Thin Solid Films 517 (2009) 1515–1521

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

The Leidenfrost effect during spray pyrolysis of nickel oxide-gadolinia doped ceria composite thin films

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ARTICLE INFO

Article history:
Received 13 October 2006
Received in revised form 22 June 2008
Accepted 12 August 2008
Available online 27 August 2008

Keywords:
Ceramics
Deposition process
Evaporation
Organic substances
Nickel oxide
Cerium gadolinium oxide
Yttria stabilized zirconia
Boiling point

ABSTRACT

$NiO–Ce_{0.8}Gd_{0.2}O_{1.9-x}$ (CGO) thin films were prepared by air blast spray pyrolysis with precursors containing nickel nitrate, cerium nitrate and gadolinium chloride in ethanol and a high boiling point organic solvent. Precursors containing solvents with boiling points between 120 and 314 °C were sprayed on sapphire, silicon, Foturan®, yttria stabilized zirconia and CGO at different substrate surface temperatures.
A maximum deposition temperature, above which film deposition ceased completely, was observed. The limiting temperature for film formation was correlated with the Leidenfrost phenomenon. At temperatures above the Leidenfrost point of the precursor, the sprayed droplets do not impact and spread on the substrate surface but levitate on a vapour cushion above the substrate and are swept away by the air stream. The Leidenfrost point of a precursor was found to depend on the solvent boiling point, the metal salt concentration and the thermal properties of the substrate expressed as the product of density, thermal conductivity and heat capacity. The maximum deposition temperature increased with increasing solvent boiling point or metal salt concentration and with decreasing product of density, thermal conductivity and heat capacity of the substrate.

1. Introduction

Spray pyrolysis of ceramic thin films involves the atomization of a liquid precursor, droplet transport towards a heated substrate, droplet impact, spreading of the liquid droplets on the substrate, evaporation of the solvent and decomposition of the deposited material [1]. Crack-free films can be obtained when the deposition temperature is above the precursor boiling point [1]. Beckel et al. [2] reported a limiting substrate surface temperature above which no continuous films can be obtained. The phenomenon was explained by an increasing number of solidified droplets due to solvent evaporation that are blown away by the air stream.

However, experimental observations of this work suggest that additional mechanisms like the Leidenfrost phenomenon [3–5] might also influence the limiting substrate temperature. When a droplet of a pure substance is deposited on a hot substrate at a temperature below the boiling point of the liquid, the droplet wets the substrate, spreads and slowly evaporates. At temperatures above the boiling point, the droplet wets the surface, spreads, vapour bubble nucleation occurs within the liquid, the droplet boils and vanishes after a short period of time. Eventually the substrate temperature becomes sufficiently high that a thin vapour layer is formed at the interface and the droplet levitates above its own vapour. This point is called the Leidenfrost point (LFP). The droplet lifetime increases by orders of magnitude at this point because of the insulating properties of the vapour layer. When the droplet is not deposited slowly but arrives with a certain initial velocity the impact dynamics also have to be taken into consideration [3]. Metal salts, salt decomposition intermediates or oxidic solids can precipitate in the droplet during evaporation for precursors containing metal salts [2].

The aim of this paper is to correlate film formation parameters and the observation of a maximum deposition temperature on sapphire with the Leidenfrost phenomenon and to extend this correlation to various substrate materials. The spray process was studied for the production of nickel oxide–cerium gadolinium oxide (NiO–CGO) thin films which can be used as anodes for miniaturized solid oxide fuel cells [6].

2. Experimental details

2.1. Spray pyrolysis setup

A schematic of the spray pyrolysis setup is given elsewhere [2]. In this study, the liquid precursor solution was fed with a glass/teflon® syringe (model 1050, Hamilton, Reno, NV, USA) and a syringe pump (model A-99, Razel, St. Albans, VT, USA) through a viton hose (Masterflex/Cole-

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0040-6090/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.tsf.2008.08.158

Table 1
Solvents used for the preparation of the precursors

Solvent	Abbreviation	Boiling point [°C]	Purity
Ethanol[1]	E	78	99.8%
1-Methoxy-2-propanol[2]	MP	119–121	99%
n-Butyl acetate[2]	BA	124–126	98.5%
Diethylene glycol[3]	DEG	245	99%
Diethylene glycol dimethyl ether[2]	DEG DME	162	99%
Diethylene glycol monoethyl ether[2]	DEG MEE	195	98%
Diethylene glycol mono *n*-butyl ester acetate[2]	BCA	245	98%
Triethylene glycol[3]	TEG	285	99%
Adipic acid di *n*-butyl ester[4]	ASDBE	305	96%
Tetraethylene glycol[4]	4EG	314	99%

Suppliers: [1]Merck, Darmstadt, DE and Scharlau, Barcelona, ES; [2]Fluka, Buchs, CH; [3]Acros, Geel, BE; [4]Aldrich, Steinheim, DE; all boiling point data from suppliers.

Parmer, Vernon Hills, IL, USA) to a spray gun (model Binks 460 with a J92P air nozzle and a J920 fluid nozzle, Binks/ITW, Glendale Heights, IL, USA). The fluid needle of the spray gun was in the fully open position and the fan spray width adjustment in the fully closed position for all experiments, resulting in a circular spot deposition of approximately 5 cm diameter at 39 cm working distance and 0.1 MPa air pressure. The air pressure was adjusted with a pressure regulator (EAR 2000, SMC, JP and Norgren/IMI, Birmingham, UK) to a precision of ±5 kPa.

