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journal homepage: [www.elsevier.com/locate/solmat](http://www.elsevier.com/locate/solmat)Revealing the innermost nanostructure of sputtered NiCrO<sub>x</sub> solar absorber cermetsL. Gaouyat<sup>a,\*</sup>, Z. He<sup>b</sup>, J.-F. Colomer<sup>a</sup>, Ph. Lambin<sup>a</sup>, F. Mirabella<sup>c</sup>, D. Schryvers<sup>b</sup>, O. Deparis<sup>a</sup><sup>a</sup> Solid State Physics Laboratory (PMR-LPS), University of Namur, Rue de Bruxelles 61, Namur B-5000, Belgium<sup>b</sup> Electron Microscopy for Materials Research (EMAT), University of Antwerp, Groenenborgerlaan 171, Antwerp B-2020, Belgium<sup>c</sup> CRM Group AC&CS, Boulevard de Colonster 57B, Liege B-4000, Belgium

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## ABSTRACT

Conversion of solar energy into thermal energy helps reducing consumption of non-renewable energies. Cermets (ceramic–metal composites) are versatile materials suitable, amongst other applications, for solar selective absorbers. Although the presence of metallic Ni particles in the dielectric matrix is a prerequisite for efficient solar selective absorption in NiCrO<sub>x</sub> cermets, no clear evidence of such particles is reported so far. By combining comprehensive chemical and structural analyses, we reveal the presumed nanostructure which is at the origin of the remarkable optical properties of this cermet material. Using sputtered NiCrO<sub>x</sub> layers in a solar absorber multilayer stack on aluminium substrate allows us to achieve solar absorptance as high as  $\alpha=96.1\%$  while keeping thermal emissivity as low as  $\epsilon=2.2\%$ , both values being comparable to best values recorded so far. With the nanostructure of sputtered NiCrO<sub>x</sub> cermets eventually revealed, further optimization of solar absorbers can be anticipated and technological exploitation of cermet materials in other applications can be foreseen.

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## 1. Introduction

Cermets are composed of metal particles embedded in a ceramic host. The ceramic matrix usually consists of oxide, boride, nitride, carbide or oxynitride components and a crystalline metallic phase is assumed to be embedded in this matrix. Such composite meta-structures allow merging specific properties of both compounds, such as high-thermal stability, corrosion resistance and hardness of the ceramic, on the one hand, electrical conductivity and ductility of the metal, on the other hand. For instance, WC–Co cermet are used as superhard coatings for cutting tools [1]. Nowadays, these microstructured coatings tend to be replaced by nanostructured coatings based on titanium nitride or titanium carbide, for instance [2]. Indeed, at the nanoscale, new opportunities are made available, not only in the above mentioned application but also in terms of light matter interactions. Thanks to their nanostructure, cermet thin films (50–100 nm thick) have peculiar optical properties, making them ideal candidates for solar absorbers, i.e. in water or air heating applications [3]. Indeed these coatings absorb efficiently the solar radiation while avoiding overwarming of the absorber material. For this reason, they are said to be “solar selective”. Aiming at reaching the best solar selective performances, many cermets compositions such

as Ni–Al<sub>2</sub>O<sub>3</sub>, Cr–Cr<sub>2</sub>O<sub>3</sub>, Al–AlN, C–SiO<sub>2</sub> or W–Al<sub>2</sub>O<sub>3</sub>, Au–SiO<sub>2</sub>, Ni–NiO [4–10] have been developed over the past 20 years and some of them are industrially produced today [11]. Although other processes such as anodization [11] or sol–gel deposition exist [12], industrial production of these advanced structural materials is only achieved by physical vapour deposition (PVD).

