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Novel sol–gel based selective coatings: From coil absorber coating to high power coating

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ABSTRACT

Single layer black selective coatings for solar thermal energy conversion were produced by low cost sol–gel dip-coating, spin-coating and coil-coating methods, the last made on the industrial line of the Alanod company (DE). For the deposition, pigment dispersion was prepared by milling a mixture of a black spinel ($FeMnO_4$) pigment, whose surface was modified with trisilanol heptaisobutyl POSS dispersant, dried and re-milled with (3-glycidoxypropyl)trimethoxysilane (GLYMO) and $Ti(i\text{-}OPr)_4$ acting as binders. The corresponding organic–inorganic hybrid consisted of silica clusters linked together with poly(ethyleneoxide) chains acting as a network former. The as-prepared nanocomposite dispersion served for the deposition of coil absorber coatings (~800 m) on aluminium coil in an industrial plant in the Alanod factory. They gave solar absorptance of 0.905 and thermal emittance of 0.12 and excellent homogeneity. The stability of the coatings at 400 °C was excellent but corrosion resistance was moderate (5 days in salt spray).

The coil absorber coating was then used for making a High Power (HIPO) solar coating with solar absorptance of 0.92 and thermal emittance of 0.075, which was achieved by exposure of the as-prepared coil to 400 °C. The isoconversion kinetics approach was used for assessing the thermal loading (time and temperature of heat treatment) required to provide a HIPO coating from the coil absorber. The improvement of selectivity was investigated by infrared spectroscopy and XPS measurements, revealing that HIPO coatings deposited on stainless steel (AISI 316) survived 1216 h at 460 °C and 400 h at 500 °C without any change of selectivity, while after exposure to 500 °C for 1216 h, thermal emittance increased to 5–7% but solar absorptance remained unchanged. Thermal emittance changes observed at thermal loading were explained with the help of infrared spectra analysis, revealing the formation of iron oxide on the surface of the HIPO coating. The deposited HIPO coating is an interesting option for temperature and corrosion stable coatings for applications in concentrated solar power (CSP) plants for solar processing heat generation.

1. Introduction

Solar energy is the cleanest (does not produce air pollutants or CO_2) renewable natural resource available. The world's energy demands are growing rapidly and the development of surfaces with high absorption of solar radiation (a_s) and low thermal emittance (e_T) is thus a driving force for the development of absorber coatings with spectral selectivity, i.e., high a_s/e_T ratio. Since the amount of sunlight that arrives at the Earth's surface is not constant, varying depending on location, time of day, time of year and weather conditions, a large surface area of solar absorbers with high spectral selectivity is required to collect the energy at a useful rate. Absorber coatings made by a coil-coating technique seem to be the best solution.

Thickness Sensitive Spectrally Selective (TSSS) paint coatings made by the deposition of black paints with controlled thickness on metallic substrates [1–5] are a cheap alternative to vacuum based coatings, even though such coatings have attracted only sporadic interest for almost forty years, mainly due to the predominant role of electrodeposited black chrome based coatings [6,7] on the market. Because toxic Cr(VI) compounds are used in

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the electroplating process, with a significant impact on the environment, interest shifted between 1990 and 1995 onto vacuum deposited coatings [8,9]. Despite the high cost of vacuum deposition equipment, the solar thermal market is currently dominated by highly spectrally selective surfaces made of various cermet materials deposited on aluminium or copper via vacuum deposition techniques [10–12]. Vacuum deposition, which is automatic and is performed on coils (roll-to-roll, R2R), enables the formation of coatings with multiple film structures and high a_s/e_T ratios (>20) (a_s ~0.95 and e_T ~0.05).

The development of TSSS paint coatings is a multifaceted problem, since selectivity strongly depends on mutually dependent parameters: thickness of the paint layer, composition of paint, which in turn depends on the pigment type and thermal emittance properties of the binder and dispersant, all affecting the pigment loading, curing and deposition conditions of the paint dispersions. Only the harmonization of all issues makes it possible to prepare paints that enable the deposition of TSSS coatings from paints with a high selectivity ratio.

A TSSS paint coating was prepared in our laboratory using a paint made of black manganese spinel pigment dispersed in polysiloxane (TEGO, Non-stick 60) resin binder with the help of (3-aminopropyl)trimethoxy silane (APTMS) [13], which served as dispersant. The use of APTMS dispersant has been found to be a major breakthrough; it has enabled the deposition of coatings with high pigment loading (33–35%), which have consequently given improved spectral selectivity (a_s ~0.90 to 0.91 and e_T ~0.20 to 0.22) and imparted excellent corrosion resistance (10 days in salt spray) and adequate abrasion resistance (H3) and temperature stability (650 h at 240 °C). Following the IEA Task 10 protocol, the last named promised a lifetime of more than 25 years. Selective absorber coils with this paint are currently manufactured by the Alanod factory (DE) on an industrial coil-coating line under the trade name Mirosol TS.

The central aim of this study was first to make a selective TSSS coil absorber coating from sol–gel precursor/pigment dispersions with solar absorptance of about 0.90–0.91 but lower thermal emittance (e_T ~0.12 to 0.14) than polysiloxane based coatings [13] and, second, to use this coil absorber coating as a starting material for the production of high power (HIPO) coatings with higher a_s/e_T ratios, i.e. $a_s > 0.91$ and e_T ~0.075. Heat treatment ($T > 400$ °C) was used for this purpose.

