Dependence of Optical and Thermal Properties on Substrate of Solar Thermal Collectors

Bhim Kafle, Rishi Lamichhane, and Sandesh Basnet
Kathmandu University

Email: bhim@ku.edu.np; rishilamichhane17@gmail.com; basnetjack.sb@gmail.com;

Abstract. The optical and thermal properties of the black chrome based Solar thermal collectors (STCs) deposited on three different substrates (aluminium, Al; galvanized iron, GI; and stainless steel, SS) were investigated. The devices were prepared by two different methods: electro-deposition and dip coating and were heat treated at 300 °C. Each STC’s performance was evaluated by measuring optical and thermal properties: Optical properties were measured with UV-Vis, Raman and IR Spectroscopy. For later measurements, all the STC samples were kept inside an air tight glass box and are exposed to the solar radiation over all the sunshine hours in summer (from 7:30 am – 5 pm, August). Then, the instantaneous temperature was recorded, simultaneously, of all samples with IR-temperature sensor. Among all the samples, the STC with black chrome coated on Al substrate showed the highest temperature, reaching the maximum value of ca. 95 °C at about 1 pm. Moreover, the STC samples fabricated by dip coating found to possess as equal optical and thermal properties as samples prepared by electro-deposition.

1. Introduction

As in the other parts of world, solar water heating systems (SWHSs) are commonly used by many households in south Asian nations as well, owing to their relatively affordable cost (around 300 USD). These systems have acceptable performance due to the relatively high solar radiation in the region. For example, in Nepal, the average daily solar radiation is around 5.5 kW h/m2 and over around 300 yearly sunny days [1].

The most crucial component of any SWHS is the solar thermal collector (STC), a device that absorbs the incoming solar radiation, converts it into heat, and transfers this heat to a fluid (e. g., water) flowing through the collector [2,3]. The solar energy thus collected is carried from the circulating fluid either directly to the hot water or a thermal energy storage tank from which can be drawn for use at night and/or cloudy days.

A preliminary survey on SWHSs in Nepalese market shows that there are, mainly, two kinds of STCs: One utilizes commercial black paint coated flat plate collector, which is attached with the galvanized iron pipes underneath. The STC exchanges heat with the GI pipes through which water is heated as it circulates by thermo-gravity. While another kind of SWHS comprises glass covered steel boxes encompassing, usually, glass tubes coated with cupper based nanoparticles. The SWHSs with STC of later kind are imported from abroad, while the former kind has been commercially fabricated in Nepal. However, both kinds of SWHSs have own problems: For e.g., former kind is less efficient and requires large surface areas to meet customers’ requirement, while on the other hand, second kind is expensive and are unaffordable unless government provides heavy subsidies for purchasing them.
Therefore, for harnessing of solar energy efficiently, the traditional material for STC (black paint) must be replaced with an efficient absorber material with low fabrication process. Specifically, efficient conversion of solar energy into thermal energy requires collector panels covered with special coatings that absorb across the solar spectrum while emitting poorly in the infrared region [4-6]. Surfaces with black paint are perfect absorbers (in the solar radiation range, 0.3 – 2.5 μm), however, have high emissive values in the infra-red range (> 2.5 μm) [7]. By contrast, so-called “selective” absorber surfaces absorb all incident radiation but show reduced emission in the infra-red region. Hence, advanced absorber substrates are typically covered with a coating that strongly absorbs in the solar radiation wavelength range in order to obtain high values of absorptivity, while yielding reduced emittance in the infrared region [8].

