (–·—·—). Cobalt electrodeposited using addition agent (– – – –).

effect of paramolybdate solution temperature is illustrated in Table III, which shows that better values of α and α/ε are obtained at a solution temperature of 60 °C rather than 80 °C. The absorptances and emittances of the coatings (prepared at 60 °C) plotted as a function of dipping time are shown in Fig. 3. α varies only slightly with dipping time while ε varies significantly. The best initial values of α and ε are obtained for a deposition time of 5 min with a selectivity factor α/ε of 9.1. (This may correspond to the optimum

TABLE III The values of α, ε and (α/ε) of Mo-black coatings on cobalt substrates at two different molybdate solution temperatures

Time of deposition (min)	Solution temperature 60 °C			Solution temperature 80 °C		
	α_s	ε_{th}	$\alpha_s/\varepsilon_{th}$	α_s	ε_{th}	$\alpha_s/\varepsilon_{th}$
5	0.91	0.10	9.1	0.89	0.13	6.8
10	0.90	0.13	6.9	0.87	0.21	4.1
15	0.88	0.18	4.9	0.88	0.26	3.4

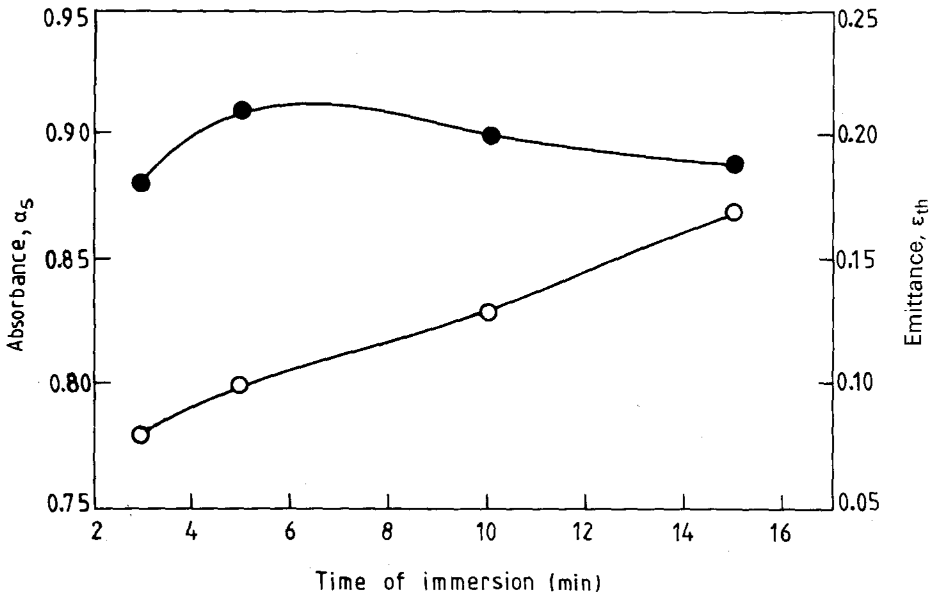


Figure 3 Variation of absorptance (●) and emittance (○) of Mo-black dip coatings with the time of immersion of cobalt-plated substrates in paramolybdate solution (at 60 °C). (Cobalt plated with addition agent in plating bath).

coating conditions for coatings prepared on cobalt plated using an addition agent.) If the deposition time is below 5 min, the coating is not sufficiently absorbing. When the deposition time is higher than 5 min, the absorptance decreases slightly and the emittance increases significantly.

A set of total reflectance spectra in the range 0.3 to 2.5 µm for Mo-black coatings prepared at 60 °C on cobalt plated with addition agent are shown in Fig. 4. Interference peaks appear in the region above 0.7 µm. These are more prominent for the coatings prepared at 80 °C (Fig. 5). The number and height of the maxima tend to increase with the increase of dipping time and temperature of the solution. (An exception to this observation is the behaviour of a coating having a deposition time of 5 min prepared at 60 °C (Fig. 4).)

