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Review

Optimization and microstructural analysis of electrochemically deposited selective solar absorber coatings

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The literature on microstructural analysis of the most common selective electrodeposits is reviewed, and the advantages and limitations of surface analysis techniques for each of the overlayers are discussed. The structures included in this review are overlayers of black chrome, black zinc, copper oxide, black cobalt, black nickel, iron oxide and pigmented aluminium oxide coatings. The optical properties and their dependence on the deposition parameters, as well as the results of optimization experiments made on these parameters, before and after heat-treatment, are also described. Finally, future work necessary for a more complete description of the coating structures, in particular through the application of optical modelling, is outlined.

1. Introduction

An important concern in the study of selective solar collector coatings has been the understanding of mechanisms of selectivity for systems with high solar absorptances and low thermal emittances [1]. Before such insight into the optical properties of collector coatings can be obtained, microstructural analyses that lead to the derivation of the relationships between optical properties and the variables of deposition of such coatings have to be made. This is particularly important since the internal film structures have a very strong influence on both the optical properties of the coatings as well as their thermal degradation behaviour [2, 3].

Among the successful selective photothermal absorber coatings, several unique structural features can be distinguished. These include geometrically roughened surfaces [4] and coatings with microcrystalline metal particle gradients [5] or artificially produced optical constant gradients formed through changes in the composition of the oxide coatings [6]. The production methods for these structures can again be subdivided into electroplated deposits, thermally or electrochemically oxidized substrates, chemical conversion coatings and vapour deposited cermets. Complicated combinations of two or more of the above-mentioned methods have also been applied for development of selective coatings [7]. All of these techniques most commonly form a very thin and complex overlayer on the metallic substrate.

Many of the most promising spectrally selective surfaces are composed of semiconductor–metal tandems [8]. Usually, the semiconductor part consists of a very thin metal oxide film. To provide suitably low reflectances throughout the solar spectrum [9], these metal oxide layers possess a refractive index gradient. This allows for a smooth increase from the index of air to that of the metal and thereby minimizes the reflectance losses in the wavelength range, however, where large reflectances are desired to minimize the thermal infrared radiation [10], selective solar coatings should be transparent to the incident radiation so that the reflectance is dominated by the substrate. This is achieved by the production of very thin films that subject the incoming photons to an abrupt change in refractive index at the oxide–metal interface [11]. To produce such thin films, electrodeposits are commonly preferred, since relatively inexpensive coatings can be deposited with good reproducibility.

Surface analysis techniques capable of analysing these thin and complex layer tandems as to their structures and chemical compositions have only recently been applied. Through the use of transmission electron microscopy (TEM), scanning electron microscopy (SEM), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), field-ion microscopy (FIM), X-ray diffraction (XRD), reflected electron diffraction (RED) and optical techniques, it has become possible to obtain information describing the internal structure of these films and to speculate on the mechanisms providing spectrally selective behaviour. Although there still is some debate on these structures, many important breakthroughs have been accomplished in this field in the last decade, and a general review paper is warranted. In this review, the literature on microstructural analysis and relations between the production parameters and structures of these thin selective structures is given, and some possible future trends in this area are also speculated upon.

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2. Structural characterization

2.1. Metal oxide – metal tandems

Many of the potential selective absorber coatings are thin metal oxides either chemically or electrochemically formed on metal substrates. They almost invariably contain excess metal in the coating, and form a gradient of this metal content. The structure of these coatings, however, is quite different from one coating to another. The coating studied in the greatest detail, electroplated black chrome, for example, is found to consist of microcrystalline chromium particles surrounded by chromium oxide in a very porous structure [12, 13]. The structure typical of black zinc, on the other hand, exhibits no evidence of microcrystalline zinc, and a relatively dense deposit forms.

Another oxide coating, thermally oxidized black cobalt, derives its selectivity from the very rough surface which is produced during the oxidizing process. Hence even in the case of the simple oxide films, complicated structures are encountered and a systematic approach has to be taken for their characterization. In the past, this approach has been in the form of detailed parametric analysis of the deposition variables and their effects on the optical properties. Subsequent microstructural evaluations of these coatings through XRD, TEM, SEM, or AES define the extent of these studies. Some of this work on oxide systems will be detailed below.

Structural analysis is most meaningful when made on coatings produced with optimum deposition conditions. Such analysis, in turn, needs to be described in conjunction with the optimization data. Although the "optimum parameters" might be different for collector systems produced on a commercial scale, it is very important to understand the changes introduced in the overlayer structures when deposition parameters are changed in the optimization. Conversely, the resulting changes in the optical properties of the coatings can provide additional information on the overall film structures [14].

