Ni-Co CO-Modified Anodized Spectrally Selective Coatings With Enhanced Corrosion and Thermal Stability

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Abstract

Ni-Co/Nanoporous Al_2O_3/Aluminum spectrally selective structures are grown using electrochemical anodization of alumina, followed by electrochemical pigmentation of Ni and Co metallic particles simultaneously. The pigmentation of Ni and Co particles into nanoporous anodized alumina (AA) is achieved using the reduction of metal ions in the aqueous electrolyte. The measured absorptivity and emittance are ~ 0.90 ± 0.05 and 0.14 ± 0.04, respectively. These structures are subjected to the ten identical thermal cycling upto 300 °C in inert N_2 and air ambient conditions. The optical performance suggests that absorptivity is nearly same with slight enhancement in the emittance values as compared to the structure without any heat treatment. The accelerated corrosion studies suggest that Ni-Co co-pigmented AA structures are relatively corrosion robust as compared to that of the AA structure.

Keywords: Corrosion, spectrally selective coatings, emittance, absorptance,

Introduction

The energy crisis during 1970-1980 implied the consequences of fossil fuel depletion, greenhouse gases and subsequently the climate change and obligated to look for alternate energy resources. Thus, renewable energy sources are gaining attention continuously and their fractions are increasing slowly. Solar energy is one of the most abundant environmentally safe renewable energy resources. The simplest and direct method of harnessing solar energy is the solar thermal conversion, where thermal energy can be utilized for possible applications later or simultaneously including power generation. The spectrally selective solar absorbers are used to convert the incident solar radiation into thermal energy by employing on receiver tube of the solar collector, which is integrated into a solar thermal systems and sub-systems for different applications including solar thermal power plants [Granqvist 1991, Behar et al. 2013]. Solar collectors can be classified into two category in general: (i) non-concentrating and (ii) concentrating. The concentration ratio for nonconcentrating solar collector is one, which is greater than one (> 1) for concentrating collectors. Non-concentrating collector such as flat plate collectors and evacuated tube collectors are mainly used for relatively lower temperatures based applications including solar hot water and drying of agricultural products, whereas concentrating collectors are used for high-temperature application such as solar thermal power and industrial applications. The initial spectrally selective coatings are mostly electrodeposited black chrome, black nickel, Nis-ZnS composites and were integrated successfully in flat plate collectors. These coatings are useful for moderate temperature applications under vacuum/inert or corrosion free ambients. The performance of a solar absorber depends on optical properties of absorber surface, employed to intercept the incoming solar radiation. For an effective solar energy collection, the spectral selective coatings are used, which are capable of absorbing the maximum of solar spectrum without emitting large thermal radiations. Thus, spectrally selective absorbers should exhibit high absorptance ≥ 0.95 in the solar spectral range 0.3 - 2.5 µm and low thermal emittance ≤ 0.05 in the infrared spectral range 2.5-25 µm [Barshilia et al. 2006]. Ideally, a spectral selective coating (SSC) should have low reflectance (ρ) ~ 0 for wavelengths (λ) ≤ 2.5 µm and high reflectance ~1 for $\lambda \geq 2.5$ µm. The cutoff wavelength may be higher or lower as the wavelength distribution of radiation emitted by a black body depends on the temeperature [Duffie 1980]. Concentrated solar thermal power systems(CSP) operate at high temperature (≥ 400 °C). For such application, SSCs should be chemically and thermally stable in the working environment under elevated temperature and thus, high thermal and structural stabilities are essential for both the combined and individual layers of the coating structures [Kennedy 2005]. The SSC performance may degrade at high-temperature not only because of oxidation in a residual environment in a vacuum or in air ambient but also

due to the thermal cycling, causing periodic thermal stresses. In addition, this may also cause interlayer diffusion and chemical reactions, leading to the poor interlayer adhesion and thus deteriorating the solar performance. The chemical reactions, especially in open ambient and moist conditions, may corrode and thus damage the coating structure. Further, the challenge is to keep the emiittance (ε) low at high temperatures as the thermal radiative losses are proportional to the fourth power of the temperature in conjunction with high absorptance. Thus, there is a tradeoff between emittance and absorptance as these are mutually exclusive properties for SSCs [Kennedy 2002].

