

Accelerated Heat Degradation Testing and Characterization of Nickel-Pigmented Aluminium Oxide Selective Absorber

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1. INTRODUCTION

Among the presently available energy resources, solar energy is considered one of the most easily or readily usable energy sources available anywhere on the earth, and thus there is demand to rapidly develop and establish technologies for effective utilization of the solar energy. The solar energy is generally obtained in the form of heat usually absorbed by a black surface, for example, a surface coated with a thin film of a black paint. While such a conventional heat absorbing surface or coating is efficient in terms of selective absorption of solar energy, its high emissivity nature creates a problem of energy loss, i.e., the solar energy or heat absorbed by such a surface tends to be emitted or radiated as infrared rays. To overcome the above disadvantage, it is important to develop a spectral-selective solar energy absorbing surface that is characterized by its high absorptance, α , of the solar energy, particularly in the visible and near-infrared regions, which is the major portion of the solar spectrum, as well as by its low hemispherical emissivity, ϵ , in the long wavelength (infrared) region. An ideal selective absorber would be a material that would absorb all the solar radiation without emitting. In practice a selective absorber can be considered good for total hemispherical emissivity $\epsilon \leq 0.20$ and absorptivity $\alpha \geq 0.90$.

Selective absorber surfaces can be obtained by, chemical [1], physical [2] and electrochemical [3] conversion of metallic surfaces such as stainless steel, zinc, copper and aluminium. Frequently anodized aluminium [4,5] is used as the matrix for encapsulation of metallic particles for the production of solar absorber materials. For example solar absorbers surfaces of nickel-pigmented aluminium oxide are produced by anodic oxidation of aluminium in phosphoric acid followed by electrochemical deposition of nickel particles in the pores of the alumina. The diameter of the aluminium pores can be as large as 30 nm and constitute up to 40% of the total volume. Such a large volume fraction of metal is suitable for obtaining high solar absorption.

In previous work [6], the effects of different impregnation parameters on the structural and optical properties of nickel pigmented alumina solar selective absorbers are described in details. In this study, the preparation, characterization, and degradation testing of nickel pigmented alumina selective solar absorbing films obtained with alternate current (ac) and reverse periodic current (rpc) technique are reported. The optical and microstructural properties of those films, with films prepared via ac impregnation technique are compared. The film stability is also investigated under high temperatures and humidity. There are so many studies were done on the thermal stability of selective absorber coatings deposited on different substrates [12].

2. EXPERIMENTAL

2.1 Substrates Preparation

A 1050a Aluminium alloy (99.95%) of rectangular shape sheet of 20 x 40mm² is used as the substrate. Samples are initially degreased in a bath made up of sodium hydroxide,

sodium carbonate and sodium gluconate for one minute. After that, a sodium hydroxide solution (25 g/l) is used for one minute (etching process).

In order to neutralize the surface, the substrate is immersed in a nitric acid bath (20%, v/v) for two minutes. All these stages, carried out at ambient temperature to enable us obtaining a satisfactory surface quality before anodic oxidation.

2.2 Anodization of Alumina

Anodic oxidation is carried out in a phosphoric acid solution. There are many experimental variables involved in the anodic oxidation of the Alumina such as: acid concentration, anodization voltage and time, etc. In order to obtain optimization of the anodization process we have made an exhaustive investigation of the effects of all these different parameters. The different oxidation parameters are reserved in the following ranges:

Acid concentration: $0.5 \text{ M} < X < 3 \text{ M}$

Anodization voltage: $5 \text{ V} < U < 25 \text{ V}$

Anodization time: $10 \text{ min} < t < 25 \text{ min}$

The anodization temperature was kept at 20°C and the electrodes distance of 4cm.

2.3 Nickel Impregnation

Nickel impregnation is carried out at ambient temperature, under ac (50 Hz) in nickel bath consisting of NiSO₄ (30 g/l), H₃BO₃ (20 g/l), (NH₄)₂SO₄ (20 g/l) and MgSO₄ (20 g/l). Reverse periodic current impregnation is performed in the same nickel solution under the following reverse periodic parameters: J_c = cathodic current density 1.0 A/dm^2 , duration 10 ms, J_a = anodic current density 0.50 A/dm^2 , duration 5.0 ms with different relaxation time t_r between the pulses.