3. Black chrome

3.1. Structural analysis

Black chrome was systematically investigated for its optical properties in 1974 by McDonald [15]. Pettit and Sowell [10] reported more extensive results and obtained as-plated absorptances of 0.95 at emittances of less than 0.25 using a proprietary bath (developed by Harshaw Chemical Co.). The thermal degradation properties of the coatings were found to depend on the substrate used, and, in particular, coatings plated on copper showed poor thermal stability [2]. The microstructure of these coatings were also found to strongly depend on the plating conditions as well as the subsequent thermal treatment given [16].

Investigations into the structure and composition of electrodeposited black chrome coatings have shown that the resulting coatings consist primarily of metallic chromium together with chromium oxide in the form of Cr_2O_3 [17]. The presence of chromium and oxygen atoms has been confirmed through AES [18], whereas the oxide bonding structure has been revealed to correspond to Cr_2O_3 by XPS. The crystal structure was determined by XRD as well as transmission and reflection electron diffraction techniques [19]. This same composition and structure have been characteristic of layers electroplated on nickel, copper, stainless steel and gold [17, 18].

Ion-sputtering through the coating, to the substrate, has evolved in the derivation of compositional depth profiles. Unfortunately, due to the inherent porosity of the coatings, such depth-profiles lead to little quantitative information on the compositional dependence of depth into the film. None the less, investigators have found that the chromium content generally increases as the distance from the substrate is reduced [20, 21]. Since the sputtering time required to pass through the substrate-film interface is roughly 40% of the total time and the porosity of the coating changes with depth, no exact profiles can be drawn from such information [22]. Integration of AES sputter profiles, however, leads to a measure of the relative amount of each constituent, if only metallic chrome and chrome oxide are assumed to be present. The relative volume fractions of Cr_2O_3 to $(Cr + Cr_2O_3)$ calculated by this method range from 0.30 to 0.44 [23].

It is generally agreed that the surface composition of the black chrome layers consists almost exclusively of Cr_2O_3, although Zajac *et al.* [18] have indicated the presence of $Cr(OH)_2$, which was previously observed primarily in the surface region layers. Other species which have been found by compositional analysis [24] include CrH_2, CrO_3, CrO, Cr_2O_4 and CrO_2, though only in small quantities, and generally only at the surface of the coatings.

Structural information on black chrome was obtained primarily by electron microscopy and diffraction studies. SEM observations show the coating to be a particulate deposit with spherical particles of approximately 50 to 100 nm diameter [12, 25]. Following the sputtering of the first 100 nm, larger elliptical particles have been observed by Ignatiev *et al.* [26]. This however, has not been confirmed in subsequent TEM analaysis. A high volume fraction of voids is observed in electron microscopy, which in turn makes the determination of film thickness very complicated. The range of thickness measured on black chrome films is typically between 0.4 and 0.7 micrometres [27].

Since only a diffuse halo electron diffraction pattern of chromium oxide can be detected in the as-plated coatings, the original structure of the coating is considered to be composed of microcrystalline or amorphous Cr_2O_3 [19]. The distribution of chromium in these crystallites is not clear, but FIM investigations confirm the presence of metallic chromium as well as chromium associated with the oxide [2]. Following heat-treatment of these coatings, the oxide crystallite size is found to increase significantly. The areal density of the deposit is measured to be approximately $5.8 \times 10^{-5}\,g\,cm^{-2}$, corresponding to an average packing fraction of approximately 33% [28, 29]. Other black chrome deposit structures, such as that observed by Spitz *et al.*, exhibit an uncommon needle-like morphology of the chromium oxide layer.

3.2. Optimization of black chrome

The deposition parameters of black chrome coatings have been optimized by various statistical methods [13, 21, 25]. A Simplex Evolutionary Operator procedure was utilized to optimize in terms of selectivity the deposition parameter, thus yielding optimum solar absorptances of 0.98 at emittances (100° C) of 0.1 in the as-plated condition. These properties were achieved through depositions of relatively low plating time (2.2 min), but correspondingly higher current densities (33 A dm^{-2}) from the proprietary Harshaw Chemical Co. mixture on nickel substrates [13]. When the absorptance of deposits on copper was optimized with a multilinear regression technique, while constraining emittance and using thermally exposed samples, the optimum coating region was defined at lower current densities and longer times. However, the enhanced degradation of the layers on copper yielded heat-treated absorptances (after 80 h at 450° C) of 0.9 at best [25]. A similar optimization of black chrome coatings on nickel-plated steel showed very good stabilities, yielding solar absorptances in excess of 0.94 even after 8 h at 450° C [30].

4. Black zinc

4.1. Structure of the coating

Following the thorough studies of zinc oxidation in sodium hydroxide and sodium nitrate electrolytes of Encheva [31], this coating system has received increasing interest in solar collector applications [32]. The structure of the optimum coatings has been reviewed in detail as consisting of zinc oxide crystallites by both TEM and RED, with an apparent constant oxygen concentration throughout the coatings as detailed by AES [33]. However, since the relationship between the concentration of covalently bonded zinc in the zinc oxide and the zinc Auger peak intensity is not well-defined, AES data do not yield much insight in the internal structure of the coating. SEM studies have found the oxide coatings to be typically from 0.5 to 1.0 μm in thickness and relatively dense. The surface morphology has been shown to consist of spherical oxide particles [34].

