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Microstructure and gas sensing properties of solution precursor plasma-sprayed zinc oxide coatings

Chao Zhang [a,*], Xin Geng [a], Hua Li [b], Peng-Jiang He [c], Marie-Pierre Planche [c], Hanlin Liao [c], Marie-George Olivier [d], Marc Debliquy [d]

[a] College of Mechanical Engineering, Yangzhou University, Huayang West Road 196, Yangzhou,Jiangsu 225127, China
[b] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China
[c] IRTES-LERMPS, Université de technologie Belfort-Montbéliard, Belfort, France
[d] Materials Science Department, Faculty of Engineering, University of Mons, Mons, Belgium

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ABSTRACT

ZnO nanostructured coatings have been prepared on Al_2O_3 substrates fitted with interdigitated Au electrodes on one side and a Pt heater on the other side, and explored as a gas sensor. The coatings were deposited by solution precursor plasma spray (SPPS) using zinc acetate $Zn(CH_3COO)_2$ aqueous solution as solution precursor. The SPPS process has proven its simplicity and reliability in fabricating polycrystalline ZnO coatings as verified by XRD structural analysis. The FE-SEM images confirmed that the coatings are nanostructured with grain size ranging from 50 to 100 nm. The surface morphology and coating grain size is influenced by the H_2 gas flow rate in plasma forming gas. The properties of the sensors based on the SPPS ZnO coatings towards NO_2 as well as other hazardous gases were characterized and the sensors showed good sensitivity to NO_2 gas in sub-ppm range. The influence of gas humidity on sensor responses was also studied.

1. Introduction

In the last decades, increasing attention has been paid on resistive-type gas sensors based on semiconducting metal oxides [1,2], because they can be widely applied for the monitoring of explosive, flammable and toxic gases in industrial communities. The sensing mechanism of semiconducting gas sensors is based on the change in the electrical resistances of the sensitive layer in presence of target gas molecules. The gas response is known to be influenced by the coating microstructure, crystal structure, chemical state, sensor design, etc. [3,4]. Nanostructured and porous sensitive coatings are well-known for obtaining high performance sensors from the viewpoints of gas diffusion and active sites [2].

ZnO is a basic material for semiconducting gas sensor [5]. Different fabrication processes, e.g., pulsed laser deposition [6], thermal evaporation [7], chemical solution deposition [8], were used for the preparation of ZnO sensitive layers. However, many researchers considered that these methods were too complex and expensive to be used as a traditional coating deposition process. The use of another deposition method, deposition from solution precursor plasma spray (SPPS) [9], was proposed for overcoming the above mentioned technological problems. In SPPS, liquid precursor droplets are injected into the plasma jet. All physical and chemical reactions, such as evaporation, pyrolysis, crystallization and coating formation, occur in one single step. However, the coating is also built up by overlapping and stacking of deposited splats. Fabricating coatings directly from solution makes SPPS technique not only a straightforward process but also an attractive method for developing nanostructures with easy control [10].

In the present paper, ZnO coatings have been fabricated via SPPS process on Al_2O_3 substrates at room temperature. The structural, morphological and electrical parameters of SPPS coatings have been investigated and correlated. Sensors based on the obtained coatings have been subjected to gas sensor testing. The sensors showed a high response to nitrogen dioxide (NO_2) when operated at different temperatures.

2. Experimental methods

2.1. Coating preparation

ZnO coatings were deposited on Al_2O_3 substrates equipped with interdigitated gold electrodes and Pt heater (C-MAC, Belgium)

* Corresponding author. Tel.: +86 514 87436008; fax: +86 514 87436008.
E-mail addresses: zhangc@yzu.edu.cn, zhangchao_cqu@hotmail.com (C. Zhang).

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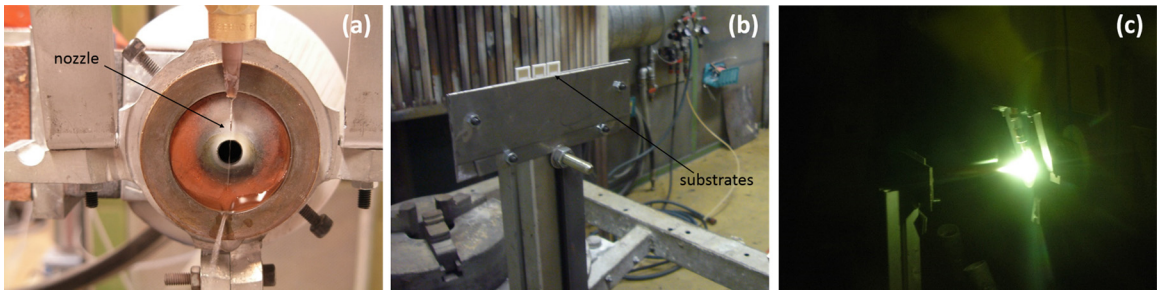

Fig. 1. Experimental setup of solution precursor plasma spraying for ZnO coating: (a) liquid nozzle; (b) sensor substrate and (c) plasma plume during deposition.

using a F4MB plasma torch (Sulzer Metco, Switzerland), which was attached to a six-axis ABB robotic arm, as shown in Fig. 1. The primary plasma gas was argon with a flow rate of 12 L min^{-1}, and the secondary plasma gas was hydrogen with a flow rate of 5 or 8 L min^{-1}. The arc current was 600 A and consequently the plasma power was 31.2 or 34.4 kW, respectively. The feedstock used was a saturated aqueous solution of zinc acetate $Zn(CH_3COO)_2$. The thickness of ZnO coating was controlled at 2.5 μm. The spray parameters were listed in Table 1.