2.4 Degradation Tests

Thermal stability tests of the samples were carried out in air. The samples were exposed to air for 48 h at different temperatures, 200°C, 250°C and 300°C. Condensation tests are carried out according to procedure reported by Wackelgard *et al.* [7]. In brief, the samples are placed (15 cm, exposed time 5 h) over hot water bath, 100°C, and the vapor condensed at the sample surface.

3. CHARACTERIZATION METHODS

3.1 Optical Properties

UV/vis/near IR spectra are diffuse reflectance. Diffuse reflection spectroscopy measurements in the UV/vis/near IR reign are carried out on a Jasco VERY-570 spectrophotometer equipped with an integrating sphere. Spectra are recorded at room temperature from 200-2000 nm with scanning speed of 100 nm/min using MgCO₃ as a reference. Hemispherical absorptivity, α , and emissivity, ϵ , are measured using absorptiometer and emissiometer (EL 510-520 ELAN INFORMATIQUE).

3.2 X-ray Diffraction

Powder X-ray diffraction (XRD) spectra are studied using a Rigaku RU-200B Rotaflex diffractometer operating in the Bragg configuration using Cu, K α radiation. Data are collected with a counting rate of 0.50° min⁻¹ and sampling interval of 0.01°. The accelerating voltage is set to 50 kV with a 150 mA flux.

3.3 Electron Microscopy

Scanning electron microscopy (SEM) images and Energy dispersive spectroscopy (EDS) are obtained using a JEOL GMC 6400 microscope at an acceleration voltage of 20 kV. The samples are dropped in 50 cc of phosphoric acid and 15 g of chromium trioxide at 75°C for 10 min. In the Transmission electron micrograph (TEM) analysis, a granule of the metal particles is placed on TEM copper grids coated with thin amorphous carbon.

4. RESULTS AND DISCUSSION

4.1 Preparation and Characterization

In order to compare the optical properties of different thin films, we will use some commonly quoted parameters for the selective surfaces such as hemispherical absorptance α and emissivity ε . The absorptivity, emissivity and the preparation conditions for different samples and nickel content are presented in Table I.

In ac plating, the impregnation process starts from threshold voltage higher than 6V and good selective absorbers are obtained at ca 9 V.

TABLE I

Alternate and Reverse Periodic Parameters with Corresponding Hemispherical Absorptivity, Emissivity and Percent Nickel Content for Selective Absorber Samples.

Sample	Preparation conditions	Hemispherical absorptivity	Hemispherical emissivity	Ni content (%)
A	ac-9V	0.95	0.16	28
B	rpc tr = 10 ms	0.92	0.11	26
C	ac-10 V	0.96	0.17	27
D	rpc tr =5ms	0.92	0.14	26
E	ac-14 V	0.97	0.23	31
F	rpc tr = 18ms	0.96	0.19	29

Note: ac, alternate current; rpc, reverse periodic current; tr, relaxation time.

