



# Spectroscopic characterization of Al<sub>2</sub>O<sub>3</sub>-Ni selective absorbers for solar collectors

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Received 20 February 1997; received in revised form 20 June 1997

## Abstract

Optical spectroscopy of electrochemically prepared Ni-pigmented aluminum oxide selective absorbers have been determined in the 200–20000 nm range. It was found that samples anodized under the same conditions and pigmented using nickel acetate resulted in better thermal emittance values when compared with nickel sulfate although both have comparable solar absorbance values. Electron spectroscopic investigation revealed that only a small fraction of Ni is present on the surface with an oxidation state of  $\geq + 2$ . The O/Al ratio determined by XPS is larger than 1.5. This information together with the measured Al 2p Auger parameter indicated that the surfaces contain additional OH groups which was also confirmed by the presence of a broad hydrogen-bonded band in the region 3000–3400 cm<sup>-1</sup> observed in the reflection-absorption IR spectra of these samples. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Spectroscopic characterization; Selective absorbers

## 1. Introduction

One of the appropriate techniques for obtaining an absorber coating with selective optical properties for solar collectors is electrodeposition of metallic films. The

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process provides coatings for large surfaces without the need for complicated/expensive equipment and/or raw materials. An important concern in the study of selective solar collector coatings has been the understanding of mechanisms of selectivity for systems with high solar absorbances and low thermal emittances. Internal film structures including thickness and porosity of the oxide coatings have a very strong influence on the optical properties [1–6]. Anodized pigmented aluminum is the most common material and salts of transition metals like Ni, Co, etc. are used for pigmentation. Anodization is usually carried out either in phosphoric or a mixture of phosphoric and sulfuric acids both of which produce a porous aluminum oxide structure with the pores perpendicular to the aluminum surfaces. During pigmentation these pores are filled with the transition metals most of which lie at the bottom of the wells away from the surface. Depth profiles using Auger Electron Spectroscopy (AES) [7] and Glow Discharge Optical Emission Spectrometry (GDOES) [8] revealed a small concentration of Ni or Co on the surface which increased on moving away from the surface and reached the highest values near the aluminum oxide/aluminum metal interface. XPS studies on Co-pigmented aluminum indicated that cobalt is partially in metallic form [7]. In our earlier studies, the solar absorption/thermal emittance values have been optimized regarding solar selectivity using nickel sulfate or nickel acetate for pigmentation [9]. Values of 0.91/0.09 and 0.93/0.15 have been obtained for nickel sulfate and nickel acetate, respectively, which compare well with reported ones [6]. However, the optimized conditions corresponded to different oxide thicknesses for acetate and sulfate. In the present study, aluminum has been oxidized under identical conditions for both of the nickel-pigmentation processes in order to eliminate the well-known effect of the oxide thickness on the properties. Analyses with regard to (i) surface versus bulk composition and (ii) the chemical state of Ni on the surfaces of Ni-pigmented aluminum selective coating have been carried out.

## **2. Experimental**

Aluminum samples consisting of  $3 \times 2$  cm flat pieces were subjected to a chemical polishing treatment consisting of alkaline (NaOH) and acid etchants ( $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ ). Anodization was achieved in phosphoric acid solution using a classical double-walled three-electrode cell coupled to an EG&G 273 Potentiostat–Galvanostat system at a current between 25–30 mA. Pigmentation was achieved using either 0.3 M nickel sulfate or acetate salts at a constant temperature of 20°C [9]. The pigmentation time was kept between 6–8 min and an AC voltage between 12–17 V was chosen.

Optical reflection/emission properties of the samples were characterized using a Jasco V500 spectrophotometer equipped with an ILN-472 integrating sphere in the UV-Visible range and a Jasco FTIR/700 and RSA-FTIR 6 in integrating sphere combination in the IR. The reflectance of the samples was recorded using a gold sphere blank as a reference. Surface characterization using XPS measurement were performed on samples cut to  $4 \times 10$  mm dimensions using a Kratos ES300 spectrometer with Mg  $K_{\alpha}$  X-rays (1253.6 eV). X-ray-induced photo and Auger electron

spectra of Al metal,  $\text{Al}_2\text{O}_3$  (sapphire), anodized aluminum together with Ni-pigmented aluminum oxide samples were recorded. For bulk analysis of the samples SEM-EDS (energy dispersed spectrometry) was used.