TEM has provided polycrystalline zinc oxide patterns and shown evidence of spherical ZnO particles of approximately 100 nm size. However, no evidence for dispersed crystalline zinc particles embedded in the coating has been found. Electron diffraction techniques show instead an abrupt change from a microcrystalline oxide to a large-crystal zinc substrate when ion-milled [19]. Since the optical properties of this coating clearly require a refractive index gradient to be present, this can only be explained by either assuming a very rough zinc–zinc oxide interface or by considering large changes in the absorption coefficient of zinc oxide by zinc additions on an atomic level [35]. Since the solubility limit of zinc in ZnO at room temperature corresponds to only a few hundred atomic p.p.m. [36], this would account for the absence of a zinc gradient in the electron diffraction and AES data.

One of the major problems associated with the analysis of this coating has been the low resistance of zinc oxide and zinc to chemical attack. Since the coating cannot easily be removed from its substrate without also removing some of the zinc in the coating, TEM cannot be successfully applied to the complete characterization of this coating, and much work is still necessary to describe the mechanism that leads to optical selectivity in this system.

4.2. Optimization of black zinc

Oxide coatings specifically designed for solar collector applications were investigated for their selective properties and optimized in terms of deposition parameters for the best optical properties. Van der Leij [32] first investigated black zinc oxide as a solar-selective surface and analysed its resistance to thermal and ultraviolet exposures. The best selective surface was obtained on polished leaf-zinc in a solution consisting of 30 g l^{-1} NaOH, 20 g l^{-1} $NaNO_3$ and 5 g l^{-1} $NaClO_2$ at a bath temperature of 40° C and a current density of 20 A dm^{-2}. These conditions were very similar to the ones described by Encheva [31], except that $NaClO_2$ was added as an additional oxidizing agent. Homuhal *et al.* [34] found a similar optimum at lower hydroxide and higher nitrate concentrations, using optical selectivity as an optimization parameter. Absorptances exceeding 0.97 at emittances of 0.2 could be obtained by Mabon and Inal [33], who oxidized leaf-zinc substrates using alternating current. They describe the optical quality of the coatings through a regression technique, observing that the chlorite addition does not contribute favourably to the optical properties. Direct current anodization in a similar NaOH–$NaNO_3$ electrolyte was also found to yield absorptances in excess of 0.97 after heat treatment, and similar equations were derived from regression analyses that describe the response surfaces for the coatings [37]. Also, the coating was found to have comparable as-plated properties when zinc plated on aluminium was anodized, although the thermal stability of such coatings was somewhat lower [38]. Previous thermal stability tests have concluded that coatings on leaf-zinc substrates possess good thermal stability at 250° C [39] at low humidity, whereas coatings on aluminium substrates are thermally stable to 200° C.

5. Black copper

5.1. Structural analysis

Coatings consisting of oxidized copper would be very attractive for photothermal collector application because of the high thermal conductivity of the substrate and the cuprous oxide band-gap energy (E = 2.1 eV) [40], which is close to the optimum cut-off wavelength of an ideal collector (E = 0.5 eV). Thermal oxidation forms a two-layer cuprous–cupric oxide stack above 700° C and the resulting solar absorptances are quite low, ranging from 0.5 to 0.7 at emittances exceeding 0.5 [41]. Although possible methods of improving such optical properties could be found by etching the copper substrate before oxidation, or subsequent etching of the oxide to induce a refractive index gradient to favour selective coatings, electrochemical copper oxidation is thought to be more successful in generating coatings with good optical properties [42]. Indeed, the optical properties resulting from the as-plated chemical or electrochemical oxides of copper are generally excellent [43], requiring very little optimization. However, one of the major problems of these coatings is an inherently low resistance to thermal exposure [44]. This factor has in the past precipitated a great deal of effort to limit the thermal degradation and to understand the attendant degradation mechanisms.

XRD and electrochemical titration experiments on copper oxide coatings, made in electrolytes composed of 10 wt % NaOH and 5 wt % $NaClO_2$ at 55° C [45], found evidence for the coating structures to consist of primarily cuprous oxide, with an average grain size of 0.2 μm, a smooth surface structure and only a thin cupric oxide overlayer [46]. In contrast to these results, Milgram [47] argues that coatings produced under similar conditions consist of mainly cupric oxide, since the optical properties of that oxide were found to correspond to the spectral reflectance response measured on black copper. The optical quality of the coatings was attributed to the unique surface geometry of the layers. Other studies confirm these observations in oxides produced with $NaNO_3$–NaOH electrolytes, which consist of primarily cupric oxide with very fragile surface layers [42].