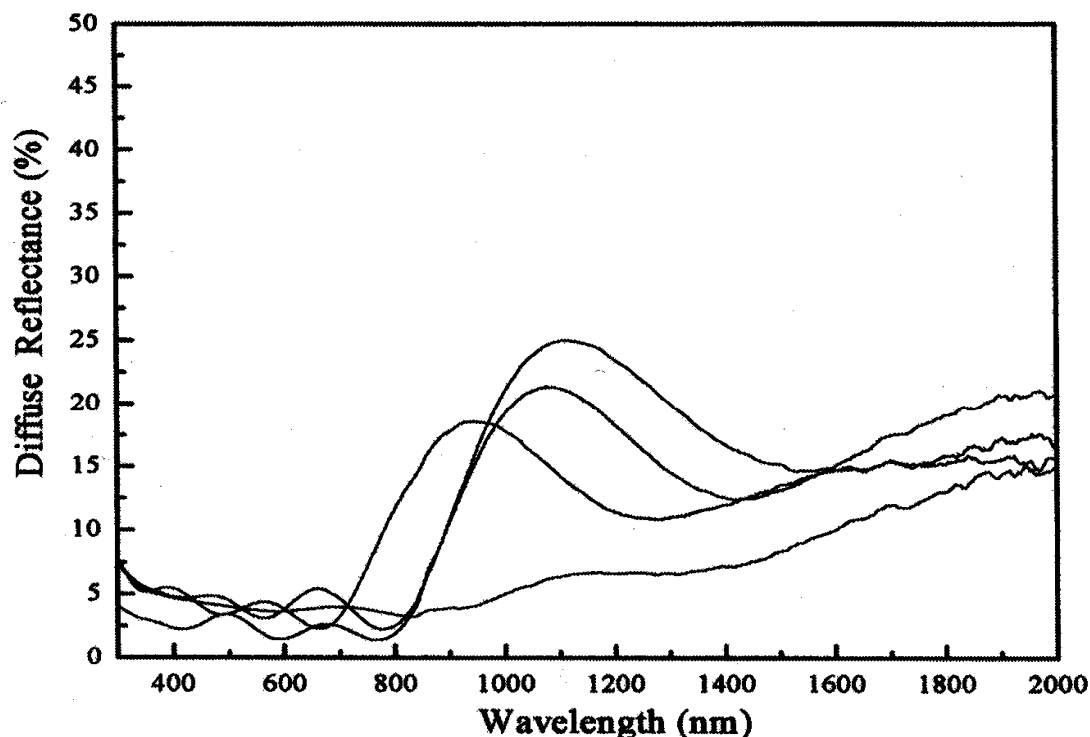


FIGURE 1 The diffused reflectance for the selective absorber samples over the solar range.

Figure 1 represents the diffused reflectance of different samples over the UV- Visible-near IR range (solar range) prepared using ac and rpc techniques for the impregnation process (electrolysis).

In general, high selective absorbers are obtained with reverse periodic technique. However, this strongly depends on the t_r between the cathodic/anodic pulses. For example the solar absorptivity and emissivity of samples plated at low $t_r = 5$ ms are relatively low in contrast to samples plated at high $t_r = 18$ ms (see Tab. I). The difference in optical properties of films deposited at various relaxation time can be attributed to many factors such as film microstructure, surface composition and morphology, film porosity, etc. Therefore, microstructure characterization of the different films is carried out.

Scanning electron microscopy surface image of films deposited under different relaxation time show almost identical surface morphology.

Figure 2 shows typical rough surface morphology of the films. At high magnification factor, the nickel particles appeared to be as thin sticks grown in the alumina pores.

We notice that, in the reverse periodic plating, more Ni particles are present on the surfaces and not in the pores.

Furthermore, X-ray diffraction of the deposited films does not add any information for the film structure. The peaks presented correspond to alumina, Aluminium substrate. No clear peaks are presented corresponding to nickel oxide. On the other hand, EDS results show high nickel content in films deposited at short t_r , for instance the Ni content in films electroplated at $t_r = 18$ ms is ca 29% while at short $t_r = 5$ ms, the Ni content in the film is ca 26%. There are few studies in the literature about the chemical composition and microstructure of nickel particles embedded in the alumina pores [8]. Most investigation [9], including the previous study [6], show that the nickel particles are in the metallic form and have the cast of the pore that embedded in.

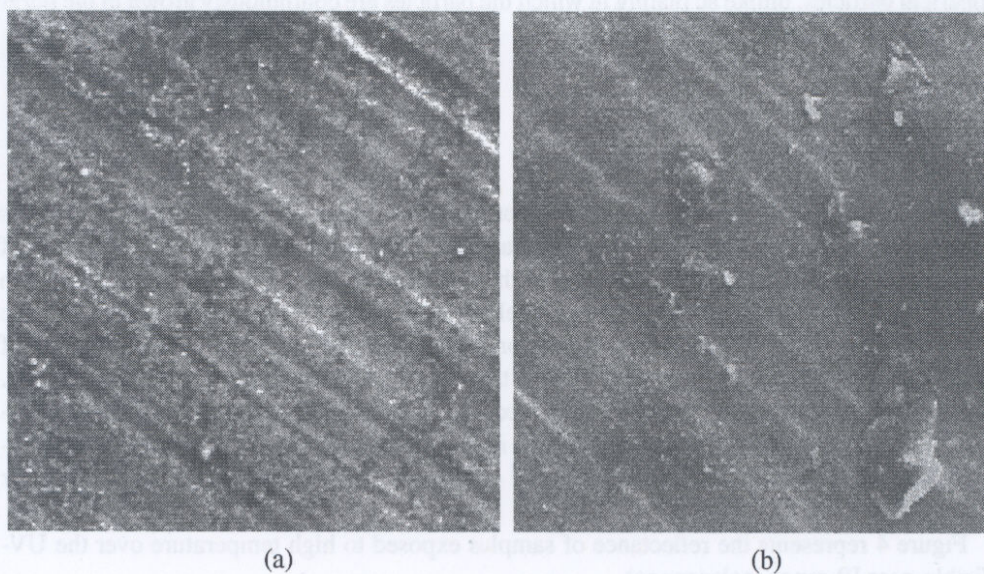


FIGURE 2 SEM of different surfaces for samples prepared by ac and rps techniques: (a) ac-normal (b) rpc-plating.