Among numerous SSCs, **cer**amic-**met**al (**cermet**) based spectrally selective absorber structures are extensively investigated and are still extensively under consideration due to their potential for solar thermal applications. Their high solar absorptance, low IR emittance and good thermal stability for mid and high temperature range make them very attractive for concentrated solar power applications [Cao et al. 2014]. The coating thickness and metal volume fraction in the ceramic matrix as well as particle size, shape and orientation can affect the spectral selectivity. For example, thicker cermet structures with smaller particle size are desired for high solar absorptance, whereas with increased thickness leads to the higher thermal emittance. Electrodeposited black chrome coatings are widely studied and used for solar hot water applications [Niklasson and Granqvist 1983, Craighead et al. 1981]. However, these are not very useful for high-temperature applications. Alumina (Al_2O_3) based cermet coating exhibit desired optical properties and thermal stabilities, showing relatively better solar thermal performance with enhanced thermal stability.The metal pigmented dielectric nanoporous structures such as anodized alumina may provide suitable cermet type spectrally selective absorber structures [Graqvist and Hunderi 1979]. The porous alumina layers with inclusion of transition metals like Fe, Co, Ni, Cu, Au, Ag, Mo, Cr, and W are widely studied [Galione et al. 2010,Salmi et al. 2000, Wackelgard 1996] for solar absorbers showing a high solar absorptance (α) of 0.93 and low thermal emittances (ε) ranging 0.04– 0.10 [Andersson et al. 1980]. In addition to the solar absorbers, metal pigmented anodized alumina is also used in nanostructured electronic devices [Sellmyer et al. 2001, Paulus et al. 2001].

Various physical and chemical deposition techniques are employed for synthesizing cermet structutre [Kennedy 2002].Among them electrochemical deposition is promising because of its easy synthesis process and the scalability for depositing coating structures on desired surfaces. This also provides the good control on synthesis parameters such as current density, electrolyte concentration, deposition time or combination of these as well to realize the optimized coating structures for possible applications. Thus, relatively good quality spectrally selective structures can be realized using electrodeposition with optimal solar thermal properties. The double anodization process is proposed by Masuda and Fukada [Masuda and Fukuda 1995] to obtain the ordered pore arrays and pores with straight side walls. The ordered pore arrays are useful when the porous alumina is used as a template, for example, in the electrodeposition of metallic or semiconducting nano-particles, wires and nanorods to achieve the metal-alumina composite matrix structure and also the specific structures for electronic device applications [Gerein and Haber 2005, Shin et al. 2009]. However, the requirement of straight pores is not so stringent for spectrally selective cermet coating structures and single step anodization process is used is followed to generate the porous alumina structure [Graqvist and Hunderi 1979, Salmi et al. 2000, Andersson et al. 1980, Cuevas et al. 2014]. These structures are obtained by anodizing aluminum in dilute phosphoric acid and electrolytically colored using nickel pigmentation. However, the stability of such structure is limited upto 250-300°C. Nahar et al and Cuevas et al also used cobalt pigmentation instead of nickel because of stronger oxidation resistance as compared to nickel [Cuevas et al. 2014, Nahar et al. 1986]. There are studies on Ni pigmented AA and Co pigmented AA spectrally selective coating structures as mentioned in Table 1 [Cuevas et al. 2014, Nahar et al. 1986, Niklasson and Granqvist 1984, Nahar et al. 1989]. However, very few studies are available on simultaneous Ni-Co pigmentation of anodized alumina for solar thermal applications in conjunction with their thermal and corrosion stabilities.

This work reports the development of Ni-Co/Nanoporous Al_2O_3/Aluminum structures. These structures are synthesized electrochemically. The anodization process has been optimized to get the desired pore size (~ 50 nm), followed by Ni and Co co-pigmentation into the nanoporous alumina structures. The detailed structural, microstructural and optical studies will be discussed in conjunction with their thermal and corrosion stabilities. The theoretical estimations are carried out to understand the impact of the metal fraction in a dielectric matrix on optical properties.

Table 1. Ni, Co pigmented anodized alumina as SSCs and their optical properties.

SSCs stucture	Absorptance	Emittance	Thermal stability	Corrosion Resistance	References
$Ni/Al_2O_3/Al$	0.93 - 0.96	0.01 - 0.20	300 °C (Air)	-	Kennedy 2002
$Co/Al_2O_3/Al$	0.92	0.28	400 °C (Air)	-	Niklasson and Granqvist 1984, Nahar et al. 1989
$Co/Al_2O_3/Al$	0.92	0.16	-	-	Cuevas et al. 2014