SEM of black copper surfaces, generated by potassium persulphate and sodium nitrate solutions, usually reveals very porous or even needle-like deposits of cupric oxide. The thickness of this structure is generally about 1 μm, and the neddles are thought to grow on top of a thin epitaxial copper oxide layer close to the surface [19]. Due to the fragile nature of these coatings, TEM has not been possible and most of the structural information comes from SEM, RED, thermal gravimetric and reflection IR observations. When the coatings are ion-milled after deposition, RED patterns obtained from that milled zone show a compositional change from cupric to cuprous oxide close to the substrate [19].

Sodium chlorite electrolytes are known to produce relatively thicker, dense deposits which have been shown to consist of mainly cuprous oxide through X-ray analysis and AES [44]. Finally, copper oxide coatings produced by anodically oxidizing copper in a NaOH electrolyte at 70° C are seen to consist largely of cupric oxide with particle sizes of approximately 25 nm distributed randomly in a porous structure. The surface structure is seen to have a large influence on the optical quality of the coatings, as was found by Milgram [48] through deposition of gold layers on the coating structure [39].

Heat treatment, although completely altering the optical properties in the high-energy infrared region, does not change the apparent surface structure. However, SEM investigations have revealed a growth in the smooth copper oxide layer underlying the cupric oxide, which could contribute to an optical property change. In the visible range, heat treatment does not change the optical response; the latter still closely corresponds to the one given for cuprous oxide. The fact that the degradation is very substrate-dependent has been shown by Milgram [48], who completely oxidized copper evaporated on platinum substrates with only little change in the optical quality of the film.

5.2. Optimization of black copper

Black copper is, at present, commercially produced as a solar coating used "Ebonol C" [14, 49] solution, or a mixture consisting of $NaClO_2$ and NaOH. Other methods of producing selective copper oxide coatings include the use of NaOH and $K_2S_2O_8$ [42]. Such oxidation of copper normally proceeds through the precipitation of a copper oxide salt on the surface, which then decomposes to produce a copper oxide film.

The resulting optical properties of such electrochemically deposited coatings were found to depend on the oxidation time, temperature and current densities used during production. Furthermore, an increase in the concentration of oxidizing salts increased the number of nucleation sites of oxide growth [50], forming a correspondingly denser but thinner film with lower thermal emittances. Higher temperatures and increased NaOH content are seen to lead to high-absorptances of 0.99 at emittances ranging from 0.4 to 0.7 were reported for films formed in such solutions [42]. Finally, RED studies on chemically produced copper oxide have shown the growth of the oxide to proceed through the formation of a smooth cuprous oxide layer on the copper, on which the cupric oxide flakes are seen to grow. This porous layer then increases in thickness, and solar absorptances of 0.97 at emittances of 0.2 are obtained in the as-plated structures after an optimization of the oxidizing parameters [42].

If such coatings are exposed to elevated temperatures (180° C for 8 h), the optical properties degrade substantially and optimum absorptances of 0.89 at emittances of 0.1 results [42]. One method of decreasing such degradation was put forward by Li and Reid [51], who developed a chromate treatment which enhanced the resistance of $NaClO_2$–NaOH layers to thermal degradation. However, even this improved coating cannot be exposed to much above 100° C without substantial degradation.

6. Black cobalt

6.1. Structure of the coating

Cobalt oxide films are known to be superior to black chrome in stability [52], but suffer from poor adhesion strength. Generally, these coatings can be produced either by plating from an oxidizing solution on to directly deposited black cobalt coatings, or deposition of a pure cobalt layer on an inert substrate (i.e. nickel) and subsequent oxidation [53].

Oxidation of cobalt in air at elevated temperatures forms a black surface with a high solar absorptance. Since selectivity requires controlled thickness of the oxide, a rather thin layer of plated cobalt is generally thermally converted to the oxide at 400° C. A needle-like structure is found to emerge from the nodular as-plated cobalt coating structure during the thermal exposure. The needles are known to consist of Co(II, III) oxide crystallites, with a metallic cobalt layer separating them from the substrate [39].

Smith *et al.* [53] determined the structures of thermal black cobalt oxides with AES and XPS to consist of flake-like oxide protruberances on a CoO layer with an increase of the cobalt XPS peak on increased sputtering time. From that information, it was concluded that the black cobalt layer consists of a Co(II, III) oxide surface layer on top of a CoO and cobalt layer and the substrate. However, the AES data generated from cobalt oxide films provide a constant cobalt signal even when the nickel substrate has been sputtered through, an artefact which obsures quantitative information being obtained with this method [53].

At higher thermal exposure temperatures (i.e. 500° C), blunting of these oxide needles takes place and oxidation of the underlying substrate is associated with the drop in solar absorptance. The latter observation is supported by the fact that when plated on gold substrates, the black cobalt oxide films are generally very stable thermally [54].