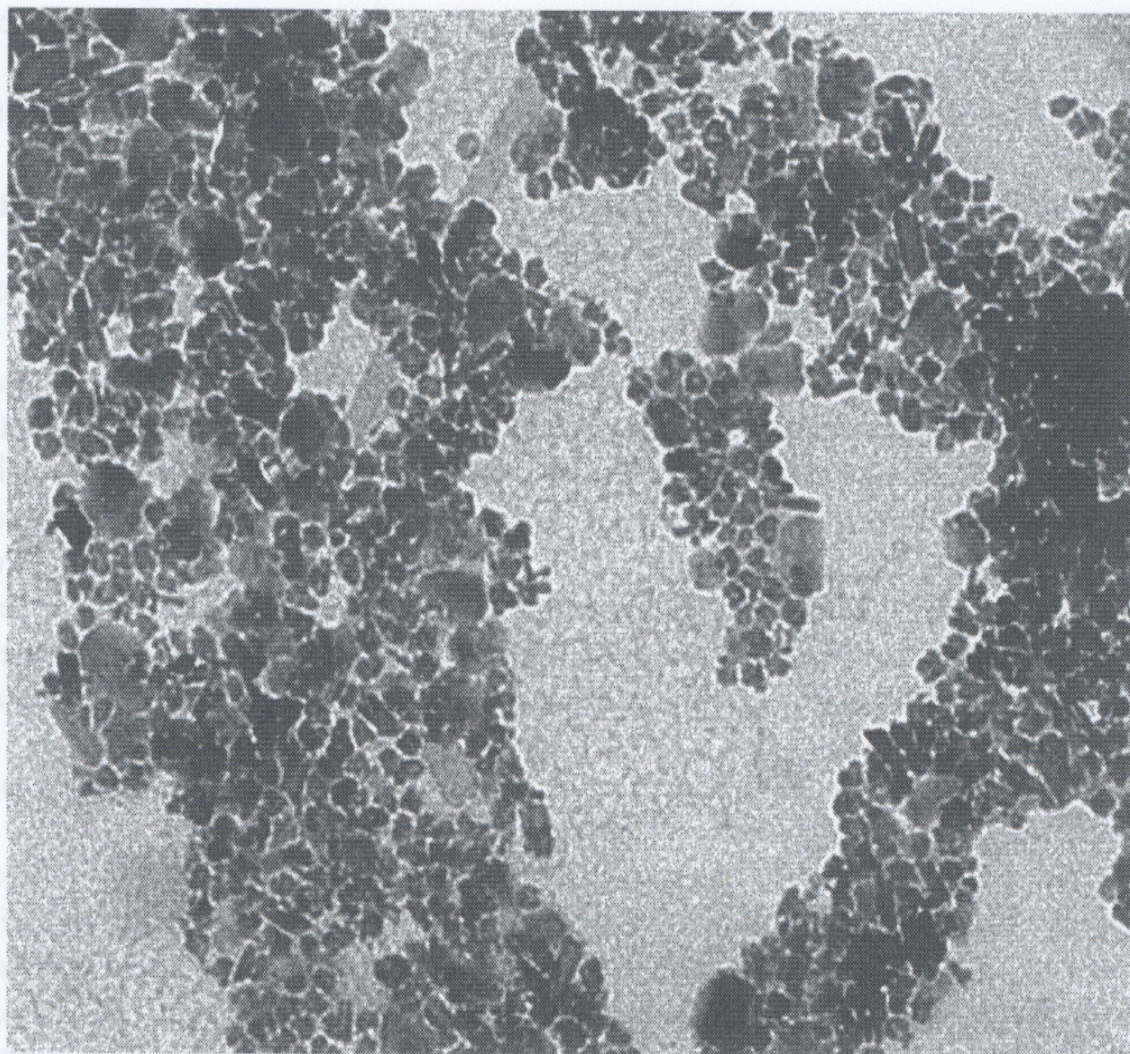


FIGURE 3 Transmission electron micrograph of Ni particles liberated for sample electroplated at long relaxation time.