Electroplated black chromium is one of the most widely used selective absorbers [9], mainly due to the possibility of large area processing. While other materials have also been investigated: For e.g., semiconductor-dielectric composites (lead sulphide, PbS, on aluminum substrate) and metal-dielectric composite selective coatings (black nickel, NiS-ZnS, on a metal substrate, stable nickel, Ni–pigmented alumina, Al2O3, cermet coating on aluminum substrates, TiN2O5 cermet coating on copper substrate, black nickel-tin coating on Cu substrate, NiOx cermet, CrNxyOy and CrAlO-based solar selective absorbing nanocomposite coating [5-7,10-14]. Among these examples, as indicated above, black chrome selective coating possesses superior optical and thermal properties [7]. Its high solar-absorbing characteristics, selectivity factor (ratio of absorbance to emittance equals to 0.92 - 0.98/0.08-0.25) and a thermal stability up to 300 0C, are a result of the micro surface light-trapping morphology [9].

However, when attempts are made to reproduce any of the published formulations, it is difficult to obtain the desired features of the coatings [15]. In particular, method of fabrication of STCs and the substrates on which they are deposited has great influence over the thermal emittance values of the solar collector due to their direct physical contact with absorber [16]. Recently, Khamlich et al. [17,18] demonstrated that preparation of STCs with “dip coating” (with a low cost chemical bath) could be one of viable alternatives to conventional electroplating. Authors showed that STCs produced with the dip coating possess comparable optical and thermal properties [17, 18]. In this work, we performed the comparative study of performance of black crome STCs prepared by electrochemical deposition and dip coating of chromium onto Al, GI and SS substrates. Also for comparison, STCs with commercial black paint as selective coating materials were also evaluated.

2. Methodology

2.1. Preparation of Cr-Cr2O3 cermet films

The chromium based STCs presented in this work were fabricated by two different methods: (1) Electrochemical deposition and (2) dip coating of black chrome onto Al, GI and SS substrates with the size 6.5cm x 5.5cm x 0.1cm. For former method, the firstly a nickel under coat layer was deposited on each substrate using a Watt-type warm bath [16]. That was followed by the fabrication of a thin layer of chromium (Cr) selective absorber coating from a near-neutral electrolyte at room temperature. Details of each step are given below.

- Before electro-deposition, each substrate’s roughness was enhanced by employing mechanical polishing with emery paper and was cleaned with the following scheme: Alkaline solution of KOH → distilled water → aqueous solution of 10% H2SO4 → distilled water. After cleaning process the substrates were dried in hot air oven at 100 0C for one hour.
- Nickel plating to thickness of about 10 microns.
- Cr plating was performed with the parameters 216 mA/cm2, 24 volts at 24 0C for 2 - 4 minutes.
- Then samples were rinsed with water, alcohol and dried (at room temp.) which was followed by heat treatment at 300 0C.

All the experiments for electro-plating the substrates were conducted in a conventional two-electrode cell. The substrate was used as the working electrode (cathode) and a Sn-Pb as anode (with Sn/Pb ratio
= 3/2). The relationship between film thickness and plating time was determined experimentally and thus the time during step (2) and (3) was adjusted to a desired thickness. For coating Ni undercoat layer, 310 g/L Nickel sulphate hexahydrate (NiSO₄·6H₂O), 50 g/L Nickel chloride hexahydrate (NiCl₂·6H₂O) and 40 g/L boric acid (H₃BO₃) was used. The employed DC current for carrying out electroplating was ca. 14 A/dm² and the pH was maintained at ca. 4. Also, a replicate of each sample was prepared for reproducibility issues. Then, thus formed nickel layer was thereafter cleaned with acetone, alcohol and distilled water and stored in a dust free environment before deposition of Cr layer. Following the deposition of the nickel layer, a thin layer of Cr selective absorber was deposited. To obtain an effective black selective absorber coating, a Cr-Cr₂O₃ cermet layer of thickness ca. 0.2 micron was fabricated, using the electro-chemical bath of 125 g/L Chromic acid (CrO₃), 20 g/L Barium carbonate (Ba₃CO₃), 10 g/L H₃BO₃, 0.5 g/L Ammonium fluoride (NH₄F) and 5 g/L Nitric acid. While with the dip coating, samples were prepared by following the method prescribed in Ref. [17]. Briefly, the cleaned substrates were immersed into the bath of only CrO₃ solution for 6 hrs at temperature 70°C. Then the as prepared sample was air dried, before thermal treatment.

