Nano structure black cobalt coating for solar absorber

G.Toghdori[1], S.M.Rozati[1*], N. Memarian[1], M.Arvand[2], M.H.Bina[3]

[1]Department of Physics, University of Guilan, Rasht42335, Iran
[2]Department of Chemistry, University of Guilan, Rasht42335, Iran
[3]Department of Materials Engineering, Esfahan University of Technology, Esfahan, Iran
* Corresponding author. Tel: +981313220912, Fax: +981313220066 E-mail: smrozati@guilan.ac. ir

Abstract: Black cobalt thin films on bright nickel plated on brass and copper substrates were prepared by the electrodeposition method. The Influence of substrate metal and heat treatment process on the surface morphology and absorptance of samples was investigated. Surface morphology and spectral reflectance of films were measured by scanning electron microscopy and spectrophotometer in the visible and near-IR region of spectrum respectively. Scanning electron microscopy images showed that the black cobalt films have porous structure. The absorptance of prepared films is over than 90%, which makes them suitable for using as solar absorbers.

Keywords: *electroplating, black cobalt, solar absorber coating, black coating.*

Nomenclature (Optional)

T *Temperature* .... *°C*
t *Time* ....*s*
α *Solar Absorptance*
ε *Thermal Emittance*

1. Introduction

The preparative aspects of cobalt oxide thin films have been a subject of investigations by various workers because of their numerous applications in various fields of technology. They are attractive in application to solar thermal energy collectors as selective absorbing layers [1]. Spectrally selective surfaces exhibiting high values of solar absorptance α and low values of thermal emittance (ε) improve the thermal performance of solar collectors by reducing the radiative heat loss component [2]. Such surfaces are employed as receiver coatings in flat plate evacuated tube and concentrating collectors and may under stagnation conditions in the latter application, experience temperatures of 500˚C. Many surface coating types have been developed which have potential for application as selective absorbers [3]. An attractive aim of selective surface research studies is the development of a single coating type which could be used for all solar collector designs. For successful industrial development such a coating would not only possess favourable optical properties but also would be readily reproducible, durable, thermally stable and inexpensive to produce. Selective solar absorber coating in solar thermal systems, working under moderate concentrations, experience operating temperatures in the rang 300-500˚C. Cobalt oxide coatings [4] are proposed as potential candidates for this use. However, little is known about their stability and the modes of degradation when operated at high temperatures. It is well known that the metal substrate microstructure strongly influences the grain size and morphology of the in-situ grown film [5]. It is also well known that the microstructure of electrodeposits varies markedly with deposition parameters and that various impurities from the plating bath may be incorporated into the deposit [5].

A general class of absorber coatings is those formed by chemical "conversion" processes. The previous works on the electrochemical preparation of cobalt oxides can be divided in to two groups: direct and indirect. In the former, a solution is prepared by dissolution of the chemical components that allow the directly preparation of black cobalt on the substrate at the cathode in the electrolysis process [6]. On the latter the formation of cobalt oxide is accomplished in two steps, i.e. first the metallic cobalt is deposited on the substrate and secondly, the cobalt is oxidized to black cobalt through chemical or thermal oxidation [6]. Because of its optical, semiconducting, magnetic and electrochemical properties, black cobalt is a promising material among transition metal oxides, which renders it attractive for solar photochemical applications and electrochemical devices as a counter electrode [7]. Today, although there are six physical mechanisms of solar absorptance [8]. It is recognized that one of the most efficient solar absorber films base their optical properties on its microstructural volume and surperficial parameters. However, in spite of all the existing mechanisms, the textured surfaces are the most dependent of the surface morphology than whatever other material is. These materials show a high solar absorptance by multiple reflection of the incident radiation among dendrites that are approximately two microns apart, while the long-wavelength thermal emittance is rather unaffected by texture. Several techniques, such as chemical conversion and thermal oxidation of metallic films and electrodeposition, are currently used to achieve such spectrally selective, black-metal, solar absorber surfaces [9]. However, the desired characteristics of the metallic coating could be better controlled by directed electrodeposition. In this paper electrodeposition of cobalt photothermal material, suitable for using in solar energy collection, has been studied.