6.2. Optimization of black cobalt

Cobalt oxide coatings formed by thermal oxidation of cobalt plated on nickel are found to be thermally stable up to 400° C. Typically, such coatings are found to exhibit absorptances of up to 0.98 at emittances of 0.4 [39]. Another method of cobalt oxide deposition is that of plating from a standard Watts or sulphate solution, with additions of oxidizing agents such as hydrogen peroxide or nitric acid. However, although McDonald and the SERI–CSM workers [54] have investigated such coatings and found absorptances of 0.9 at emittances of 0.2, these values are not very reproducible. Conversely, co-deposition of the cobalt and the oxide [55] was performed by Smith *et al.* [53], who reported a very flaky layer of cobalt hydroxide and cobalt oxide on the surface with solar absorptance of 0.98. These coatings tend to degrade considerably to values of 0.9, at best, after exposure to 450° C.

7. Iron oxide

Black iron coatings can be deposited using Ebonol S, a commercially available plating solution (Ethone Inc., Bridgeview, Illinois). The best optical properties reported by Mar *et al.* [56] consisted of solar absorptances of 0.85 at emittances of 0.08. Longer plating times, higher solution temperatures and higher solution concentrations could produce thicker coatings with a corresponding shift of the reflectance spectrum to the right, but higher solar absorptance values could not be achieved. This feature is explained by the fairly high refractive index of iron oxides, which causes large reflection losses at the surface of the coatings. If this surface is coated with a polymer, these losses are minimized and solar absorptances of 0.90 at higher emittances (0.4) could be attained. Such coverage was, however, only thought to provide a 2% increase in collector efficiency. The degradation observed in black iron after exposure to humid environments was limited to the formation of minor rust pinholes. To the authors' knowledge, no optimization programme has been carried out for the deposition of these coatings.

8. Black nickel

Black nickel, which has been studied extensively by Tabor [57], Jurisson [58], and several other investigators [59], is described as an Ni–Zn–S complex. Black nickel deposits are produced industrially by electrodeposition of nickel in the presence of zinc and sulphides. Tabor developed the first black nickel coatings on copper and nickel substrates in 1955. These coatings are known to possess solar absorptances of 0.94 at emittances of 0.06 [60], but these properties degrade substantially in humid environments. Deposits on copper substrates were found to be completely degraded after exposures to 200° C due to the oxidation of the copper [58].

There are a number of different black nickel plating solutions, of which only the sulphate and the chloride bath are suitable for plating of solar coatings. The major problem with the sulphate bath is the degradation of this electrolyte during the plating process [10], and thus the chloride bath is generally preferred.

The structure and composition of black nickel coatings has been investigated by Lin and Zimmer [60], who also performed controlled humidity experiments on both single- and double-layer black nickel coatings. AES data obtained show the initial coating to contain nickel, zinc, and their oxides and sulphides [60]. The surface structure of the resulting films was found by RED to consist of microcrystalline nickel and zinc oxides, with crystallite sizes well below 30 nm. Other work by Patel *et al.* [61] showed that the degradation of black nickel on copper at low temperatures was primarily due to the oxidation of the sulphur, whereas at higher temperatures substrate oxidation could be observed. Optimized solar absorptances after heat treatments of 200 h at 200° C provided solar absorptances above 0.95 at emittances of 0.25. However, these optimized coatings are also expected to substantially degrade upon humidity exposures.

9. Pigmented aluminium oxide

9.1. Structure of the coating

Although pigmented aluminium oxide coatings are commercially used as solar collectors, they are generally not considered to be very selective [62]. However, little research has been conducted on thin films of pigmented anodized aluminium for solar collector purposes. Selective coatings can be produced from aluminium oxide by intrinsic colouration of aluminium during anodization, by adsorption–precipitation pigmentation, or by electrolytic deposition of metal into pores of the anodic film [63]. Previous research on adsorption–precipitation pigmentation, of cobalt sulphide into aluminium oxide coatings provided initial solar absorptances of 0.96 at emittances of 0.2. However, these layers were found to possess very little resistance to even mild (150° C) thermal degradation [7]. Nickel pigmentation of aluminium oxide was also investigated, and the resulting layer was modelled using an effective medium approach. Preliminary studies show that with absorptances above 0.96 and emittances of 0.25, such coatings are very promising and reasonably stable. However, long-term thermal stability tests have to be completed before this kind of pigmented oxide film can be compared to other coatings [64]. Finally, since the structure of anodized aluminium has previously been described in detail as a function of the anodizing conditions [65], optical models of the coating