Our focus on Ni–NiCrO<sub>x</sub> cermets was mainly driven by its high durability and suitability to many applications (electrochromic properties among other) [13]. Indeed, NiO<sub>x</sub> oxide is well-known as p-type semiconductor with Ni vacancies, enabling good electrical conductivity of the oxide material [14], while the optical transmittance is kept very high in UV–visible range. This material was extensively studied by Wäckelgard and coworkers for solar selective applications [15]. Not only does it show good performances in absorbing the solar radiation in UV–visible range, while keeping low thermal radiative losses (performances are discussed in the following section), but it does also exhibit good performances in durability tests. In spite of the fact that NiCrO<sub>x</sub> cermet has been intensively studied for solar absorber applications, the only Transmission Electron Microscopy (TEM) image reported in the literature did not give any direct evidence of the segregated particles, certainly because of the challenging TEM sample preparation [16]. In this study, we focus on NiCrO<sub>x</sub> cermet with the aim of proving the existence of a nanostructure in sputtered NiCrO<sub>x</sub> layers. In order to achieve this objective, we carried out a comprehensive experimental analysis, based on X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and TEM imaging techniques.

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The latter involved a variety of techniques such as high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) and high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM).

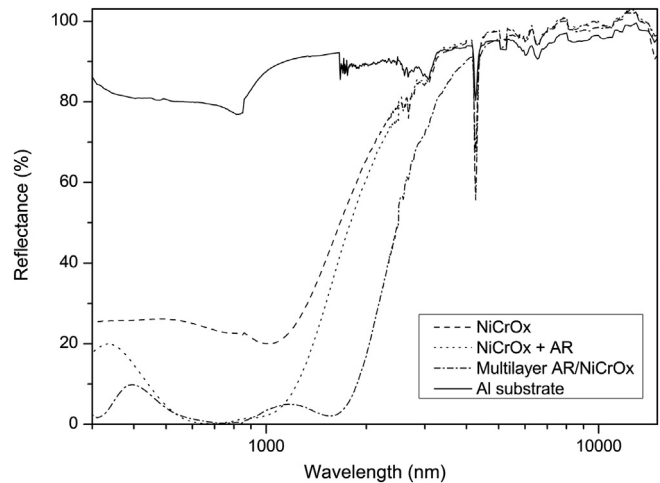
## 2. Experimental

Fine tuning of the magnetron sputtering process was performed through a systematic study of the deposition parameters. NiCrO<sub>x</sub> layers were deposited by reactive magnetron sputtering of NiCr target (8–20 wt%—purity 99.8%) under 0.7-sccm O<sub>2</sub> and 50-sccm Ar atmosphere on a 0.4-mm thick aluminium substrate which was previously cleaned with ethanol. The substrate was an industrial laminated Al product exhibiting grooves in the lamination direction (roughness parameters:  $R_a=0.31\ \mu\text{m}$ ,  $R_z=1.12\ \mu\text{m}$ ). A working pressure of 5 mTorr was used. Optical reflectance was measured using a UV–visible–NIR Perkin Elmer lambda 950 spectrophotometer equipped with a 150-mm integrating sphere. Composition and chemical bonding in the layer were studied using a PHI-Quantum 2000 XPS instrument after one minute of argon sputtering to reach the core of the layer. The crystalline structure was identified using a grazing incidence Bruker D8 diffractometer. A 500-nm thick sample was sliced by focused ion beam (FIB) to observe the cross-sectional structure of the layer. The nanostructures were studied by selected area electron diffraction patterns (SAED), high-resolution electron microscopy (HRTEM), and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) using a Tecnai G2 microscope.

## 3. Results and discussion

### 3.1. Sputtered cermet as efficient solar absorber

The aim of solar selective materials is to absorb solar radiations as much as possible while keeping the generated heat inside the material, i.e. the solar absorptance should be maximised whereas the thermal emittance should be minimized. Usually a single cermet layer deposited on a substrate is not able to reach alone this double criterion. Therefore, the layer is incorporated in a multilayer stack which is designed to act as an optical trap for light. Such a stack is usually designed to provide a gradual refractive index matching across the layer stack by step-wise decreasing the real part of the refractive index from the top to the bottom of the stack [17]. Besides, absorption enhancement is also provided by step-wise increasing the imaginary part of the refractive index from layer to layer. The multilayer design is the basis of a typical solar absorber [18]. In the stack, the active role of converting solar energy into heat is provided by the NiCrO<sub>x</sub> layer. With the aim of producing a layer that meets all these requirements a careful optimization of the NiCrO<sub>x</sub> layer thickness was performed in a previous work by some of the authors of the present study [19]. As predicted by wave optics theory, a slight change in the coating thickness led to a significant shift of the reflectance spectrum. Based on our previous results and theoretical simulations, the critical tuning of the thickness was determined to be around 70 nm [19]. The performances of the coating/substrate system are described by a double criterion combining two quantities: the solar absorptance  $\alpha$  and the thermal emissivity  $\varepsilon$ . They are calculated from  $\alpha = [\int (1-R(\lambda))B_s(\lambda)d\lambda] / [\int B_s(\lambda)d\lambda]$  and  $\varepsilon = [\int (1-R(\lambda))B_a(\lambda)d\lambda] / [\int B_a(\lambda)d\lambda]$  respectively, where  $R(\lambda)$  is the reflectance spectrum,  $B_s(\lambda)$  is the normalized Air Mass 1.5 (AM 1.5) solar irradiance spectrum, (corresponding to the irradiance of the sun – blackbody at 5000 K – taking into account atmosphere