### 3. Results and discussion

Variation of the potential during the application of constant current gives some idea about the oxide layer formation as shown in Fig. 1a. The steep rise at the onset is due to the barrier oxide layer formation on aluminum. The decrease in the potential after formation of a certain oxide thickness has been interpreted as a transformation to the porous phase through which some electrical conduction can be achieved. Fig. 1b shows the reflectance of a Ni-pigmented sample using nickel acetate in the 200–20000 nm region which is used to calculate the solar absorbance,  $\alpha$ , between 300

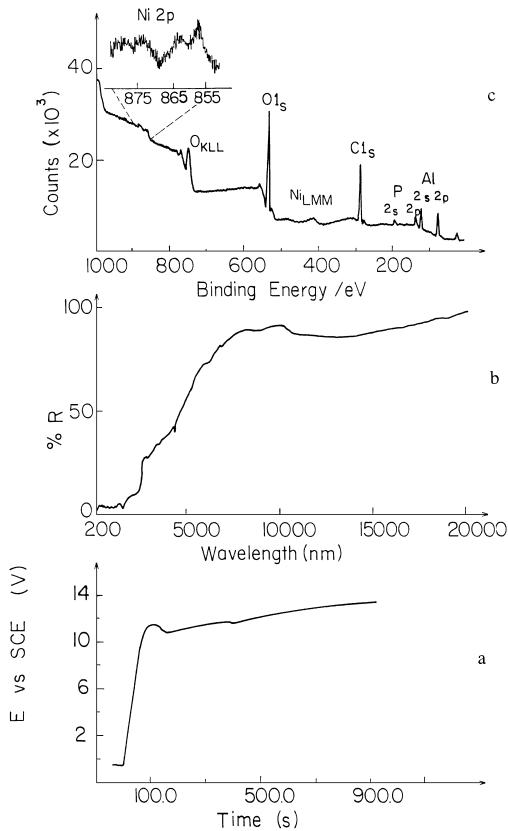


Fig. 1. (a) Variation of the anode potential as a function of time during oxidation of aluminum at 30 mA in phosphate solution. (b) Reflectance of the same sample in 200–20000 nm range. (c) XPS spectrum of the same sample.

Table 1

Solar absorbance ( $\alpha$ ) and thermal emittance ( $\epsilon$ ) values together with the Ni/Al atomic ratios using XPS and SEM-EDS

	$\alpha$	$\epsilon$	Ni/Al atomic ratio	
			XPS (surface)	SEM-EDS (bulk)
NiSO <sub>4</sub>	0.95	0.41	0.10	1.8
Ni(Ac) <sub>2</sub>	0.93	0.16	0.04	0.6

Table 2

Measured binding and kinetic energies of various peaks together with their atomic ratios

	O1s (BE, eV)	Al2p (BE, eV)		Al KLL (KE, eV)		Auger parameter (BE + KE, eV)		Atomic ratios	
		Al <sup>+3</sup>	Al <sup>0</sup>	Al <sup>+3</sup>	Al <sup>0</sup>	Al <sup>+3</sup>	Al <sup>0</sup>	O/Al <sup>+3</sup>	Ni/Al <sup>+3</sup>
Al (m)	531.8	75.7	73.0	1385.7	1393.1	1461.4	1466.1	1.8	–
Al <sub>2</sub> O <sub>3</sub>	531.2	74.4	–	1387.7	–	1462.1	–	1.6	–
Al (anod.)	531.9	75.6	–	1385.5	–	1461.1	–	1.8	–
Al (Ni-pigm.)	532.1	75.8	–	1385.7	–	1461.5	–	1.8	0.04

and 4000 nm, as well as the emittance,  $\epsilon$ , between the limits 2000–20000 nm of this sample [7]. The observed low reflectance values in UV–visible and increasing ones in IR ranges are the desirable parameters for a selective coating. The calculated values are  $\alpha = 0.93$  and  $\epsilon = 0.16$  for this sample and 0.95 and 0.41 for the sample prepared using nickel sulfate (Table 1). The data of Table 1 shows that high absorbance values could be obtained for both of the chosen nickel salts. However, the thermal emittance decreased considerably when nickel acetate salt was used. Although the aluminum oxide thicknesses are the same for both cases, an improvement in the thermal emittance from 0.41 to 0.16 will considerably increase the efficiency of a flat-plate collector. Fig. 1c depicts the X-ray photoelectron spectrum of the same sample. O 1s, C 1s, Al 2s and Al 2p are the major features and weak features due to O KLL Auger, Ni 2p, Ni LMM Auger and P 2s and P 2p peaks are also observed. Carbon is always present on the surface due to both hydrocarbon deposits and the presence of phosphorus is due to phosphoric acid used for anodization. The binding energies and other relevant data are given in Table 2.