2.2. Coating characterization

The phase composition of the coatings was determined using X-ray diffraction with a Cu Kα radiation (XRD, D5000, Siemens, Germany). The XRD patterns were collected in a 2θ range from 20 to 75° with a scanning rate of 1° min^{-1}, and from 30 to 39 °C with a rate of 0.05° min^{-1}. A field-emission scanning electron microscope (FE-SEM, SU8020, Hitachi, Japan) was used to characterize the coating morphology.

2.3. Gas sensor testing

Sensing characteristics of the sensors based on the ZnO coatings were measured in a Teflon chamber. The sensors were connected to a home-designed system to measure electrical resistances. For each testing condition, three same samples were used. Once the electrical resistances of the sensors were stable in reference air and waiting for another 30 min, 10 ppm NO_2, 100 ppm NH_3, 200 ppm SO_2, 4000 ppm CO or 4000 ppm H_2 (commercial gas, Praxair NV, Belgium) was introduced in the reference air with controlled flow rates to get the desired concentrations of the target gases. The concentrations of the target gases were calculated by doing a division of the flow rates of the commercial gas and total gas (commercial gas + reference gas). In this work, 0.12–1 ppm NO_2, 2.5–20 ppm SO_2, 1.2–10 ppm NH_3, 50–400 ppm CO and 50–400 ppm H_2 were used as target gases. The gas sensors were tested at temperatures ranging from 250 to 325 °C. A sensor response was defined as $S = R_{gas}/R_{air}$ in which R_{gas} and R_{air} were the resistances of coatings in the presence of target gas and reference gas, respectively. Response time is defined as the time needed for the electrical resistance starting from R_{air} to reach 90% of R_{gas} while recovery time represents the time required for resistance decreasing from R_{gas} to 110% of R_{air}. Relative humidity (R.H.) of the reference gas was measured at 25 °C before being introduced in the test chamber by mixing dry air and wet air (after bubbling in deionized water). In this study, the moisture level of reference air was controlled at R.H. 50%, unless specially mentioned.

Table 1
Solution precursor plasma spray parameters.

Parameters	Value
Arc current	600 A
Spraying distance	100 mm
Argon volume flow rate	30 L min^{-1}
Hydrogen volume flow rate	5 or 8 L min^{-1}
Argon powder carrier gas	0.5×10^5 Pa
Nozzle diameter	0.24 mm
Flow rate of solution	13.5 mL min^{-1}
Anode internal diameter at torch exit	6 mm

3. Results and discussion

3.1. Coating microstructure

Fig. 2 shows XRD patterns of the ZnO coatings. XRD patterns also show Au and Al_2O_3 peaks which were emitted from the Al_2O_3 substrates and gold electrodes below the coating. These results confirm that the as-sprayed coatings deposited with 5 L min^{-1} or 8 L min^{-1} H_2 have a polycrystalline nature and hexagonal wurtzite crystal structure (PDF: 36-1451). In Fig. 2b, it can be observed that the peak of 5 L min^{-1} H_2 coating (abbreviated as 5 L coating in this paper) was slightly broader compared with 8 L min^{-1} H_2 coating (abbreviated as 8 L coating). The crystallite size of the two SPPS coatings were calculated from XRD line broadening using Debye Scherrer formula, $d = K\lambda/\beta\cos\theta$, where λ is the wavelength of the X-ray radiation (Cu Kα = 0.15406 nm), K is a constant taken as 0.89, β is full width at half maximum height and θ is the diffraction angle. To estimate the average crystallite sizes, the three most intense peaks, i.e., (1 1 0), (0 0 2) and (1 0 1) at 31.77, 34.42 and 36.25°, were used. The average crystallite sizes for the two coatings are 31.8 nm and 39.4 nm respectively. As well known, the hydrogen flow rate in the plasma gas has an important influence on the plasma enthalpy and plasma thermal conductivity. The increase in hydrogen flow rate enhances the evaporation, precipitation, and pyrolysis of the solution droplets, and induced larger crystallite size in the deposited coating.

Figs. 3 and 4 present the surface morphology of the two ZnO coatings. It can be found that the temperature of plasma plume (H_2 flow rate) plays an important role in the coating microstructure. The 5 L coatings exhibit a smooth surface whereas the 8 L H_2 coatings exhibit a rough surface. The agglomeration in 5 L coating was smaller compared to that in the 8 L coating. The droplets of the zinc acetate solution undergo accelerated chemical reactions in the high temperature plasma flame to form semi-molten/molten particles before impacting on the substrate. The following reaction can be used to describe the pyrolysis in the plasma jet.

$$Zn(CH_3COO)_2 + H_2O \rightarrow ZnO + CH_3COOH$$

In the 5 L coating, it seems that ZnO particles were deposited one by one. On the contrary, ZnO particles existing in the form of agglomerates were present in the 8 L coatings, which involves a rougher surface. The formation of agglomerates may be attributed to higher temperature of the plasma plume when 8 L min^{-1} H_2 is used. The particles formed during precipitation and pyrolysis of the