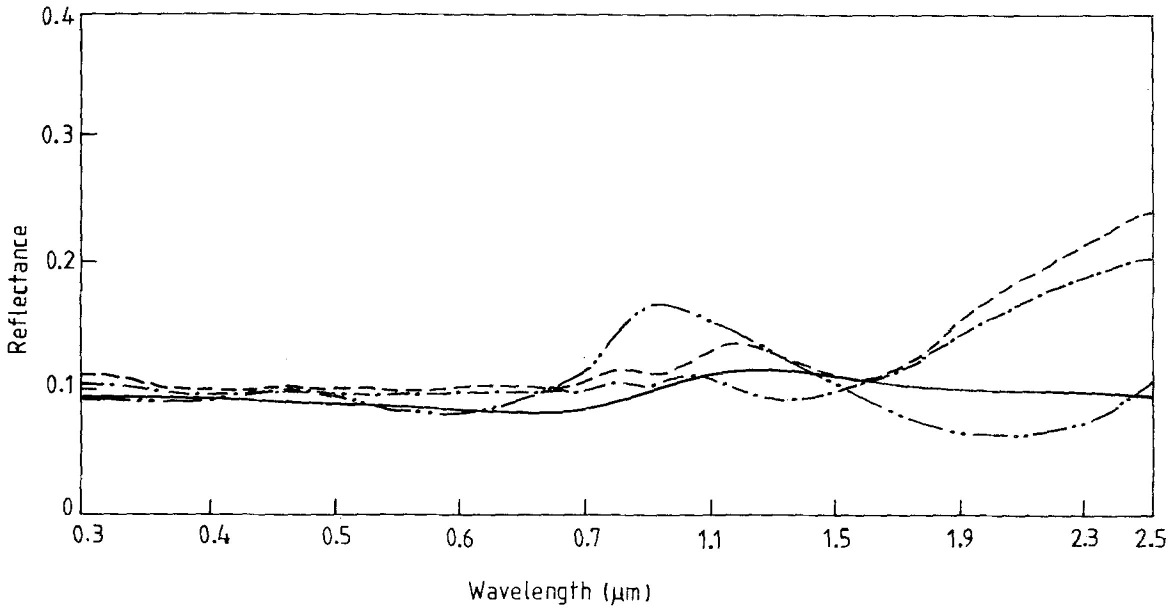


Figure 4 Spectral reflectance spectra of Mo-black dip coatings on cobalt-plated substrates (cobalt electrodeposited using addition agent) for various paramolybdate solution immersion times at 60 °C, 3 min (—··—··—), 5 min (——), 10 min (–·—·–), 15 min (– – –).

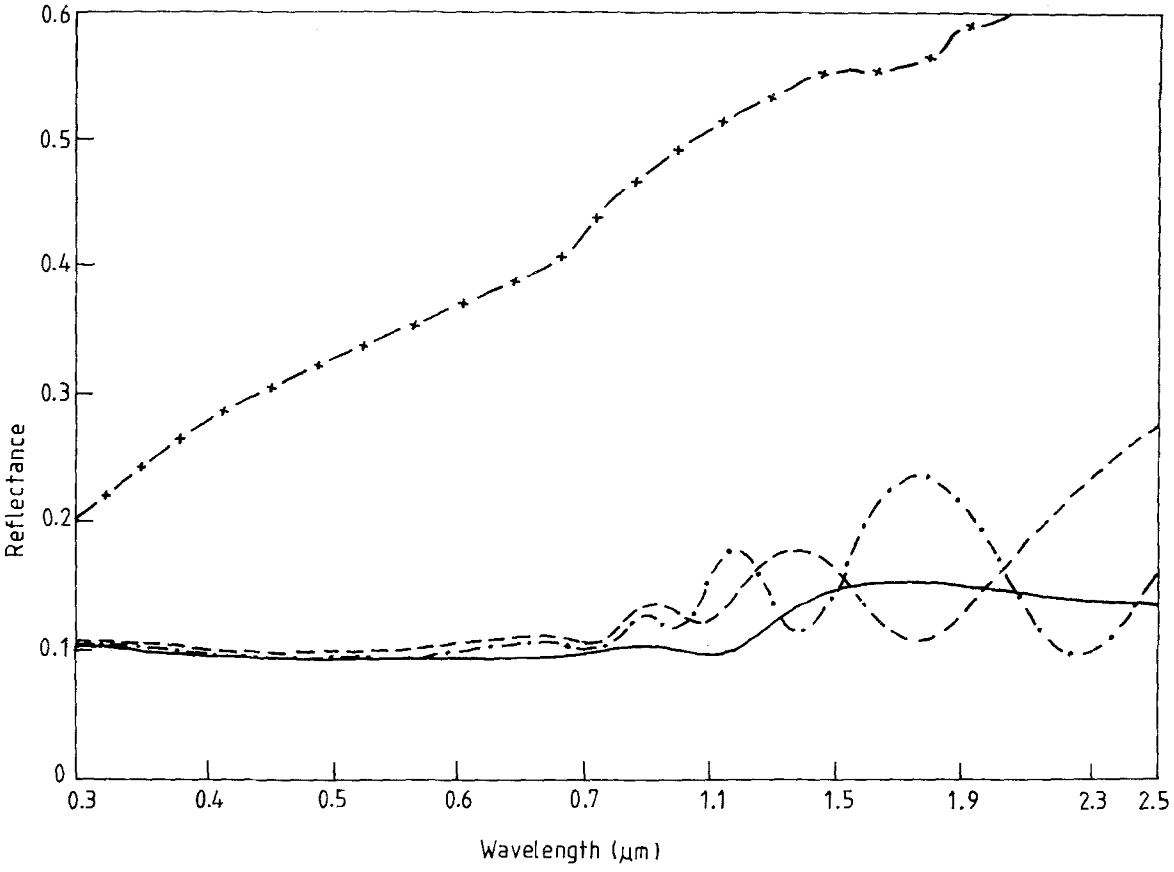


Figure 5 Spectral reflectance spectra of Mo-black dip coatings on cobalt-plated substrates (cobalt electrodeposited using addition agent) for various paramolybdate solution immersion times at 80 °C, 5 min (—), 10 min (– – –), 15 min (–·–·–) Spectral reflectance spectrum of electrodeposited cobalt substrate on nickel-plated copper (– x – x –).

The reflectance curve is flatter than that of the coating deposited by immersion for 3 min. This accounts for the maximum in the solar absorptance after an immersion time of about 5 min. The spectral reflectance spectrum of a plated cobalt substrate (with addition agent) on nickel-plated copper is also shown in Fig. 5. The value of α obtained from the cobalt substrate is 0.56.

Fig. 6a shows the effect of dipping time of Mo-black on IR specular reflectance spectra in the range 2.5 to 50 μm for coatings prepared at 60 °C. As the deposition time increases, the IR reflectance decreases. The increase of coating thickness (with the deposition time) results in a reduction of IR transmittance of the coating which leads to an increase in emittance. The IR reflectance also decreases with the rise of solution temperature for the same time of deposition (Fig. 6b).