Figure 3 represents the TEM image of nickel particles embedded in the alumina pores for sample electroplated at long relaxation time (sample F, $t_r = 18$ ms). The nickel particles are spherical or ellipsoid in shape, in contrast to the rod-like shape typically observed in films electroplated with ac. The average crystals size ranged from approximately 150-300 Å, which corresponded well with the alumina pores sizes. It should be noted that for films deposited at high relaxation time the average crystals size is bigger, 300-500 Å. The X-ray shows high degree of crystalline and the crystals electron diffraction rings is corresponding to metallic nickel. The small crystallinity and spherical shape can be realized as a result of the reverse periodic plating mechanism. For a long time, it has been known that pulse plating usually yields a finer grained deposit. The underlying principle of reverse periodic deposition is that the high current densities (as in our situation) induced fast nucleation rates on the substrate, giving, many small nuclei and thus smaller crystal size with spherical shape. The spherical shape is probably due to the relaxation time duration. During each pulse, the crystals can be grown by the deposition of new crystals or by the pre-existing nucleus. Additional pulses (in plating) introduced discontinuous in crystal growth, which can produce spherical particles, unlike ac plating in which the particles are continuously grown in the pores to form rod-like shape.

4.2 Degradation Test

The optical properties of solar absorber materials are varying with time because of various degradation processes [10]. The chemical stability of the nickel particles and hydration of the aluminium oxide are the prime cause of the degradation processes. The first degradation mechanism is the oxidation of metallic nickel which decreases the solar absorptance of the films, mainly at high temperatures. The second degradation mechanism is the hydration of aluminium oxide to boehmite ($\gamma\text{-AlO}\cdot\text{OH}$) or to pseudoboehmite ($\text{AlOH}\cdot\text{XH}_2\text{O}$, $X = 0.1\text{-}1$). This increases the thermal emittance which requires high humidity. Other degradation mechanisms are the electrochemical oxidation of nickel to nickel oxide or nickel sulfate. However, this mechanism is negligible in normal conditions and only present in high sulfur air pollution.

Figure 4 represents the reflectance of samples exposed to high temperature over the UV-Visible-near IR range (solar range). The fracture in the surfaces is seen clearly due to high temperature effect