2. Experimental Details

Black cobalt thin films on bright nickel plated on brass and copper substrates were prepared by the electrodeposition method. The core part of the electroplating process is the electrolytic cell. In the electrolytic cell a current is passed through a bath containing electrolyte, the anode and the cathode. The workpiece to be plated is the cathode (substrate). The Anode is a metal which is coating on the cathode surface. Electrolyte is the electrical conductor in which current is carried by ions rather than by free electrons (as in a metal). When a direct electric current passes through an electrolyte, chemical reactions (Oxidation/Reduction) take place at the solution. Reduction takes place at the cathode, and oxidation takes place at the anode. Electrolyte completes an electric circuit between two electrodes. Upon application of electric current, the positive ions in the electrolyte will move toward the cathode and the negatively charged ions toward the anode. The metallic ions of the salt in the electrolyte carry a positive charge and are thus attracted to the cathode. When they reach the negatively charged workpiece, it provides electrons to reduce those positively charged ions to metallic form, and then the metal atoms will be deposited onto the surface of the negatively charged workpiece.
Brass and copper plates were thoroughly degreased and cleaned, then subjected to a 1-min acid etch in 5% sulphuric acid prior to bright nickel deposition. According to watts bath [10] bright nickel deposition was carried out under the conditions mentioned in table 1. A piece of nickel metal with 99.9% purity was used as anode.

Table 1: Deposition condition and bath composition for deposition of bright nickel.

Composition bath		Current density	Temperature
Nickel sulphate	250 gl^{-1}	0.5 A/dm^2	70°C [11]
Nickel chloride	50 gl^{-1}		
Boric acid	50 gl^{-1}		

After bright nickel plating, the panels were rinsed with distilled water. Finally black cobalt deposition was carried out under the conditions described in table2 according to McDonald electrolyte bath [6]. The anode was cobalt metal with 99.9% purity and bright nickel plated brass and copper was used as cathode.

Table 2: Deposition condition and bath composition for deposition of black cobalt.

Composition bath		Current density	Temperature	pH
Cobalt sulphate	400 gl^{-1}	3 A/dm^2	30˚C	4
Cobalt chloride	50 gl^{-1}			
Cobalt nitrate	4 gl^{-1}			
Boric acid	40 gl^{-1}			

The cobalt sulphate is the main source of cobalt ions, the cobalt chloride helps to improve the conductivity of electrolyte solution and the boric acid is a leveling agent. Cobalt nitrate was added to the bath to obtain a black layer on the sample.
The films deposited on brass substrate and bright nickel plated brass substrate annealed in the air environment at temperature 400 ˚C for 20 Min to study their physical properties after heat-treatment. The absorptance was calculated from the equation 1-R, in the visible region [12]. Where R is the room temperature reflectance measuremement. Reflectance in the visible region was determined with a Carry 500 spectrophotometer. The morphology of the surfaces is detected by scanning electron microscope (SEM) model Philips XL30.

3. Results and Discussion

3.1. SEM Analysis

Figure 1 depicts the surface morphology of black cobalt films deposited on different bright nickel plated substrates. Fig.1.a is for a brass substrate and Fig.1.b belongs to a copper substrate. It is obvious that the crystal structure of black cobalt film deposited shows a porous structure. There is no evident difference between the morphology of films deposited on different substrates. While by changing the substrate metal the porous sizes have changed from micro, for copper substrate, to nano-sized porous structure for brass substrate. Figure 2 shows the surface morphology of black cobalt films deposited on brass substrate, (a) before heat-treatment and (b) after heat-treatment. From figures 1 and 2 it is clear that the films deposited on brass substrates after annealing had more cracks on the surface and the porosity of the structure was increased. By comparing fig.1a and fig.2a it is evidence that the presence of bright nickel middle layer causes a more uniform structure without any crack in the surface of electrodeposited black cobalt films on brass substrate. In addition by using the bright nickel middle layer the porosity of structure increased. This porous structure results enhanced the absorptance in coatings and makes these layers suitable for solar absorber application.