Thermal stability testing of the coatings was performed in air in an oven at temperatures of 200 and 300 °C for a rather short time. The results of the tests are given in Table IV. There was very little change in the radiative properties of the coatings. The solar absorptance decreases by no more than about 1% after heat treatment. The emittance of the coatings on cobalt prepared without addition agent decreases after heat treatment but increases for coatings on cobalt plated using an addition agent. This indicates that the coatings on the former substrate are more stable than those on the latter substrate.

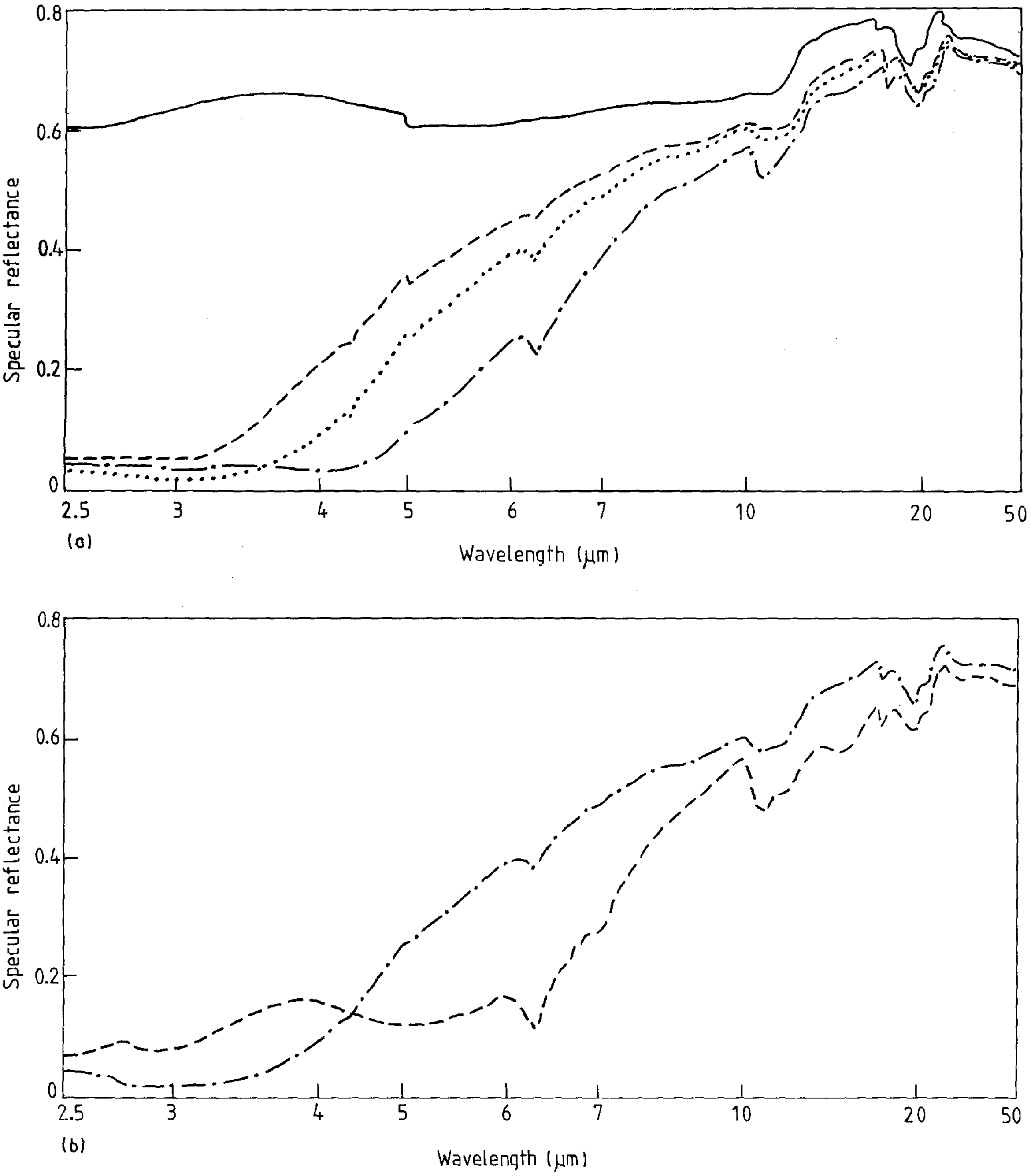


Figure 6 (a) IR specular reflectance spectra of Mo-black dip coatings on cobalt-plated substrates (cobalt electrodeposited using addition agent) for various paramolybdate solution immersion times at 60 °C. 5 min (– – –), 10 min (. . . . . .), 15 min (–·–·–) reflectance spectrum of aluminium reference mirror. (——) (b) IR specular reflectance spectra of Mo-black dip coatings prepared with a 10 min paramolybdate solution immersion time at two different solution temperatures on cobalt-plated substrate (cobalt electrodeposited using addition agent). 60 °C (–·–·–), 80°C (– – –).

TABLE IV Effect of heat treatment on radiative properties α, ε of Mo-black coatings on cobalt substrates

Substrate types	Heat treatment	As-prepared		After heat treatment	
		α_s	ε_{th}	α_s	ε_{th}
Cobalt plated without addition agent	5 h at 300 °C	0.94	0.29	0.94	0.24
		0.90	0.26	0.89	0.21
	2 h at 400 °C	0.94	0.33	0.94	0.29
		0.90	0.25	0.89	0.23
Cobalt plated with addition agent	5 h at 300 °C	0.91	0.10	0.89	0.11
		0.90	0.13	0.89	0.16
	2 h at 200 °C	0.89	0.13	0.89	0.16
		0.88	0.20	0.88	0.20

Fig. 7 shows another set of spectral reflectance spectra in the solar region for Mo-black coatings on cobalt substrates prepared at relatively low temperatures, with low current densities (about 25 mA cm^{-2}) for short times as indicated in Table V. The reflectances are low (resulting in high absorptance) and do not change significantly throughout the solar region. These coatings have high IR reflectance resulting in low emittance. Long deposition times of Mo-black do not affect the emittance of the coatings. These coatings were prepared at a relatively high paramolybdate solution pH value of 3.2, which may reduce the deposition rate of Mo-black coatings. An absorptance of 0.91 together with an α/ε value of 10.1 was the best combination of values obtained using this method of coating preparation. No durability testing has, however, been performed on this type of coating.

