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## Innovative smart selective coating to avoid overheating in highly efficient thermal solar collectors

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### Abstract

Highly efficient solar thermal systems generally undergo stagnation conditions with temperature inside the solar collectors as high as 190-200°C, as soon as the domestic hot water demand is poor or when the system is off while the collectors are still submitted to a strong solar radiation ( $> 950 \text{ W/m}^2$ ). These stagnation conditions are known to be one of the major problem of thermal solar systems and often lead to vaporization and glycol degradation, loss of performances, and the need for regular maintenance with associated costs for the end user. Thanks to a novel smart selective coating, characterized by a strong increase of its infrared emissivity (thermochromic effect) at a critical temperature, stagnation temperatures can be reduced to 150°C for solar radiation and ambient temperature of  $1000 \text{ W/m}^2$  and 35°C, respectively. As the novel smart selective coating presents a high solar absorption coefficient ( $>94\%$ ) and a low emissivity ( $\sim 6\%$ ) at low temperature, and because the thermochromic effect starts at a temperature around 70°C, the high performance of the new thermochromic thermal solar systems is guaranteed for domestic hot water heating. The properties of this new generation of selective coatings, based on a mixture of vanadium and aluminum oxides ( $\text{VO}_2/\text{V}_n\text{O}_{2n+1}/\text{Al}_2\text{O}_3/\text{SiO}_2$ ), are presented and discussed with regard to composition, structure and optical properties analysis. FTIR spectroscopy and infrared camera pictures clearly show the strong increase of emissivity for temperature higher than 70°C. Aging performances (high temperature, humidity, thermal cycling) are also presented in order to guarantee a minimum life time of 25 years for the new generation of thermochromic solar collectors. Finally, stagnation temperatures recorded under the same natural sun radiation on scale one ( $2.3\text{m}^2$ ) standard and thermochromic collectors are compared.

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## 1. Introduction

Thermal solar systems equipped with highly efficient flat plate thermal solar collectors (i.e. solar absorption  $\alpha > 94\%$  and infrared emissivity  $\varepsilon < 6\%$ ) generally reach stagnation conditions in summer, as soon as the domestic hot water demand is poor or when the system is off, while collectors are still under a high sun radiation (holidays, electrical power breakdown, ...). In such stagnation conditions the temperature inside the collector can be as high as 190-200°C, which leads to glycol/water medium vaporization/condensation and degradation (glycol starts to evaporate at roughly 170°C). Without regular maintenance to replace the medium, or without the use of additional and costly regulation/purge systems (drain-back for example), the solar thermal system gradually loses its efficiency, and serious damages can occur in the system such as mud formation in the piping and inside the thermal exchanger.

Thanks to a patented innovative smart selective coating, based on a mixture of vanadium and aluminum oxides ( $\text{VO}_2/\text{V}_n\text{O}_{2n+1}/\text{Al}_2\text{O}_3/\text{SiO}_2$ ), with a reversible change of its infrared emissivity for a critical temperature close to 70°C, stagnation temperature in highly efficient thermal solar systems can be reduced by more than 35°C, while keeping the high performance of the system until 70-80°C. A maximum stagnation temperature of 150°C was recorded with the new smart selective and thermochromic coating. Thus the medium (glycol/water) is fully protected and the new generation of smart thermal solar collectors does not need maintenance anymore. Moreover, the strong stagnation temperature reduction contributes to the cost reduction and the simplification of the thermal solar installation without system performance losses.

In this paper, composition, structure, optical properties, and aging performances of this innovative smart selective and thermochromic coating are presented and discussed. Finally, the evolution of the absorber temperature recorded for scale one (2.3 m<sup>2</sup>) standard and thermochromic collectors submitted to the same sun radiation (1000 W/m<sup>2</sup> - 35°C) are presented and discussed.

## 2. Experimental details

$\text{VO}_x/\text{SiO}_2$  and  $(\text{V}, \text{Al})\text{O}_x/\text{SiO}_2$  coatings were deposited on aluminum substrates (solar quality: thickness of 0.4 mm,  $R_a < 0.3 \mu\text{m}$ , initial infrared emissivity  $< 3\%$ ) and silicon wafers by means of magnetron sputtering of vanadium (99.5%), aluminum (99.9%) and silicon (99.9%) targets in argon and argon/oxygen atmospheres. A 30 liters vessel equipped with 2 planar magnetrons (2 inches in diameter) and a rotating/heating substrate holder was used for lab scale samples (50x50mm<sup>2</sup>) whereas an industrial in line coater equipped with 1.4 m long magnetrons was used to produce scale one (2.3m<sup>2</sup>) thermochromic thermal absorbers taken from coated aluminum coils (1 m width and 900 m long). As the as-deposited  $\text{VO}_x/\text{SiO}_2$  and  $(\text{V}, \text{Al})\text{O}_x/\text{SiO}_2$  coatings are amorphous, an annealing process at high temperature ( $>500^\circ\text{C}$ ) for duration ranging from 120 to 300s is needed to obtain coatings with crystalline vanadium oxides. Detailed experimental conditions can be found in the patent PCT/FR2014/050590.

A Bruker D8 Advance X-ray diffractometer equipped with  $\text{Cu K}_{\alpha 1}$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) and set in the Bragg-Brentano configuration was used to determine the film structure. The composition of the coatings, especially the vanadium and aluminum contents, was determined using a Philips XL 30.S scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). Auger electron spectroscopy (AES) was also employed using a VG Microlab350 system with an high voltage of 10 kV and a probe current of 2 nA to detect the formation of aluminum oxide after the annealing process, and to perform composition depth profiles (1x1 mm<sup>2</sup>).

Optical properties of the annealed coatings in the ultraviolet, visible and near infrared range (250 to 2500nm) were determined thanks to a Agilent Technologies Cary5000 spectrometer equipped with an integration sphere, whereas a Nicolet 6700 Fourier transform infra-red (FTIR) spectrometer equipped with a heating substrate holder (Linkam THMS600) was used to determine the evolution of the infrared emissivity of the samples for a wavelength of 8  $\mu\text{m}$ , and for various temperatures between 30 to 160°C. Infrared pictures of the thermochromic coatings at low and high temperature were recorded thanks to a Fluke Ti-100 infrared camera set to a constant emissivity of 40%.

In order to guarantee a final life time of at least 25 years for the new generation of thermochromic collectors, aging tests were performed according to the normalized TASK X procedure (ISO 22975-3) [1]. As the new

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