TABLE I Decomposition conditions and properties of films

Coating	Substrate	Electrolyte	Conditions	Optical Properties		References
				Absorptance	Emittance	
Black chrome (plated)	Nickel	Chromic acid 327 to 337 g l^{-1} Addition agent 24.5 to 26 g l^{-1}	140 to 190 mA cm^{-2} 3 to 5 min 15 to 20° C	0.97 0.94 after 8 h at 450° C	0.12 0.1	[30]
Black chrome (plated)	Copper	Chromic acid 24 vol % Addition agent 345 g l^{-1}	26 A dm^{-2} 4 min 18° C	$\geqslant$0.97 0.97 after 8 h at 450° C	0.46 0.22	[25]
Black zinc (anodized)	Zinc	NaOH 15 g l^{-1} $NaNO_3$ 15 g l^{-1} Zn 0.52 g l^{-1}	14 A dm^{-2} 47° C	$\geqslant$0.97 0.96 after 320 h at 300° C	0.27 0.22	[33]
Black zinc (anodized)	Zinc-plated aluminium	NaOH 12.8 to 14 g l^{-1} $NaNO_3$ 15 to 40 g l^{-1} $NaClO_2$ 0 to 10 g l^{-1}	8 A dm^{-2} 33 to 42° C 1.5 to 2.0 min	$\geqslant$0.98 0.96 after 200 h at 200° C	0.14 0.12	[38]
Black copper (oxidized)	Copper	NaOH 60 g l^{-1} $K_2S_2O_8$ 20 g l^{-1}	7.5 min 60° C	0.97 0.83 after 900 h at 160° C	0.17 0.10	[42]
Black cobalt (plated–oxidized)	Nickel	$CoSO_4 \cdot 7H_2O$ 450 g l^{-1} Boric acid 33 g l^{-1} KCl 16 g l^{-1}	Plated 8 min, 36° C 350 A m^{-2} Oxidized 400° C	0.96 0.96 after 200 h at 450° C	$\geqslant$0.40 0.40	[53]
Black nickel (plated)	Copper	NaCNS 8 to 12 g l^{-1} $NiCl_2$ 80 to 100 g l^{-1} NH_4Cl 10 to 30 g l^{-1} $ZnCl_2$ 20 to 30 g l^{-1}	1.2 to 1.5 A dm^{-2} 0.63 to 0.7 min 20 to 30° C	$\geqslant$0.97 0.95 after 200 h at 200° C	0.50 0.25	[61]

structure as well as the degradation phenomena can be characterized in a straightforward manner.

10. Discusssion and conclusions

Deposition and properties of films are collected in Table I. Optimization of electrodeposited coatings enables not only the definition of the optimum plating regions and the relative importance of the plating variables, but also gives an indication of the reproducibility of the properties of the deposits. Indeed, most of the above-mentioned electrochemically formed coatings can reproducibly provide high solar absorptances at low thermal emittances at relatively low cost. Finally, if a multilinear regression is used, the optimization routine can also generate empirical relationships between structure (dependent on plating parameters) and the optical property of a given coating. This information is quite necessary before meaningful analysis can be performed, since (as can very effectively be seen in the case of black copper or black chrome), different plating conditions can provide completely different microstructures. Since information on the structures and prediction of these is only desired for optimized coatings, optimization provides the natural precursor to any structural analysis.

Information has been generated on the strucures of important oxide coatings that are potentially useful for solar collector applications. The surface morphology of these coatings has been described and, although it is often very difficult to analyse the internal structures of these complex oxides, some direct and indirect observations have been cited that qualitatively characterize the attendant mechanisms yielding selective behaviour. TEM analysis has, for example, provided direct insight into black chrome coating structures and given a description of the particle sizes and internal compositions of these layers. Other approaches to deduce such information, which were used on black zinc, black cobalt and black copper films, consist of the description of the film growth sequence and subsequent ion-milling of the coatings to define the resulting structures [39]. AES and XPS studies on black nickel and black chrome have also provided detailed information on the film structure as well as the chemical species constituting the film. All of these structural analysis methods have thus contributed to qualitative development of structural models of the coatings, but none allow verification in a quantitative manner.

Since the optimum coatings in most of these oxide systems are less than 1 μm in thickness and exceedingly complex, the resolution limit of most surface-analysis techniques is pushed to the limit. Therefore, it is necessary to make use of the unique spectral reflectance behaviour inherent in these coatings which provides the selective behaviour. This information can be used to verify that a presumed structural model indeed reproduces the measured reflectance behaviour.

In the black chrome and pigmented alumina systems, modelling of the optical properties has successfully been applied by Granqvist and Niklasson [66] and Ignatiev *et al.* [16] by assuming a simple structural model, calculating the reflectance against wavelength response and matching this to the experimentally observed one. Since several different structures can be used to reproduce such reflectance responses, a novel approach has been taken by Sweet *et al.* [67]. who modelled the changes in the optical properties of black chrome coatings during heat treatment. This approach allows more confidence to be placed in the resulting model.

Although such optical modelling has been very successful in obtaining structural information of selective coatings, there are several problems inherent in this approach. Since "effective medium approximations", which are generally used to provide the relationship between the dielectric properties of a composite coating to its structural constituents, rely on distinct regions of definable dielectric constants, doped semiconductive films are very difficult to treat by such modelling. Therefore, many of the above-mentioned oxide coatings require very careful insight [68] before optical modelling can be performed. Furthermore, the optical data of the individual constituents are often not readily available or too imprecise to use for modelling purposes. However, provided that the thin films of interest are described in enough detail, such limitations can be overcome with relative ease. Indeed, the microstructures of most of the above-mentioned absorber coatings are understood to the extent that allows for optimal modelling.