3.2. Micromorphology

As the reflectance is a surface property, it changes with the surface morphology. A systematic study was made of surface morphology for both Mo-black coatings and plated cobalt. The resulting micrographs show that the surface topography of the coatings depends upon the plating conditions of cobalt and also Mo-black. A typical SEM micrograph of a Mo-black coating on a cobalt substrate plated without addition agent is shown in Fig. 8a. The surface of the coating consists of a large number of fibrous protruberences with a few nodules. They are uniformly distributed and oriented in different directions parallel to the substrate. The high proportion of surface voids and the surface roughness may be responsible for the high solar absorptance (0.94). Fig. 8b shows the surface of another Mo-black coating which consists of a modified fibrous structure. Due to this coarse surface texture, the emittance of the coating was comparatively high (0.35). The Mo-black coating was prepared under the same conditions in both samples, but in the latter case, cobalt was plated at a relatively high temperature with high current density.

The surface topography of the coating changed when an addition agent was used in the plating

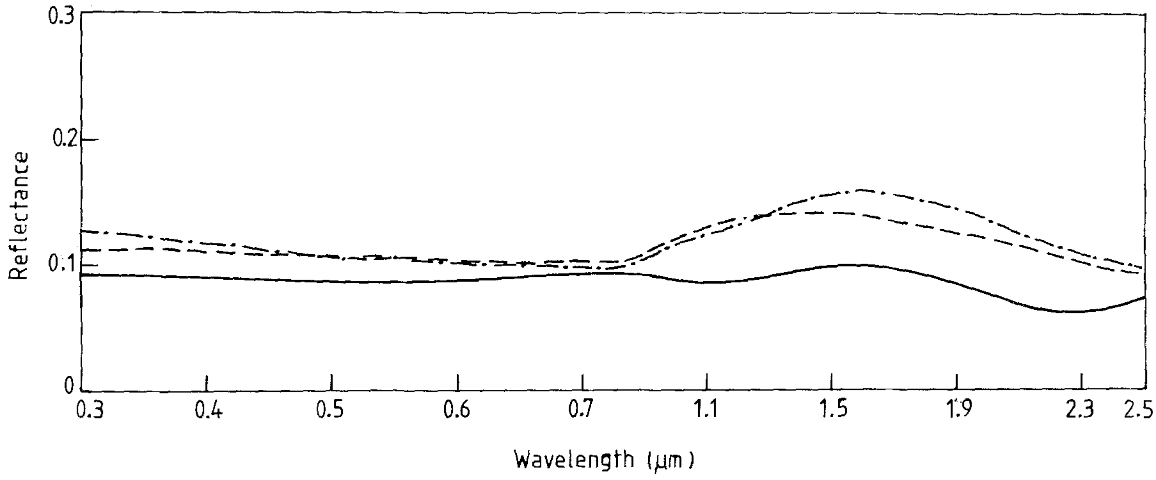


Figure 7 Spectral reflectance spectra of Mo-black dip coatings on cobalt-plated substrates (cobalt electrodeposited at 45 °C and about 25 mA cm^{-2}) current density without addition agent) for various paramolybdate solution immersion times, 5 min (——), 8 min (-·-·-), 12 min (- - -).

TABLE V Absorptance α, emittance ε and selectivity factor (α/ε) of Mo-black coatings on cobalt substrates (without addition agent)

Cobalt plating			Mo-black plating		Thermal radiative properties		
Current density (mA cm^{-2})	Temperature of the solution (°C)	Plating time (min)	Temperature of the solution (°C)	Deposition time (min)	α_s	ε_{th}	$\alpha_s/\varepsilon_{th}$
25.1	45	4	60	5	0.91	0.09	10.1
24.9	45	4	60	8	0.89	0.10	8.9
25.2	45	4	60	12	0.88	0.09	9.7