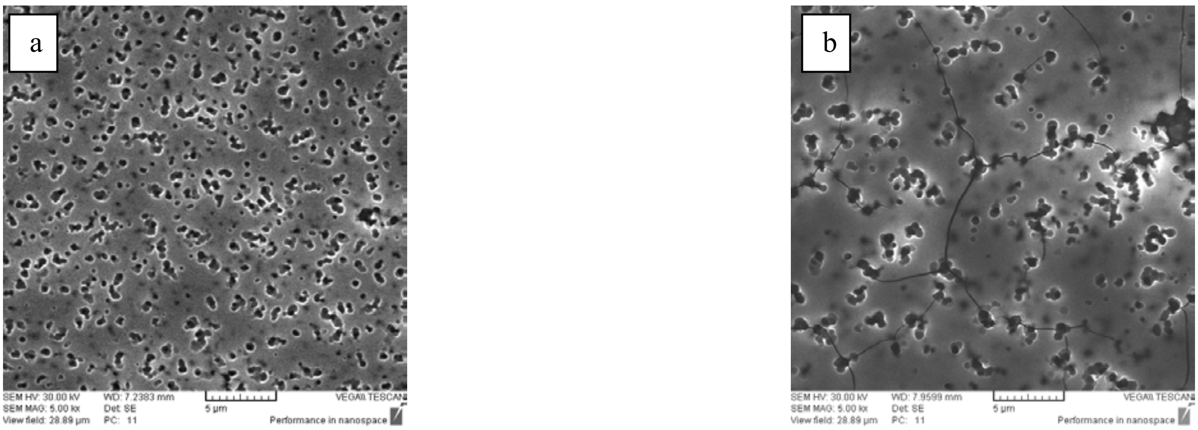

Fig. 1. The surface morphology of black cobalt film deposited on bright nickel-plated substrates (a) for brass substrate (b) for copper substrate.

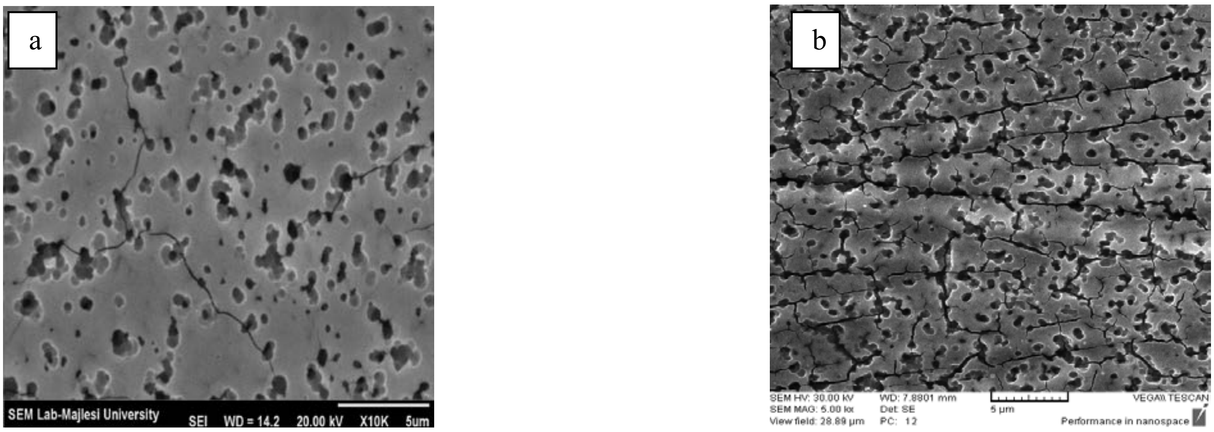

Fig. 2. The surface morphology of black cobalt films deposited on brass substrate (a) before annealing (b) after annealing.

3.2. EDAX Analysis

Figure 3 and table 3 show the elements in electrodeposited cobalt film on brass substrate by EDAX analysis. These Data expressed that the main elements in black cobalt coating, is cobalt metal.