2.Experimental detail

The development of Ni-Co co-pigmented anodized alumina as the spectral selective coatings involve the three successive steps: (i) pre-treatment of substrate surface, (ii) electrochemical anodization for porous alumina structure and (iii) electrochemical co-pigmentation of nickel-cobalt in anodized alumina. The process is explained schematically in Fig 1. The pretreated degreased 80 mm × 40 mm × 1 mm aluminum 'Al' sheets are used as working electrodes and a 7 mm x 10 mm x 3 mm graphite plate as the counter electrode [Bostrom et al. 2003, Green et al. 2007]. The anodization is carried out at constant voltage 15 V_{DC} for about 15 minutes at room temperature (~ 25℃) in 2M phosphoric acid electrolyte solution. This led to the porous aluminum oxide structure with 50 ± 10 nm diameter pores. Further, aqueous electrolytic bath, containing 0.11M $CoSO_4$, 0.11 M $NiSO_4$, 0.2 M H_3BO_3 and 0.1 M ascorbic acid, is used for co-electrodeposition of Ni-Co metallic nanoparticulates inside the porous alumina structure. This is achieved under AC electrodeposition conditions at ~10 V_{AC} (frequency ~50 Hz) for 10 minutes [Foyet et al. 2008]. The solar thermal properties of these structures are investigated using UV-Vis and IR spectroscopic measurements. The accelerated corrosion tests are carried out in 3.5 wt% NaCl electrolyte solution at room temperature. The thermal treatments are carried out under ambient and inert N_2 gas environments. The microstructural and surface properties are investigated using Carl Zeiss EVO 18 especial edition scanning electron microscope (SEM). The elemental compositions are measured using the energy dispersive X-ray (EDX) instrument (OXFORD make); equipped with SEM system. The optical reflectance is measured using UV–Vis-NIR spectrophotometer (Carry 5000) in 0.2-25 µm wavelength range to understand the spectral response. These reflectance measurements are used to calculate the room temperature solar absorptance $\alpha(\lambda)$ in 0.2 - 2.5 µm wavelength range and thermal emittance $\varepsilon(\lambda)$ in 2.5-25 µm respectively.
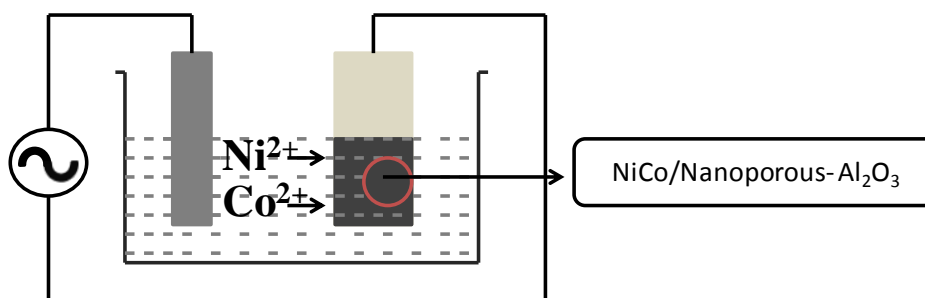

Fig.1: The schematic diagram explaining electrodeposition setup for Ni-Co pigmentation into the nanoporous Al_2O_3 structure.

3. Results and discussion

The SEM micrographs are shown in Fig. 2 (a) and 2(b) for anodized alumina and Ni-Co co-electrodeposited anodized alumina, respectively. The respective schematic structures are shown as the insets. The pore size of the anodized alumina is estimated using higher magnification image of anodized alumina, as shown in inset, in Fig. 3 (a)). We observed pore size ~ 40 ± 10 nm. For elemental composition determination, EDX measurement was performed and estimated results are shown as the insets in respective figures. The introduction of Ni and Co can be observed in anodized alumina structures, as shown in Fig. 2 (b). In spite of equimolar ratios for Ni and Co precursors, the electrodeposition of Co is preferred and larger Co fraction is deposited as compared to that of Ni in these Ni-Co co-pigmented anodized alumina structures.
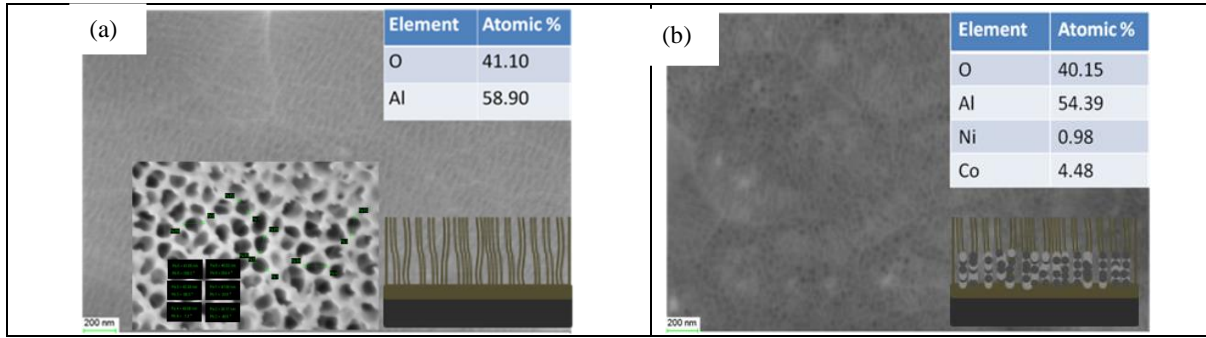
Fig. 2: SEM micrograph of the anodized alumina (a) and Ni-Co co-electrodeposition in anodized alumina (b)