Examination of Ni2p binding energies and surface composition reveals two facts: Firstly, the nickel to aluminum ratio is at least 15 times lower than that of the bulk composition determined by EDS. Secondly, the measured binding energy of Ni 2p is 856.6 eV which is higher than that of Ni 2p in NiO (854 eV) or metallic Ni (853 eV). The tabulated 2p binding energies for Ni<sub>2</sub>O<sub>3</sub> and Ni(OH)<sub>2</sub> are very close to each other at approximately 856 eV [10,11]. Variations in binding energies up to 1 eV depending on chemical/physical environment is usual, hence an exact assignment of the

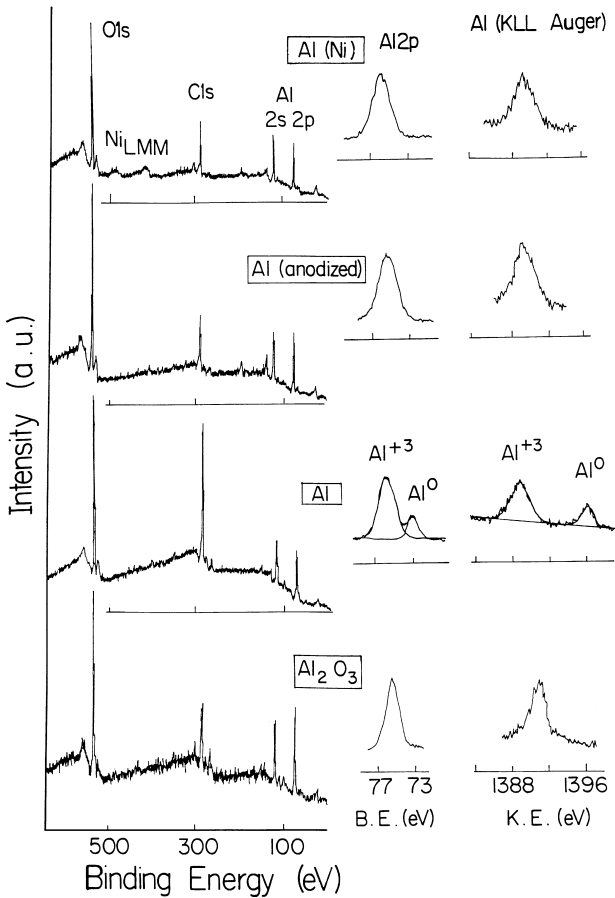


Fig. 2. XPS spectra of Al (metal),  $\text{Al}_2\text{O}_3$  (sapphire), anodized and nickel-pigmented aluminum.

oxidation state of nickel is difficult, but, it is definitely not in the metallic state on the surface and has an oxidation state of at least +2 or higher. This is consistent with our studies on Co and Cr pigmented selective surfaces. In our XPS analyses no metallic cobalt or chromium could be identified [12].

In Fig. 2, the electron spectra of  $\text{Al}_2\text{O}_3$ , Al metal, anodized aluminum and Ni-pigmented aluminum are given. Except in the case of the metal, only a single oxide peak is observed. The metal contains approximately 40 Å of native oxide layer on the surface, hence, the zero-valence metal peak underneath also shows up [10,11]. The absence of the zero-valence peak is an indication that the oxide/pigment layer on top of the aluminum substrate is thicker than 100 Å which is a typical sampling depth in XPS. The observed O/Al atomic ratio is close to the stoichiometric value of 1.5 in the  $\text{Al}_2\text{O}_3$ , but is much larger in the others. The Auger parameter (the sum of binding and kinetic energies) of the Ni-pigmented sample is also similar to that of anodized one

rather than to that of  $\text{Al}_2\text{O}_3$ . Furthermore, the IR reflection/absorption bands (not shown) of anodized and pigmented samples are similar and contain a broad hydrogen-bonded OH band in  $3000\text{--}3400\text{ cm}^{-1}$  region. The presence of extra OH moieties is also consistent with the greater than 1.5 O/Al ratio measured by XPS.

Although the aluminum oxide thicknesses are the same for both cases, an improvement in the thermal emittance from 0.41 to 0.16 will considerably increase the efficiency of a flat-plate collector. Comparing these two samples according to their emissivity values it is observed that the emittance increases about 2.5 times with increasing Ni/Al ratios of the same order both on the surface and in the bulk. An interesting result of this work is the reconfirmation of the marked difference between the surface and bulk compositions of nickel and aluminum in relation to solar absorption and thermal emittance values. Nickel content should mainly be at the bottom of the oxide pores and nickel on the surface may be a reason for radiation losses.

## Acknowledgements

This research was partly supported by NATO's Scientific Affairs Division within the framework of the Science for Stability Programme and partly by TÜBİTAK, the Scientific and Technical Research Council of Turkey through the grant TBAG-COST-1.

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