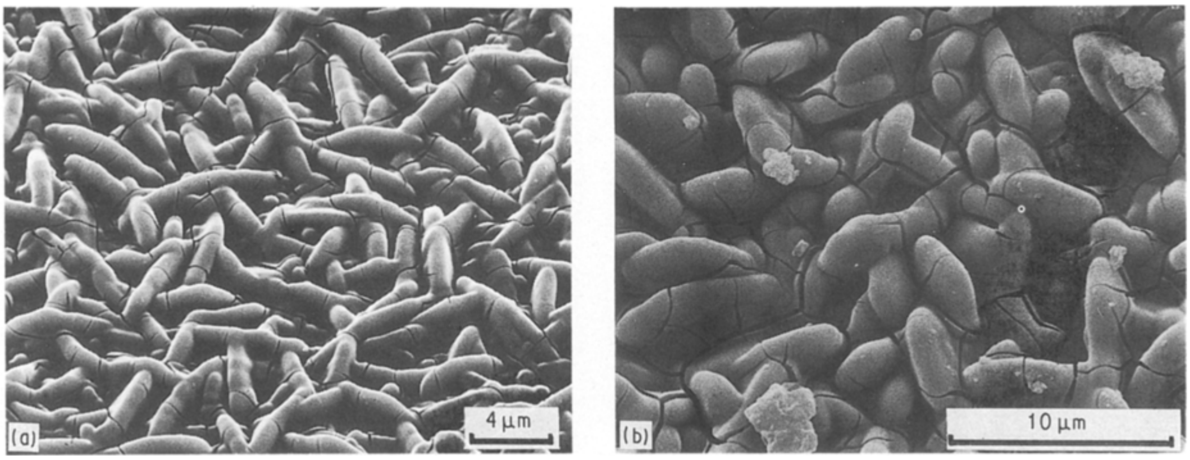
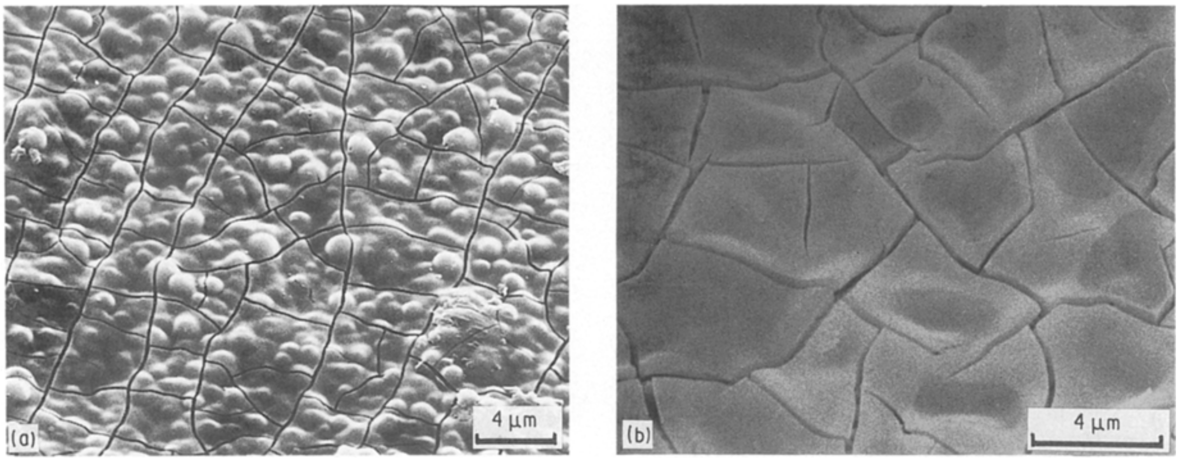


Figure 8 (a) SEM micrograph of a Mo-black dip coating on a cobalt-plated substrate (cobalt electrodeposited at 50 °C and current density of 25 mA cm^{-2} without use of an addition agent) showing a fibrous like structure ($\alpha = 0.94$, $\varepsilon = 0.28$). (b) SEM micrograph of a Mo-black dip coating on a cobalt-plated substrate (cobalt electrodeposited at 60 °C and current density of 34 mA cm^{-2} without use of an addition agent) showing a modified fibrous structure. ($\alpha = 0.92$, $\varepsilon = 0.35$).



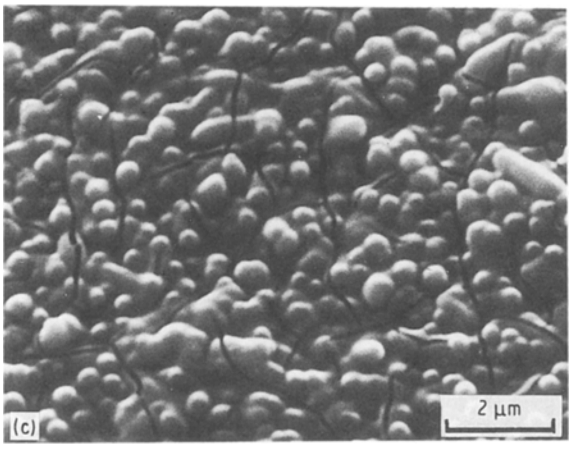


Figure 9 (a) SEM micrograph of a Mo-black dip coating on a cobalt-plated substrate (cobalt electrodeposited using an addition agent) showing nodular structures ($\alpha = 0.90$, $\varepsilon = 0.12$). (b) SEM micrograph of a Mo-black dip coating prepared at a paramolybdate solution temperature of 80 °C on cobalt-plated substrate (cobalt electrodeposited using an addition agent) showing flat, plate-like structure ($\alpha = 0.87$, $\varepsilon = 0.21$). (c) SEM micrograph of a Mo-black dip coating on a cobalt-plated substrate (cobalt electrodeposited at 45 °C at 25 mA cm^{-2} without addition agent). ($\alpha = 0.91$ and $\varepsilon = 0.09$).

solution of cobalt. A typical SEM micrograph of a Mo-black coating prepared at 60 °C on cobalt plated using an addition agent is shown in Fig. 9a. The coating surface consists of large numbers of nodules of about 1 to 2 µm in size range. The surface of the coating became smoother when the deposition time (or temperature) of the Mo-black coating increased [10]. Fig. 9b shows the SEM micrograph of another coating which was prepared at 80 °C. The surface is quite smooth and flat and this is probably due to the relatively large thickness of the coating. The values of α and ε obtained from this surface are 0.87 and 0.20, respectively. When the cobalt was plated at a comparatively low temperature (45 °C) with low current density (25 mA cm^{-2}), and no addition agent, the surface of Mo-black consisted of submicrometre-sized nodules as shown in Fig. 9c.