**Fig. 1.** Reflectance spectra measured on a single NiCrO<sub>x</sub> layer (dash line), a NiCrO<sub>x</sub> layer with antireflective (AR) coating on top of it (dot line), a multilayer stack consisting of two NiCrO<sub>x</sub> layers and two AR coatings (dash-dot line) and the bare substrate (solid line). All layers were deposited on rough aluminium (Al) substrate. The dip at around 4200 nm is due to residual water on the sample surface.

absorption bands,  $B_a(\lambda)$  is the irradiance of the blackbody heated at 373 K (water boiling point), corresponding to the absorber sheet. Note that the absorption spectrum  $A(\lambda)$  of the coated substrate is equal to  $1-R(\lambda)$  because, due to the use of a metallic substrate, the transmittance spectrum  $T(\lambda)$  is equal to zero in the wavelength range of interest (i.e.  $A=1-R-T$  with  $T=0$ ). Fig. 1 shows the reflectance spectra corresponding to the bare aluminium (Al) substrate, a single 70-nm NiCrO<sub>x</sub> layer, a 70-nm NiCrO<sub>x</sub> layer with an antireflecting (AR) dielectric layer on top of it and a multilayer stack containing two NiCrO<sub>x</sub> layers and two AR layers (all the layers were deposited on Al substrate). The multilayer stack contains two cermet layers. The AR/NiCrO<sub>x</sub> stack gives  $\alpha=91.2\%$  (solar absorptance) and  $\varepsilon=1.5\%$  (thermal emittance). The multilayer AR/NiCrO<sub>x</sub> stack gives  $\alpha=96.1\%$  and  $\varepsilon=2.2\%$ . In comparison, record values of  $\alpha=97\%$  and  $\varepsilon=5\%$  were reported earlier on NiCrO<sub>x</sub> [15]. Therefore, our multilayer stack absorbs slightly less but features less thermal losses, clearly making it suitable for high performance solar absorber applications. As a matter of fact, NiCrO<sub>x</sub> is a very competitive basic layer for solar absorbers.

Aiming at investigating NiCrO<sub>x</sub> composite fine structure, we relaxed on the choice of the layer thickness, which does not need to match the optimal thickness for solar selective performances (70 nm). Therefore, in the following study, a larger layer thickness (500 nm) has been used to facilitate experimental characterizations, e.g. to get high enough signal-to-noise ratio in XRD peak intensity, and preliminary sample preparation.

### 3.2. Elemental composition and structural analysis

According to literature state-of-the art, NiCrO<sub>x</sub> is supposed to be formed of metallic particles embedded in a dielectric matrix. Aiming at verifying the chemical species present in composite, XPS analysis have been performed with emphasis on characteristic Ni 2p, Cr 2p and O 1s core lines. Quantitative information extracted from those indicated a global composition of 56% Ni, 30% O and 14% Cr in the material. Using several NiCrO<sub>x</sub> samples produced with different amounts of oxygen, we observed that chromium and oxygen XPS spectra were identical for all samples, whereas the nickel XPS spectra were different according to the sample used. Regarding the Cr and O spectra (Fig. 2a and b), the following conclusions were drawn: Cr only exists as an oxide (Cr<sub>2</sub>O<sub>3</sub>) and hydroxyl compound (Cr(OH)<sub>3</sub>), O is bound to a metal (Ni and Cr). Seen the very close electron affinity of Cr and Ni, discrimination of

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