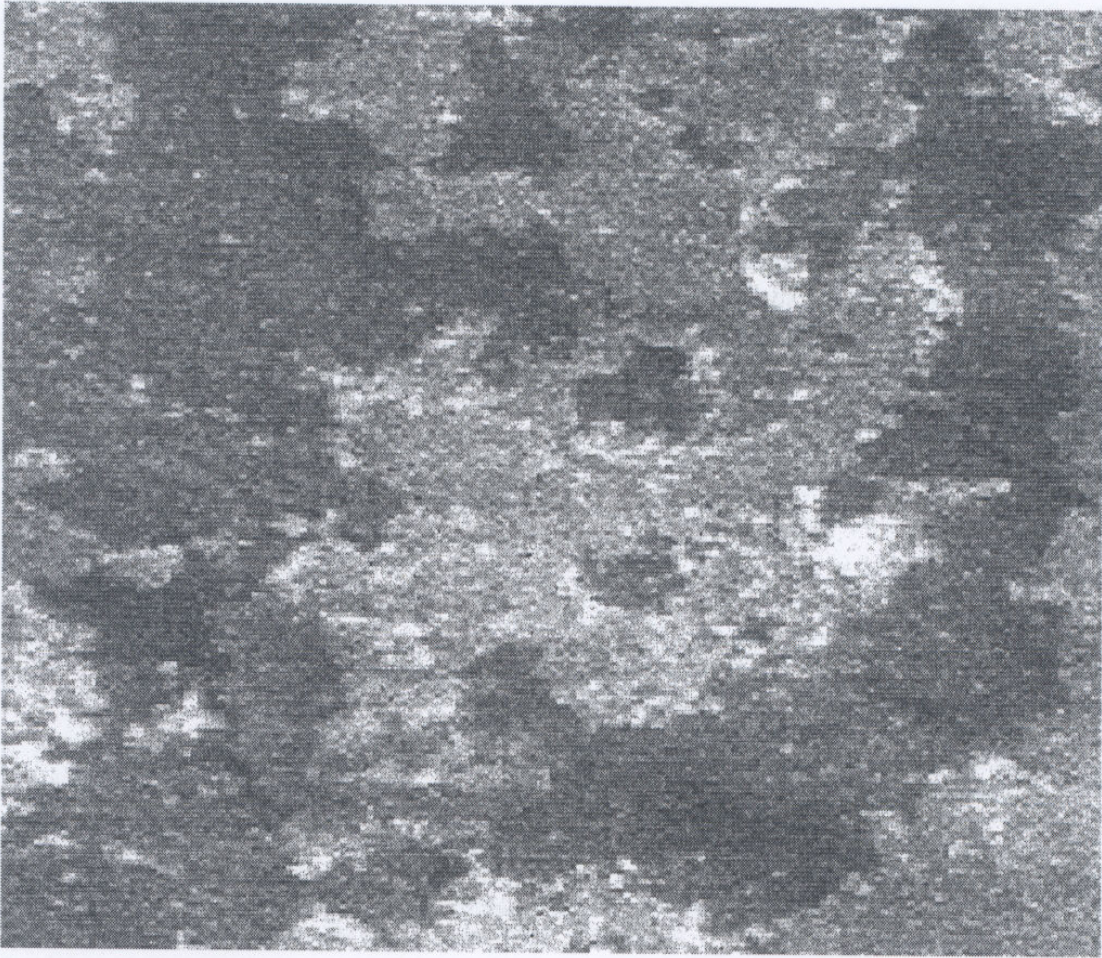


FIGURE 4 Scanning electron microscopy for the selective absorber samples after the exposure to air for 48 h at 300 °C.

The solar absorptivity is reduced in all films and a large reduction is observed in films electro-deposited at short relaxation time. The decrease of the solar absorptivity in films electrodeposited with ac technique is less significant than in reverse periodic-plated films.

As we see from Figure 5, X-ray peak at ca 53 is due to NiO (oxidization of nickel).

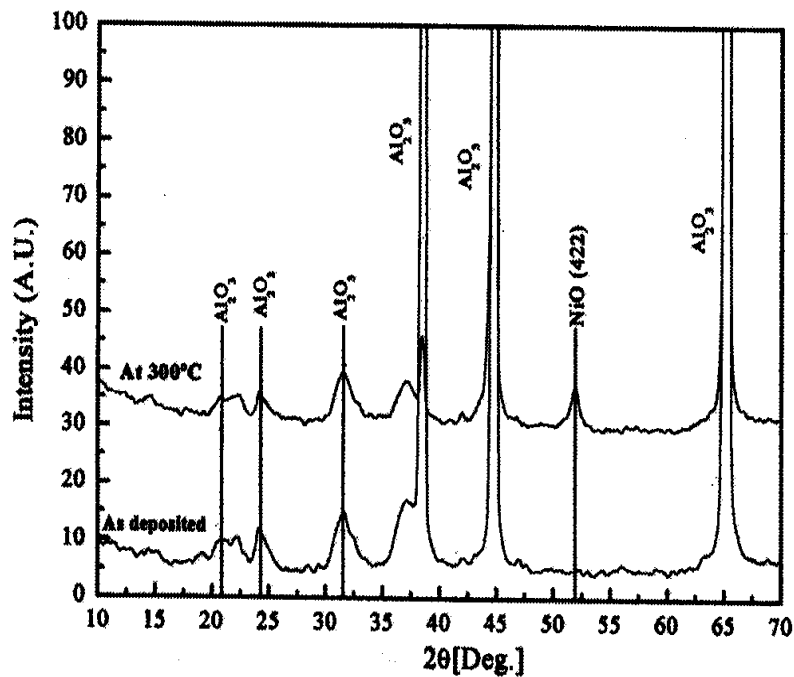


FIGURE 5 X-ray of the reverse periodic plating samples followed by condensation (10 cm, exposed time 5 h, over hot water bath, 100 °C).

5. CONCLUSION

Two techniques of electrolysis are used for the preparation of the selective absorber samples, ac and rpc plating techniques. The nickel ion (from nickel sulfate solution) is reduced and deposited inside the alumina pore as metallic nickel. The ac produced the rod-like metal nickel particles. However, the rpc technique produces the spherical metal particle. No nickel oxide was observed inside the alumina pores. In the rpc electrolysis, more metal nickel particles are found on the surface than the ac electrolysis. The degradation tests at high temperatures and humidity show that the main cause of degradation is the oxidation of nickel. In addition, fractures of the surface are seen from the SEM measurements at high temperatures. These selective absorber samples are tested for solar thermal performance in previous work [11].

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