The representative UV-Vis-NIR reflectance measurement is shown in Fig 3(a) for Ni-Co/Nanoporous Al_2O_3/Aluminum spectrally selective coatings ~ 0.2 – 25 μm wavelength range. The effective medium approach is used to simulate the reflectance for these structures [Niklasson et al. 2007] and is shown in Fig 3(a) in conjunction with experimentally measured reflectance. The materials parameters such as dielectric and optical constants are borrowed from references [Andersson et al. 1980, Palik 1998]. The metallic fraction is varied to achieve the best fit for the experimentally recorded reflectance, as shown in Fig. 3(a).

The simulated reflectance trend is similar to the experimentally measured reflectance and is in good agreement towards higher wavelength region. However, the simulated and measured reflectances are not showing good agreements and the difference is attributed to ignorance of the surface irregularities and lack of reliable materials parameters in the desired wavelength regions. The measured absorptance and emittance values are 0.95 and 0.14, respectively for the pristine spectrally selective structures. The measured absorptance is in close agreement with the simulated absorptance whereas the emittance value is slightly higher as compared that of the simulated emittance for optimal 25% metallic fraction in anodized alumina ceramic matrix. Further, these coating structures are thermally heat-treated at 300°C for 50 hours and respective reflectance results are summarized in Fig. 3(b) & (c). The emissivity value increased from 0.14 for as prepared structure to 0.20 and 0.22 for thermally treated structures in inert N_2 and air ambient conditions, suggesting that these structures are relatively thermally stable with a small increase in their emissivity values.
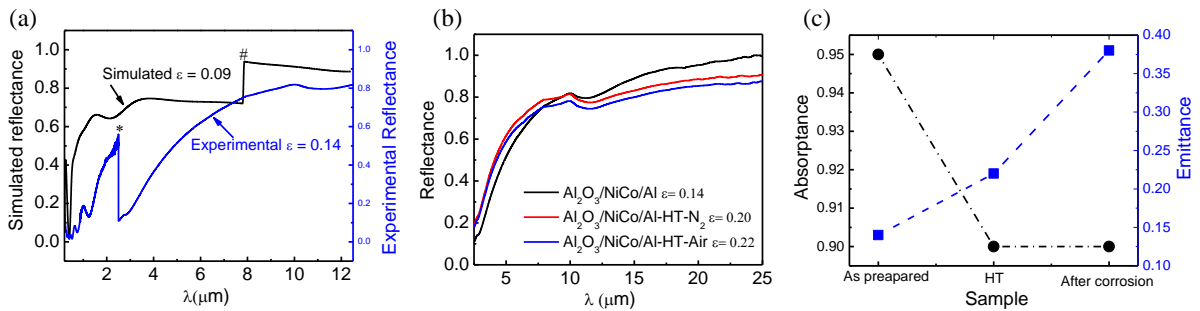

Fig. 3: Reflectance curves for (a) pristine Ni-Co/Nanoporous Al_2O_3/Aluminum coating, experimentally measured one with blue color and simulated one with black color (* glitch at 2.5 μm is the instrumental error, while changing the wavelength range near NIR region and # glitch in data taken from references at 7.8 μm); (b) high temperature (HT) thermally treated Ni-Co/Nanoporous Al_2O_3/Aluminum coatings, with respective emissivity values and (c) absorptance and emittance for as prepared, HT and after corrosion treatment of Ni-Co pigmented Ni-Co/Nanoporous Al_2O_3/Aluminum coatings.