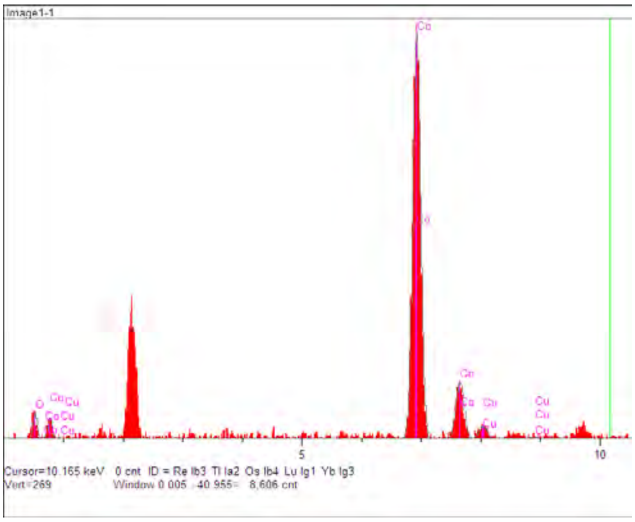

Fig. 3. EDAX of black cobalt as-deposited on brass substrate.

Table 3. The elemental concentration of black cobalt film deposited on brass substrate.

Intensity(c/s)	Conc. (Wt %)	Element
14.11	4.648	O
420.67	90.610	Co
13.34	4.742	Cu

3.3. Solar Absorptance Analysis

The changes in absorptance of layers by the wavelength for bright nickel-plated brass and copper substrates are shown in Fig.4. And the films absorptance of black cobalt films deposited on brass substrate before heat treatment and after heat treatment in visible region of wavelength are shown in Fig.5. The optimal solar absorptance was 98%-99.55% at wavelength range 400-1200 nm for the as-deposited films and films after heat treatment.

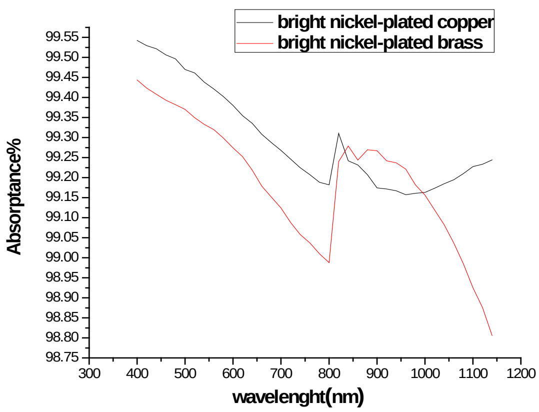

Fig. 4. The relationship between the absorptance and wavelength of black cobalt films deposited on different substrates.

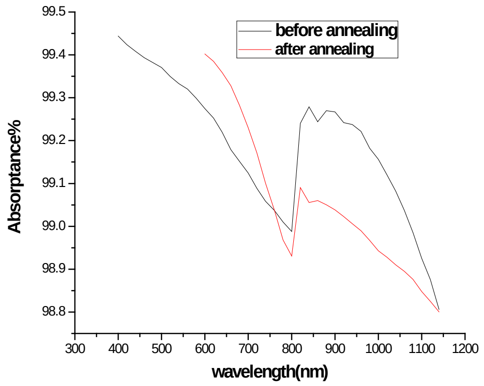

Fig. 5. The relationship between the absorptance and wavelength of black cobalt deposited on brass substrate (a) before heat treatment (b) after heat- treatment.

4. Conclusions

Black cobalt coatings on bright nickel plated on brass and copper substrate were prepared by the electrodeposition method. The influence of heat treatment on optical absorption and surface morphology of black cobalt films deposited on brass substrates has been studied. Heat treatment of black cobalt films deposited on br ass substrates caused cracks in the surface structure. Heat treatment of black cobalt deposited on br ass caused a slight decrease in an absorption in the near-IR region. Due to high absorption in visible region the best substrate for a black cobalt solar absorber coating is bright nickel-plated on copper substrate.

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