2.2. Thermal treatment of the electrodeposited Ni-Cr films
In order to submit the fresh Cr-Cr₂O₃ cermet film to a similar thermal treatment as that for a solar collector, samples were heated in a muffle furnace to 300°C for 6 h. Then the selective absorber coated samples were analyzed to characterize their effectiveness in harnessing the incident radiation by measuring it optical and thermal properties. Thermal treatment of the electrodeposited Ni-Cr films In order to submit the fresh Cr-Cr₂O₃ cermet film to a similar thermal treatment as that for a solar collector, samples were heated in a muffle furnace to 300°C for 6 h. Then the selective absorber coated samples were analyzed to characterize their effectiveness in harnessing the incident radiation by measuring it optical and thermal properties.

2.3. Optical and photo-thermal response analysis of STC
Tests were conducted to evaluate STCs’ optical and photo-thermal responses for their potential in solar thermal energy scavenging. This section describes the testing and test setups for these experiments.
Spectral reflectance measurements in UV-Vis and Near IR regions were carried out to investigate the optical selectivity of each sample. Reflectance measurements for all the samples in the wavelength range 0.28 – 1.1 microns were performed on a Reflectometric Spectrophotometer (Amstec., US). All the reflectance measurements were taken at near normal incidence at room temperature (ca. 20°C). Raman spectra were also recorded with Raman Spectrometer (Model RIRM, RI Instruments and Innovation, India).

The study of optical properties was followed by analysis of thermal performance of the collector samples. That represented a key element of the STC characterization effort. The ability of the collector to achieve high temperature is critical for SWHSs. Hence, the temperature profile of each STC plate was characterized to determine the ability of the collector to transform solar radiation into heat. For this measurement, the experimental setup consisted of three kinds identical STC films. The first system (C1), a substrate (Al) of size 6.5cm x 5.5cm coated with commercial black paint as STC. The second system (C2), substrate (Al) of same size coated with black crome layer as STC (prepared by electro-deposition), and the third system (C3), substrates (Al, GI and SS) coated with black crome layer as STC (prepared with deep coating). Each solar collector plate (C1, C2, C3) has total surface area of about 35.75 cm². The temperature measurements were conducted using a IR thermometer which was calibrated using a calibrated digital thermometer. All temperatures were recorded every hour from 7:30 am to 5 pm for consecutive two days on the first week of August, 2016 to ensure the reproducibility and reliability of the experimental output. Measured maximum radiation flux in the spot was about 900 W/m².
3. Results

3.1. X-Ray analysis
The X-Ray diffraction (XRD) patterns of the synthesized and annealed chromium/chromium oxide, Cr/Cr$_2$O$_3$ particles deposited on Al and GI substrates using electroplating and dip coating are demonstrated in Fig. 1. In between, black crome and substrate a Ni undercoat layer was coated for better adsorption of chromium STC. It can be seen that even though the samples were prepared with different techniques and at different substrates, all the samples show intense peaks in the planes [110], [024], [300] and [311] at $2\theta = 45.24^\circ$, $52.58^\circ$, $65.75^\circ$ and $78.82^\circ$, respectively. Observation of these peaks is in line with earlier contributions [17,18]. However, the intensities of all the peaks observed with the samples prepared with electroplating found to be significantly higher (For. e.g., the intensity peak [110] was higher by the factor of ca. 8).

![Figure 1. X-Ray diffraction patterns of the Cr/Cr$_2$O$_3$ particles deposited on Al and GI substrate.](image)

3.2. Optical Properties of STC
Fig. 2 shows the spectral reflectance from UV to near IR region (wavelength $\approx$ 0.2 $\mu$m – 1.2 $\mu$m) for Al substrate and for thin film of black crome fabricated by electro-deposition and dip coating (represented with red blue and black solid lines, respectively). As expected, one can clearly observe magnificent reduction in the reflectance of the thin film of black crome compared to that of Al substrate. Moreover, the reflectance curve observed from the sample C2 (with electroplating process) almost overlapped with that of C3 (with dip coating process), which confirms that the film prepared by later process is also of good quality.