The elemental composition of the coatings was analysed by energy dispersive X-ray analysis (EDX) using the SEM instrument. The EDX spectra indicated the presence of Mo and Co in the coatings. A systematic study of a number of coatings of varying deposition time indicated that the percentage of cobalt decreases with the increase of deposition time of Mo-black whereas the percentage of Mo increases [10].

This suggests that the cobalt signal originates mainly from the plated cobalt substrate.

A metallographic cross-section of a coating on a cobalt substrate was prepared and examined in SEM. The SEM micrograph of the metallographic section of the coating is shown in Fig. 10. The X-ray line scans for Mo, Co and Ni are superimposed on the metallographic cross-section. This Figure shows the presence of three successive layers of Mo, Co and Ni on the copper substrate.

3.3. XPS study

The elemental compositions of the Mo-black coatings and also the chemical states of the elements comprising the Mo-black coating were analysed by X-ray photoelectron spectroscopy. This indicated that the main elements near the coating surface are molybdenum and oxygen but cobalt was also detected. The estimated binding energy of the electrons associated with the Co($2p_{3/2}$) peak was about 780.0 eV. (using C1s as a reference peak corresponding to an electron binding energy of 284.9 eV). A strong satellite of the Co($2p_{3/2}$) peak was observed at a binding energy about 6 eV higher than that of the main peak. These features may indicate the presence of cobalt oxide (CoO) [11, 12]. Reflection electron diffraction also provided evidence for the presence of some CoO in the coatings [10]. A symmetric peak of 0 1s (of binding energy 530.1 eV) may have been due to the presence of metal oxides [13]. The Mo 3d doublet peak was well resolved. Several coatings were studied and the average electron binding energies of Mo($3d_{3/2}$) and Mo($3d_{5/2}$) are given in Table VI.

For comparison, the standard oxides, MoO_2, MoO_3 and Mo metal were also studied in the same spectrometer. The binding energies of the Mo 3d doublet for these standard materials [14] are also included in Table VI. Comparison of the binding energy of Mo($3d_{5/2}$) peak from the coatings with that of the standard materials indicates that that the oxidation state of Mo in the coating is between + 4 and + 6. The coatings were also examined after heating in air at 400 °C for 2 h and heating inside the spectrometer chamber at a temperature of 300 °C for 2 h. The results obtained from these investigations are also given in Table VI. On air heating the binding energy of Mo$3d_{5/2}$ electrons increases by about 0.3 eV towards that of MoO_3 while on vacuum heating the binding energy of the same electrons decreases by about 0.4 eV towards that of MoO_2. X-ray diffraction studies have indicated formation of MoO_3 or MoO_2 in Mo-black coatings on other substrates after similar heat treatments [2].

Argon ion bombardment was used to profile the coatings. The binding energy of the Mo 3d doublet shifted towards a value associated with a lower oxidation state after etching with Ar^+ions (Table VI). The effect of Ar^+ ion bombardment on the Mo 3d doublet of the coating is displayed in Fig. 11. Using the XPS elemental sensitivity factors [10] the atomic ratios of Co, Mo and O were calculated. At the surface of the coating, the ratio of the elements Mo:Co:O is 1:0.22:2.31. After 10 min of etching, the ratio becomes 1:0.21:1.84. The reduction of O to Mo ratio could be due to the Ar^+ etching as it reduces the Mo-oxide to the lower oxidation state. The ratio of the elements after 10 min of etching remains almost constant up to 370 min of etching as shown in Fig. 12.

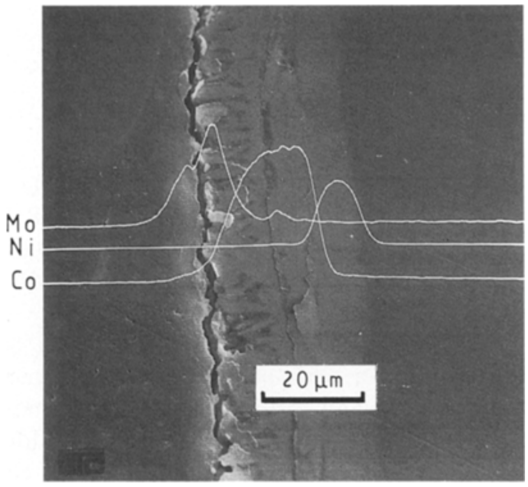


Figure 10 SEM micrograph of a metallographic cross-section of a Mo-black dip coating on cobalt-plated (on nickel-plated copper) substrate with Mo, Co and Ni characteristic X-ray line scans.

TABLE VI XPS data for Mo-black dip coatings on cobalt substrates and standard materials including shift in binding energy (BE) of Mo $3d_{5/2}$ with respect to that of Mo-metal

Sample	Electron binding energy (eV)			Mo 3d doublet breadth[a] (eV)	Shift in BE (eV)
	Mo $3d_{3/2}$	Mo $3d_{5/2}$	0 1s		
As-prepared coating	235.0 ± 0.1	231.9 ± 0.1	530.1 ± 0.2	5.2	4.9
Heated in air at 400 °C for 2 h	235.3 ± 0.1	232.2 ± 0.1	530.6 ± 0.1	4.6	5.2
Heated in vacuum at 300 °C for 2 h	234.7 ± 0.2	231.5 ± 0.1	530.6 ± 0.2	5.6	4.5
Etched with Ar^+ ions	232.1	229.0	–	–	2.0
Mo-metal	230.2 ± 0.2	227.0 ± 0.1	–	–	0
MoO_2	232.4 ± 0.2	229.3 ± 0.2	529.9	–	2.3
MoO_3	236.1 ± 0.1	233.0 ± 0.1	529.9	4.4	6.0

[a] Half peak breadth.