In conclusion, the mechanisms contributing to selectivity in electrodeposits or anodically produced oxides commonly used for solar absorber surfaces have been defined through microstructural analysis. To allow for quantitative insight as well as a comparison of thermal degradation behaviour and the optical performance among these deposits, however, optical modelling as well as more precise analysis of the coatings (through Rutherford back-scattering spectroscopy or secondary ion mass spectroscopy, SIMS) have to be undertaken.

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References

1. B. O. SERAPHIN, in AIP Conference Proceedings No. 40, edited by J. C. Garland and D. B. Tanner (American Institute of Physics, New York, 1978).
2. O. T. INAL, J. C. MABON and C. V. ROBINO, *Thin Solid Films* **83** (1981) 399.
3. G. ZAJAC and A. IGNATIEV, *J. Vac. Sci. Technol.* **16** (1979) 233.
4. R. B. STEPHENS and G. D. CODY, *Thin Solid Films* **45** (1977) 19.
5. C. G. GRANQVIST and O. HUNDERI, *Phys. Rev.* **B16** (1977) 1353.
6. G. ZERLAUT, in "Critical Materials Problems in Energy Production", edited by C. Stein (Academic Press, New York, 1976) p. 899.
7. A. SCHERER and O. T. INAL, *Thin Solid Films* **101** (1983) 311.
8. A. B. MEINEL and M. P. MEINEL, "Applied Solar Energy – An Introduction" (Addison-Wesley, Reading, Massachusetts, 1979) p. 279.
9. I. T. RITCHIE and B. WINDOW, *Appl. Optics* **16** (1977) 1438.
10. R. B. PETTIT and R. R. SOWELL, *J. Vac. Sci. Technol.* **13** (1976) 596.
11. R. A. BUHRMAN and H. G. CRAIGHEAD, in "Solar Materials Science", edited by L. E. Murr (Academic Press, New York, 1980), p. 294.
12. C. M. LAMPERT, *Thin Solid Films* **72** (1980) 73.
13. O. T. INAL, M. VALAYAPETRE, L. E. MURR and A. E. TORMA, *Solar Energy Mater.* **4** (1981) 333.
14. H. C. HOTTEL and T. A. UNGER, *Solar Energy* **3** (1959) 10.
15. G. McDONALD, "A Survey of Coatings for Solar Collectors", NASA Technical Memorandum TMX–71830 (1974).
16. A. IGNATIEV, P. O'NEILL, C. DOLAND and G. ZAJAC, *Appl. Phys. Lett.* **34** (1979) 42.
17. L. E. MURR, O. T. INAL and M. VALAYAPETRE, *Thin Solid Films* **72** (1980) 111.
18. G. ZAJAC, G. B. SMITH and A. IGNATIEV, *J. Appl. Phys.* **51** (1980) 5544.
19. A. SCHERER and O. T. INAL, *Thin Solid Films* **119** (1984) 413.
20. M. VALAYAPETRE, O. T. INAL, L. E. MURR, A. E. TORMA and A. ROSENTHAL, *Solar Energy Mater.* **2** (1980) 177.
21. P. O. MAY, O. T. INAL and I. H. GUNDILER, *ibid.* **9** (1983) 253.
22. G. ZAJAC and A. IGNATIEV, *ibid.* **2** (1980) 239.
23. P. H. HOLLOWAY, K. SHANKER, R. B. PETTIT and R. R. SOWELL, *Thin Solid Films* **72** (1980) 121.
24. O. T. RICHIE, S. K. SHARMA, J. VILIGRAF and J. SPITZ, *Solar Energy Mater.* **2** (1980) 167.
25. J. C. MABON, O. T. INAL and A. J. SINGH, *ibid.* **7** (1982) 357.
26. A. IGNATIEV, P. O'NEIL and G. ZAJAC, *ibid.* **1** (1979) 69.
27. C. M. LAMPERT and J. WASHBURN, *ibid.* **1** (1979) 81.
28. J. N. SWEET and R. B. PETTIT, "Optical Modeling of Black Chrome Solar Selective Surfaces", SAND–82–0964 (Sandia National Laboratory, New Mexico).
29. G. ZAJAC and A. IGNATIEV, *Appl. Phys. Lett.* **41** (1982) 435.
30. R. B. PETTIT, R. R. SOWELL and I. J. HALL, *Solar Energy Mater.* **7** (1982) 153.
31. M. A. ENCHEVA, *J. Appl. Chem. USSR* **45** (1972) 318.
32. M. VAN DER LEIJ, *J. Electrochem. Soc.* **125** (1978) 1361.
33. J. C. MABON and O. T. INAL, *Thin Solid Films* **115** (1984) 51.
34. C. HOMUHAL, O. T. INAL, L. E. MURR, A. E. TORMA and I. GUNDILER, *Solar Energy Mater.* **4** (1981) 309.
35. G. HEILAND, E. MOLLWO and F. STOECKMANN, in "Solid State Physics", Vol. 8, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1959) p. 193.
36. K. I. HAGEMARK and P. E. TOREN, *J. Electrochem. Soc.* **122** (1975) 993.
37. P. O. MAY and O. T. INAL, to be submitted (1985).
38. S. N. PATEL and O. T. INAL, *Thin Solid Films* **113** (1984) 47.
39. A. SCHERER and O. T. INAL, *ibid.* (1984) 112.
40. J. BLOEM, *Philips Res. Rep.* **13** (1958) 167.
41. D. L. DOUGLASS and R. B. PETTIT, *Solar Energy Mater.* **4** (1981) 383.
42. A. SCHERER, O. T. INAL and A. J. SINGH, *ibid.* **9** (1983) 139.
43. D. K. EDWARDS, J. T. GIER, K. E. NELSON and R. D. REDDICK, *ibid.* **6** (1962) 1.
44. A. ROOS, B. WESTERSTRANDH, A. KAMF, R. SUNDBERG, S. E. HOERNSTROEM, L. PETTERSON and S.-E. KARLSSON, *Thin Solid Films* **90** (1982) 411.
45. A. A. MIGRAM, *J. Appl. Phys.* **54** (1983) 3640.
46. A. F. REID and A. F. WILSON *Solar Energy Prog. Austr. N.Z.* (1974) 23.
47. A. A. MILGRAM, *J. Appl. Phys.* **54** (1983) 1053.