There were several reasons for choosing sol–gel precursors instead of polymeric siloxanes [13]. Surprisingly, there are no commercial selective absorber coatings prepared from sol–gel based pigment dispersions, even though sol–gel coatings are used in practice in many applications [14–17]. Tetraethoxysilane (TEOS) seems to work well, as reported by Morales et al. [18], as antireflective and protection coatings for solar absorbers, while Rincon et al. [19] made sol–gel based TSSS absorber coatings from titanium(IV) isopropoxide (TIP) with added carbon soot and carbon nanotubes as pigments. Selective absorber cermets (33% Au/67% TiO_2) have been made by inexpensive sol–gel techniques, with good optical selectivity a_s/e_T (400 °C)=0.80/0.01 and high thermal durability (>500 °C in air) [20,21]. However, such sol–gel pigment dispersions have low viscosity and seem to be more suitable for dip and spin-coating depositions than for much faster coil coating and other less sophisticated but more common paint deposition methods.

Basically, two different wet deposition preparation routes exist: in situ preparation of a black sol–gel coating from a mixture of silanes or titaniumalkoxyde and metal salt precursors followed by heat treatment and a *standard route* used for the preparation of paints, in which the pigment particles are milled in the presence of silanes serving as binders. By following the first route, Kaluza et al. and later Vince et al. [22,23] demonstrated that it is possible to make black $CuCoMnO_x$ and $CuTiMnO_x$ spinel crystalline thin films (300 nm) with a solar absorptance of 0.86 and thermal emissivity of 0.11. The added Ti-alkoxide acted as a binding phase, which connects the black spinel pigment particles formed after heat treatment at 400–500 °C (few h). Using sol–gel and spin-coating deposition, Bostroem et al. [24] obtained similar black spinel based coatings with thermal emittance below 0.05, which absorbed 97% of the incoming solar energy. Bayon et al. [25–27] obtained highly selective coatings based on Cu–Mn–Si oxides that show excellent optical performance. A solar absorptance of 0.95 combined with thermal emittance of 0.035 was achieved for coatings on aluminium substrates. Recently, Joly et al. [28] reported sol–gel based Cu–Co–Mn–Si–O nanocrystalline multilayer thin films, in which TEOS acted as a binding phase and depositing the precursor solution on steel by the dip-coating technique and application of inductive heating considerably shortened duration of heat treatment. Multi-layered coatings showed high spectral selectivity (a_s ~0.94 and e_T ~0.12) but single layer films exhibit much smaller a_s values (a_s ~0.81), due to the inherent high reflection of the formed spinel/silica coating. Temperature stability was checked at 400 °C and was adequate, but corrosion resistance (acid drop test) was about 3 times worse than for electrodeposited black chrome coating. Despite the use a special heat treatment procedure [28], the in situ fabrication of black crystalline manganese spinel films seems to be time consuming, especially because an additional layer(s) is/are needed in order to decrease the inherently high reflection of the crystalline material. Sol-gel based cermets [29,30] could also be ranked among coatings in which the absorbing phase forms in situ during the preparation. In situ preparation of the sol–gel black TSSS coatings from sol–gel solutions is undoubtedly time consuming and wet deposition of TSSS coatings the sol–gel dispersions is a better option.

In general, alkyltrialkoxysilanes ($R\text{-}(Si\text{-}OR')_3$, where R=mercapto, glycido, methyl, acryl, vinyl,… and R′ – alkoxy groups) are promising alternative to existing tetraalkoxysilane binders because the viscosity of the pigment dispersions and compatibility of the dispersed pigment particles can be relatively easily adjusted by choosing the appropriate alkyl (R) groups. Namely, alkyltrialkoxysilanes, during the course of condensation, form organic–inorganic hybrid materials with highly condensed and cross-linked silica organic–inorganic networks with a nanocomposite structure (ORMOCER) [31–33]. Organic–inorganic hybrids have already been used for making Thickness Insensitive Spectrally Selective (TISS) paint coatings with added aluminium flakes [34,35] but the spectral selectivity was much lower than for TSSS paint coatings, even though selective paint coatings with different colors have also been produced [36].

In this study, (3-glycidoxypropyl)trimethoxysilane (GLY for short) was selected as a binder because this popular precursor has already been used as precursor for many organic–inorganic hybrid coatings [14,16]: hard coatings for plastic ophthalmic lenses [37], low temperature coatings for glass coloration [38,39], organic dye-doped hybrid sol–gel coatings [40], planarization layers for microelectronics [41] and generally for multifunctional coatings [42]. However, it has not been used for selective coatings yet.

An additional reason for choosing GLY as a binder for the sol–gel TSSS coatings in this study was that GLY has lower thermal emittance per coating thickness than polysiloxanes and other organic binders [43–45]. GLY is actually one of the simplest organic–inorganic hybrid precursors, which consists after polymerization of silica clusters (short linear, cyclic, ladder and partially octameric silsesquioxanes), covalently linked into polyether (poly(ethylene oxide), PEO) chains formed by direct reactions between the epoxy rings (Fig. 1) [46]. Ring opening is achieved by the presence of a metal (Zr, Ti, Al, and Sn) alkoxyde, such as titanium tetraethylate ($Ti(OEt)_4$), Al sec$(OBu)_3$ [47] or AlO(OH) boehmite nanoparticles [37]. The boehmite nanoparticles thus have a