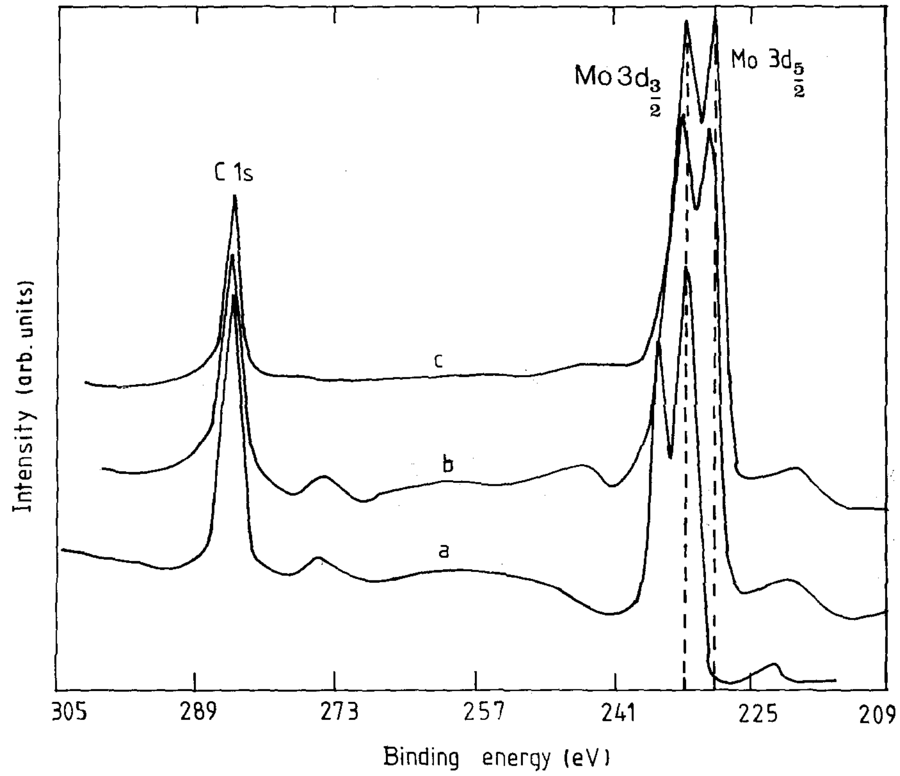


Figure 11 XPS doublet (Mo3d) obtained from Mo-black dip coating on cobalt-plated substrate (a) as-prepared (b) after etching for 10 min, (c) after etching for 70 min (using Ar^+ ion bombardment).

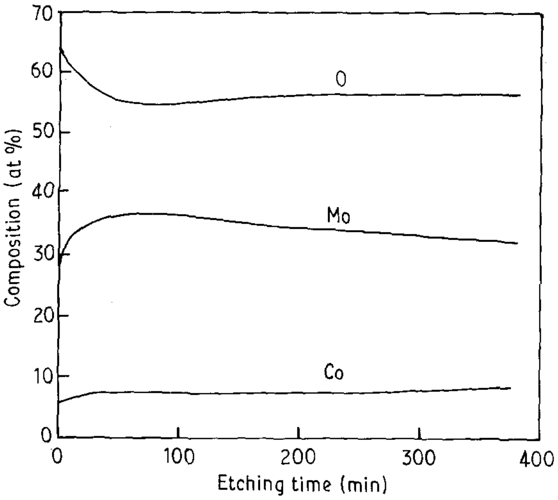


Figure 12 Composition depth profile of a Mo-black dip coating on a cobalt-plated substrate obtained using XPS and Ar^+ ion bombardment.

4. Discussion

The spectral reflectance spectra (Fig. 1) of some of the Mo-black coatings prepared in the present work show that they are good intrinsic absorbers. No strong interference peaks are evident especially in the visible region. The high absorptance of the coatings may be mainly due to surface morphology. The presence of front surface relief and possible high porosity of the coatings and the underlying cobalt layer reduces the front surface reflections giving high absorptance. By assuming that the coatings have a negligible imaginary part of refractive index, (like most oxide semiconductors [15]) the real part of refractive index n can be calculated using the equation

$$R = (n - 1)^2/(n + 1)^2$$

where R is the reflectance of the coatings. The estimated value of n is within the range 1.5–1.8. The values of n for these coatings are comparable with the values obtained by Smith and Teytz [7] for Mo–Co coatings.

The coatings prepared on cobalt plated at 60 °C without use of an addition agent exhibit generally higher emittances and absorptances (Table I) than the coatings on cobalt plated at 60 °C using an addition agent (Table II). These differences appear to be related to differences in the surface roughness of the two coating types, e.g. increased microroughness may enhance the solar absorptance due to multiple reflections. Information concerning the surface microroughness was obtained using a Rank Taylor Hobson Talystep. The central line average roughness value of samples of each type of coating was 0.3 μm (without addition agent) and 0.13 μm (with addition agent). Differences in the surface morphology of the underlying cobalt layers (plated with and without addition agents) probably account for the observed differences in surface roughness of Mo-black coatings [10]. Reduction of the cobalt deposition temperature to 45 °C together with relatively slow deposition of cobalt and Mo-black yields similar benefits to the use of an addition agent according to the data in Table V and also modifies the coating microstructure (Fig. 9c). This requires further investigation.