48. *Idem, ibid.* **54** (1983) 4692.
49. D. M. MATTOX and R. R. SOWELL, *J. Vac. Sci. Technol.* **11** (1974) 793.
50. V. L. LAINER and N. T. KUDRYATSEV, "Fundamentals of Electroplating 2," 3rd Edn, (US Department of Commerce, New York, 1957) p. 192.
51. C. LI and A. F. REID, "Amcro Solar Selective Surfaces: Composition and Formation", CSIRO Report (Commonwealth Scientific and Industrial Reasearch Organization, Australia, 1979).
52. P. KOKOROPOULOS, E. SALAM and F. DANIELS, *Solar Energy* **3** (1959) 19.
53. G. B. SMITH, A. IGNATIEV and G. ZAJAC, *J. Appl. Phys.* **51** (1980) 4186.
54. G. McDONALD, *Thin Solid Films* **72** (1980) 83.
55. L. D. BURKE and O. J. MURPHY, *Electroanal. Chem.* **112** (1980) 379.
56. H. Y. B. MAR, R. E. PETERSON and P. B. ZIMMER, *Thin Solid Films* **39** (1976) 95.
57. H.TABOR, in "Low Temperature Engineering Applicatiuons to Solar Energy", edited by R. C. Jordan (New York, 1969) p. 41.
58. J. JURISSON, R. E. PETERSON and H. Y. B. MAR, *J. Vac. Sci. Technol.* **12** (1975) 1010.
59. R. E. PETERSON and J. W. RAMSEY, *ibid.* **12** (1975) 174.
60. R. J. H. LIN and P. B. ZIMMER, "Optimization of Coatings for Flat-Plate Solar Collectors", Phase II (Honeywell Inc. Systems and Research Council, Minneapolis, 1977) p. 85.
61. S. N. PATEL, O. T. INAL, A. J. SINGH and A. SCHERER, *Solar Energy Mater.* **11** (1985).
62. L. W. MASTERS, J. F. SEILER, E. J. EMBREE and W. E. ROBERTS, "Solar Energy Systems – Standards for Absorber Materials", NBSIR Report 81–2232, (US National Bureau of Standards, 1981).
63. K. WADA, T. HATANO and K. UCHIDA, *J. Appl. Electrochem.* **9** (1979) 445.
64. A. ANDERSON, O. HUNDERI and C. G. GRANQVIST, *J. Appl. Phys.* **51** (1980) 754.
65. W. HUEBNER and C. T. SPEISER, "Die Praxis der Anodischen Oxidation des Aluminiums", 3rd Edn. (Aluminium Verlag, Duesseldorf, 1977).
66. C. G. GRANQVIST and G. A. NIKLASSON, *J. Appl. Phys.* **49** (1978) 3512.
67. J. N. SWEET, R. B. PEITIT and M. B. CHAMBERLAIN, *Solar Energy Mater.* **10** (1984) 251.
68. R. W. BALLUFFI, C. B. DUKE, L. L. KAZMERSKI, K. W. MITCHEL, R. REIFENBERGER and R. F. WOOD, *Mater. Sci. Eng.* **53** (1983) 93.

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