A glass ceramic hot plate (model CT10 with 1.8 kW, Harry Gestigkeit GmbH, Düsseldorf, DE) was used for heating the substrates. A circular aluminium plate of 150 mm diameter and 6 mm thickness was placed on the hot plate to ensure temperature homogeneity of better than 1 °C over the sprayed area. The plate was polished before each experiment with silicon carbide abrasive paper grade 1200 to eliminate strong radiative heat transfer from black residues to the sprayed droplets and to ensure temperature homogeneity by good thermal contact with the substrate. The temperature of the aluminium plate was adjusted with a 1 mm diameter type K thermocouple (MTS Messtechnik, Schaffhausen, CH) and a temperature controller (model 3216, Eurotherm, West Sussex, UK) to limit temperature fluctuations over time to less than ±0.5 °C. The thermocouple was situated in a hole parallel to the plate surface with the tip in the centre underneath the substrate. All substrate surface temperature measurements were carried out with a calibrated handheld surface probe of type K (Model 88108, Omega, Stamford, CT, USA). The error for substrate temperature measurements under flowing air was estimated to be ±5 °C with a reproducibility better than ±2 °C, and without air flow ±2 °C with a reproducibility better than ±1 °C. The greatest care has to be exerted in substrate placement and temperature measurement as temperature changes of 10 to 20 °C can result in a doubled film growth rate under certain conditions.

2.2. Characterization

The morphologies of the deposited films were analyzed with a light microscope equipped with a digital camera (Polyvar MET and Leica DC300, Reichert-Jung/Leica Microsystems, Wetzlar, DE). Film thicknesses were measured by scratching off a small portion of the film with a scalpel and measuring the step height between the substrate and an averaged height within about 1 mm scan length of the film with a surface profiler (Alpha Step 500, KLA Tencor, San Jose, CA, USA). Surface tensions were measured at 25 °C in a saturated environment with a profile analysis tensiometer (PAT-1, SInterface, Berlin, DE). Droplet volume distributions of the spray were measured with a laser diffraction droplet size analyzer (Helos, Sympatec, Clausthal-Zellerfeld, DE). Viscosities were measured at 20 °C in the shear rate range from 5 to 200 s^{-1} with a rheometer (Gemini with DG 24/27 Ti double gap measurement system, Bohlin/Malvern, Worcestershire, UK).

Temperatures of the air stream between the heating plate and the spray gun were measured with a 1 mm diameter type K thermocouple placed horizontally with the tip in the centreline of the air stream.

2.3. Precursor composition and properties

The liquid precursors consisted of a mixture of ethanol and one or more higher boiling point solvents as well as metal salts in the desired stoichiometry. The metal salts were dissolved in ethanol under stirring and after complete dissolution the higher boiling point solvents were added. The total concentration of all metal salts was 0.1 mol/l with an intended composition of the final layer of 60 vol.% metallic nickel and 40 vol.% $Ce_{0.8}Gd_{0.2}O_{1.9-x}$. The ceramic film itself was deposited in the oxidic state as a mixture of NiO and CGO. Nickel-II-nitrate hexahydrate (98% purity, Fluka, Buchs, CH), cerium-III-nitrate hexahydrate (99.5%, Alfa Aesar, Karlsruhe, DE) and gadolinium-III-chloride hexahydrate (99.9%, Alfa Aesar) were used for all spray solutions with 2.46 g, 0.54 g and 0.115 g respectively dissolved per 100 ml of total solvent volume. The crystal water content and resulting molar mass of the salts were verified by thermogravimetry before the solution preparation. Table 1 gives an overview of all solvents used throughout this work with the respective boiling points, purities, suppliers and abbreviations. All solvents were completely miscible with ethanol in a volume ratio of 1:9.

The liquid properties of primary importance for spray generation are density, viscosity and surface tension [7]. Measured values for viscosities and surface tensions of the pure solvents, the solvent mixtures and two precursors are given in Table 2. All liquids exhibited Newtonian behaviour in the investigated range. The viscosity of the 1:9 E:4EG precursor with metal salts was stable to ±5% of the initial value over a period of 4 weeks. Adding metal salts to the solvent had almost no influence on surface tension and only a slight influence on viscosity. Consequently, a measured droplet distributions of solvent mixtures without salts should reflect the distribution during spraying of precursors with salts.

2.4. Substrate materials

Sapphire single crystals (Stettler, Lyss, CH) with a $(11\bar{2}0)$ orientation parallel to the surface, a diameter of 10 mm and a thickness of 1 mm were used as substrates. Small pieces with a size of approximately 10×10 mm^2 of tape-cast polycrystalline 8-YSZ $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ with a thickness of 500 μm (Kerafol, Stegenthumbach, DE), Foturan® in the

Table 2
Surface tensions and viscosities of solvents, solvent mixtures and precursors

Solvent or solvent mixture [volume ratios]	Surface tension at 25 °C [$\times10^{-3}$ N/m]	Viscosity at 20 °C [$\times10^{-3}$ Pas]
Ethanol	21.8 [22]	1.2
Water	72.0	1.0
1:1:1 E:MP:BCA	25.9	2.1
1:1:1 E:MP:BCA with salts 0.1 mol/l	25.7	–
BA	25.1[a]	0.74 at 25 °C[a]
1:9 E:BA	26.5	1.3
DEG	48.2	38.5
1:9 E:DEG	39.1	21.2
DEG DME	29.5[a]	0.99 at 25 °C[a]
1:9 E:DEG DME	30.5	1.7
DEG MEE	29.5[a]	3.9 at 25 °C[a]
1:9 DEG MEE	–	3.9
BCA	30[a]	3.02 at 25 °C[a]
1:9 E:BCA	29.1	2.5
TEG	45.2[a]	49[a]
1:9 E:TEG	39.6	25.9
4EG	44.1[a]	44.6 at 25 °C[a]
1:9 E:4EG	40.2	35.5
1:9 E:4EG with salts 0.1 mol/l	40.6	38.0

[a] Data of pure substances taken from [27].