![Figure 2. Reflectance from bare Al substrate and black crome (deposited on Al substrate by both the electroplating and dip coating).](image)
Figure 3. Reflectance for C3 samples (black crome films coated on Al, SS and GI substrates prepared by dip coating). All three spectrums found to overlap each other.

Fig. 3 shows the spectral reflectance from UV - near IR regions for sample set C3: Black crome films deposited by dip coating on substrates Al, SS and GI. All three samples showed less than 2% reflectance for all the scanned wavelengths below 1 µm, above which one would expect gradual rise in the spectrum (noise in the upper edge is due to upper limit of our spectrophotometer). The findings from present study are consistent with that the results of Khamlich et al. [18].

Figure 4. Raman spectra for black crome films coated on Al, SS and GI substrates (prepared by dip coating).

Fig. 4 displays the Raman spectra for black crome film coated on Al, SS and GI substrates. The Raman spectra are due to presence of chromium, as the contribution of the substrate has been eliminated in base line correction for each peak. Furthermore, a peak ca. 475 cm\(^{-1}\) confirms the presence of Cr\(_2\)O\(_3\).

3.3. Photo-Thermal response Analysis of STC

Fig. 5 shows the setup for thermal behaviours measurement of our STCs, which comprises an air tight transparent glass box with wooden base on which samples are placed horizontally. The temperature profile of each STC was monitored in real sun condition. To verify the increase in collectors’ temperature is only due to absorption of solar radiation by the STC, the temperature of the surrounding (which serves as baseline), substrate and of all STC samples was simultaneously monitored. In Fig. 6, temperature as a function of time duration (hr) of radiation exposure on the surface of black chrome coated STCs samples C1, C2 and C3 are demonstrated. Also, included are the temperature
profiles of Ni undercoat layer and of Al substrate. Temperature measurements were carried out in every 5 minutes time interval, in order to monitor gradual change in temperature with the radiation exposure time. As displayed in the Fig. 5, monotonic increase of the temperature was observed for both the STC and for Ni coated plate and substrate until 12:30 pm, but decreasing trend was observed thereafter. Notice, the large difference in temperature during mid day between STC and Al substrate (differ by a factor of ca. 4).

Figure 5. Setup for thermal measurement which comprises an air tight transparent glass box with wooden base on which samples are placed horizontally with the surface.

Figure 6. Temperature as a function of time (hr) recorded on the surface of black chrome coated STC. Also, included are the temperature profiles of Ni undercoat layer and of Al substrate.

Figure 7. Temperature of STCs as a function of time (hr).

Fig. 7 displays the temperature as a function of time (hr) recorded on the surface of samples C3. Also, included is the temperature profile of sample C1, STC prepared by coating of commercial black paint (B.P.) on the Al substrate. One can apparently notice higher temperature for all the time duration of radiation exposure for STCs with black chrome selective coating compared to that of black paint. Also, very interestingly, the fluctuation in the later spectrum is due to cloud cover in the sky (decrease in temperature directly reflects the higher emissivity of the film fabricated with black paint). Although
very nominal, the STC with Al substrate always showed higher temperature compared to that of STCs prepared on GI and SS substrates.

4. Conclusion
The STCs deposited by “dip coating” showed similar optical and thermal properties to that of STCs prepared by “electro-deposition”. Results on optical properties from present study are consistent with that the results of Khamlich et al. [17] and provide a further evidence (basis) for employing this low cost technique to fabricate commercial solar collectors. Moreover, about 20 % higher temperature observed with STCs with Cr-Cr₂O₃ than that of STCs with black paint likely to influence the performance of solar water heater system (and also of solar dryers) by the same factor. However, the films fabricated with dip coating were not as homogeneous as of “electro-deposited” one. Therefore, further study on this matter is required and is in progress.

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