For corrosion studies, potentiodynamic polarization measurements are carried out in 3.5 wt% NaCl electrolyte solutions for anodized alumina and fabricated SSCs structure at room temperature. The corrosion experiments were performed using Autolab (Metrohm) workstation in three electrode configuration, where platinum is used as counter electrode, Ag/AgCl as reference electrode and sample as working electrode. In both the corrosion measurements, sample was immersed in 3.5% NaCl solution for half an hour to establish open circuit potential (OCP). The OCP for anodized alumina was ~0.56 mV and -0.65 for fabricated SSC sample. So, measurement were performed in -1.5mV to 0 to cover the OCP range. The measured voltage versus logarithmic of current measurement is summarized as Tafel plots in Fig. 4(a). The respective corrosion parameters are calculated using Nova software, provided with Autolab (Metrohm) workstation and are summarized in Table 1. The polarization

resistance is measured using Stern-Geary relation, $R_p = \frac{b_c \times b_a}{2.3 \times i_{corr}(b_c + b_a)} (K\Omega cm^2)$, where b_a and b_c are anodic and cathodic curve slope. The corrosion current (i_{corr}) is lower ~0.182µA cm^{-2} for Ni-Co/Nanoporous Al$_2$O$_3$/Aluminum structure as compared to that of ~ 0.936µA cm^{-2} for anodized alumina at a scan rate of 10 mVs^{-1}, suggesting that corrosion resistance has increased for pigmented structure. The corrosion potential and polarization resistance (R_p) also showed higher values for fabricated SSCs with respect to that of anodized alumina. The corrosion rate after metal pigmentation is observed much lower as compared to that of anodized alumina. These results suggest that the Ni-Co/Nanoporous Al$_2$O$_3$/Aluminum structure is better corrosion resistant with respect to the anodized alumina. This is desirable for a SSC structure for longer lifetime in open environmental condition. After corrosion measurement, the optical characterization was performed to estimate the absorptance and thermal emittance. The observed absorptance of these corrosion treated samples remains nearly unaffected, whereas the emittance values showed enhancement upto 0.38 as shown in Fig. 4(b). This is mainly attributed to the increased surface roughness due to microstructure evolution, introduced during the accelerated corrosion testing.
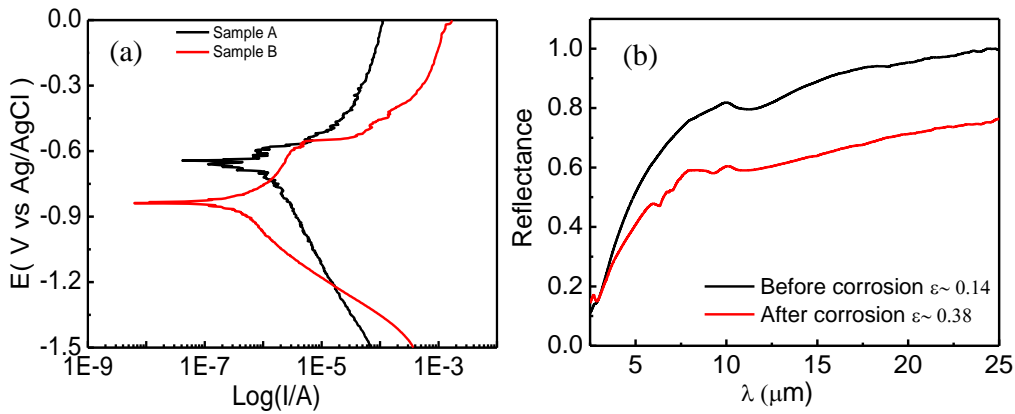

Fig. 4: (a) Potentiodynamic polarization curves and (b) respective reflectance curves for anodized alumina (black) and Ni-Co/Nanoporous Al$_2$O$_3$/Aluminum SSCs (red).

Table 2.The estimated corrosion parameter of anodized Al and Ni-Co/Nanoporous Al$_2$O$_3$/Aluminum SSCs

Sample	E$_{corr}$ (V)	i$_{corr}$ (µA/ cm^{-2})	R$_p$ (KΩ)	C. Rate (mm/y)	b$_a$ (V/dec)	b$_c$ (V/dec)
Sample A	-0.6589	0.936	40.66	0.0108	0.100	0.359
Sample B	-0.837	0.182	135.03	0.0021	0.049	0.050

4. Conclusion

We demonstrated successful deposition of Ni-Co/Nanoporous Al$_2$O$_3$/Aluminum SSCs using simple electrodeposition process. These structures showed optimal absorptivity ~ 0.95 and emissivity ~ 0.14. Further, these structures showed enhanced thermal resistance without degrading their optical properties significantly. The corrosion studies suggest that Ni-Co co-pigmented SSCs structures are relatively corrosion resistant as compared to that of the bare anodized alumina substrate. The observed absorptance is nearly unaffected whereas the emittance values enhanced to ~ 0.38 for corrosion treated SSC structures. Thus Ni-Co co-pigmentation in anodized alumina structures may provide a thermally stable and corrosion resistant spectrally selective structure.

5. Acknowledgement

6. References

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