The benefit of use of an addition agent in the cobalt plating solution can be reduced if the paramolybdate solution temperature is too high. In the present study,

α and ε values obtained from the coatings prepared at a paramolybdate solution temperature of 80 °C are comparable with the results reported by Smith and Teytz [7] for Mo–Co coatings. It was observed that the coatings prepared at a solution temperature of 60 °C have better selectivity (Table III) than those prepared by Smith and Teytz. This may be due to the increase of coating thickness with deposition temperature (for a given deposition time) which generally leads to smoother coatings as the influence of the cobalt substrate is reduced. It is also observed that as the coatings become smoother and thicker interference peaks appear in the NIR region (Fig. 5). These are similar to the spectra obtained by Smith and Teytz [7]. For thicker coatings small IR absorption peaks at about 10.5, 11.6 and 14.3 μm are observed in the IR reflectance spectra (Fig. 6b). These absorption peaks together with the absorption peaks of water (2.9 and 6.2 μm) reduce the IR reflectance of the coating and lead to an increase in emittance. The optimum coatings are thin enough to be transparent in the IR region.

The XPS study of these coatings shows the presence of a small amount of cobalt near the coating surface (possibly in the form of CoO). The ratio of Mo to Co was found to be 4.55. This is higher than that obtained by Smith and Teytz [7] for Mo–Co coatings. They reported that in an outer layer of about 80 nm thickness, the ratio of Mo to Co is 2.0 and after that it becomes 1.18. The higher percentage of Co in their coatings may be due to their use of cobalt sulphate in the Mo-black plating solution. It is then more likely that cobalt would be deposited with molybdenum oxide. They suggested the composition of the coatings is close to $MoCoO_2$ or $MoCo(OH)_2$. It might also be a compound containing Co_2O_3 mixed with a molybdenum oxide.

In the present analysis of the XPS results [10] and comparing the binding energies with the published data [14], the estimated oxidation state of Mo is + 5.4, which is close to the oxidation state of Mo_4O_{11} [16]. The ratio of Mo to O is also similar to that in Mo_4O_{11}. X-ray diffraction investigations of Mo-black coatings prepared on cobalt (together with zinc and aluminium) substrates using the same solution as in the present work suggest the presence of Mo_4O_{11} in the Mo-black coatings [10]. Potdar *et al.* [17] reported that the ratio of O to Mo is consistent with Mo_4O_{11} in Mo-black coatings prepared by electrodeposition on nickel-plated copper substrates.

Argon ion bombardment shifts the Mo 3d doublet towards the lower binding energy (+ 4) oxidation state. No further shift in binding energy is observed after a prolonged time of bombardment. Reduction of the oxide to the lower oxidation state by Ar^+ bombardment is very common for most of the metal oxides [18]. In the case of MoO_3 it was, however, reported by Kim *et al.* [19] that after prolonged bombardment with Ar^+ ions, the final product is MoO_2. The same effect was observed in the Mo-black coatings on other substrates (Al, Zn) after Ar^+ bombardment [10]. It is, therefore, unlikely that the observed shift in the binding energy of the Mo 3d doublet is due to an actual variation in the oxidation state of Mo with depth in the coating.

Smith and Teytz [7] have reported that their Mo–Co coatings are stable to 400 °C. Further work is needed on durability testing of the present coatings.

5. Conclusions

The conclusions are as follows.

1. The morphology of Mo-black coatings on cobalt-plated substrates depends on the preparation conditions. The coatings have a nodular structure and comparatively smooth surface when prepared on cobalt-plated substrates using an addition agent in the plating solution. On cobalt-plated substrates without an addition agent (at a bath temperature of 60 °C or higher) the coatings consist of a number of fibrous structures with few nodules.

2. These coatings have high solar absorptances (0.92–0.94) mainly due to the surface morphology together with the structure of the underlying cobalt layer (when it is prepared without addition agent). Their emittance is rather high (0.25–0.35).

3. Use of an addition agent in the cobalt plating solution leads to a reduction in emittance to about 0.1 with a slight decrease in solar absorptance. This is thought to be related to a decrease in surface microroughness of the Mo-black coating.

Coating emittance increases steadily with coating thickness due to the occurrence of absorption bands (including those due to water) in the IR region of the coating reflectance spectrum. A maximum in the curve of absorptance as a function of paramolybdate solution immersion time (at 60 °C) is probably associated with a decrease in the coating roughness as the influence of the cobalt substrate is diminished. The corresponding absorptance is 0.91 while the α/ε ratio is 9.1. These are the optimum initial values of α and α/ε obtained in the present work for coatings prepared on cobalt substrates plated using an addition agent.

4. X-ray photoelectron spectroscopy (XPS) studies indicate that the oxidation state of Mo-black coatings on cobalt-plated substrates is about + 5. This is close to that of Mo_4O_{11}. Bombardment of coatings with Ar^+ ions reduces the oxidation state to + 4. The atomic ratio of Mo to Co indicated by XPS is about 5 and has a comparatively small variation with ion bombardment time. The cobalt may be present in the form of CoO.

5. The coating refractive index is estimated to lie in the range 1.5 to 1.8.

6. Short term heat treatment (e.g. 5 h at 300 °C) leads to little change in α and ε. The coatings, however, prepared on Co previously plated (at 60 °C) without use of an addition agent in the plating bath appear to be rather more stable than those on Co prepared with an addition agent. XPS studies shows that there is a tendency for MoO_3 to form on heating the Mo-black coatings in air while heating *in vacuo* leads to formation of MoO_2.

7. An initial α value of 0.91 together with an α/ε value of 10.1 has been obtained for coatings prepared on cobalt deposited at a relatively low temperature of

45 °C (without the use of an addition agent) and at a relatively low current density of 25 mA cm^{-2} for short times. The durability of such coatings has not been investigated.

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