$LaMnO_3$ PEROVSKITE THIN FILM DEPOSITION, FROM AQUEOUS NITRATE SOLUTIONS OF La AND Mn, IN A LOW PRESSURE PLASMA EXPANDED THROUGH A NOZZLE

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Abstract

In the inductively coupled RF Plasma Expanded Through a Nozzle (PETN) of Ar + O_2 mixtures, perovskite thin fims as $LaMnO_3$ were deposited from La and Mn nitrate aqueous solutions. The PETN using aqueous solutions is a new method to deposit thin films of ceramic oxides. An ultrasonic nebulizer operating at atmospheric pressure introduce the precursors aerosol through a valve in a pulsating mode. The aerosol passing the RF Ar + O_2 plasma produces a shock wave prior to the nozzle, evaporating the excess of H_2O and decomposing the H_2O and the nitrate of La and Mn. The molecular spectra of LaO and MnO was measured in the shock wave prior expanding through the nozzle. This is a new low-temperature process for ceramic oxide thin film deposition.

INTRODUCTION

Numerous properties of perovskite ceramic oxides make these materials very promising for different industrial applications. $LaMnO_3$ is one of the ceramic oxides which are going to be developed as the cathode for the solid oxide fuel cells (SOFC). To increase the efficency of SOFC devices, the structural and electrical properties of their components should be improved. Controlling the thickness of these oxides can lead to increase their electrical conductivity while the cost of fabrication could be reduced as well. Therefore plasma processings are one of the most suitable tools for thin film deposition of SOFC components. From a literature review only two plasma techniques have been reported for this purpose, namely plasma spraying [1] and sputtering techniques. Both of these techniques need a high energy density and have several disadvantages. Among these we can notice the rate of deposition, which is very low by sputtering (0.5 μm/h) and very high by plasma spraying (1g/mn). For these reasons plasma deposition of SOFC components is still in the stage of research and developement. The results presented in this work are the outcome of the developement of a new low-pressure plasma coating process [2-3].

I - EXPERIMENTAL SET-UP & DIAGNOSTICS

I.1 - Experimental set-up

A schematic diagram of our experimental set-up is shown in figure 1. The tubular reactor is made of pyrex glass with a convergent nozzle located after the inductive coil. The plasma discharge is formed before and after the nozzle where the glow discharge couple with a substrate-holder made of stainless steel.

The reactor is equiped with a carrier gas inlet (Ar), a vaccum gauge, a reactant gas inlet (O_2) and a R.F. generator at a frequency of 40 MHz. The reactor is evacuated by an oil rotary pump to a pressure of less than 0,1 mbar prior to the deposition. A liquid nitrogen trap and a dust filter are inserted between the reactor and the rotary pump to avoid contamination caused by oil backstreaming. O_2 and Ar are used as plasma gases at a ratio of almost 1. The reactant solution of lanthanum and manganese is then injected upstream after nebulizing. An ultrasonic nebulizer at a frequency of 1,7 MHz and an input power range of 40 Watts is used for this purpose. The precursors are then introduced into the plasma stream by a pulse injection which is controlled by an electrovalve. Deposits were done on quartz and YSZ substrates located on the metallic substrate holder further downstream. The temperature of the substrate holder can be controled up to 750°C by a resistive heater.

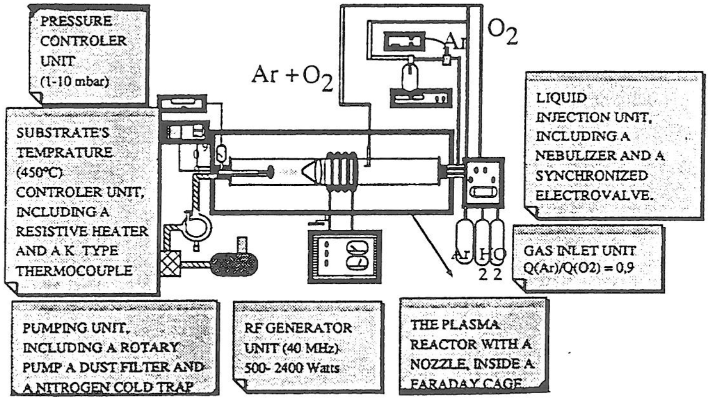


Figure 1: Plasma deposition experimental set-up

I.2 - Plasma stream characterization

The characterization of the plasma was performed by two techniques, namely Optical Emission Spectroscopy (OES) and Laser Doppler Anemometry (LDA) which led to the optimisation of the plasma parameters for deposition. The OES technique led to the identification of OH, H, MnO and LaO transitions [2-4].The LDA technique led to the detection of the particles in the plasma stream before and after the nozzle, confirming the possibility of cluster formation in the reactor [2-4]

II - ANALYSIS TECHNIQUES

Analytical techniques used for the characterization of the solutions and the deposits were ICP-OES, ICP-MS analysis, conventional XRD and the TEM-XRD techniques, FTIR, SEM-EDX and Image analysing of micrographes, Dynamique focalisation profilometry, XPS, TG-DTA and resistance measurement as a function of temperature by the four points probe technique. In this paper we will presente some of these results.

III - QUANTITATIVE ANALYSIS OF THE SOLUTIONS

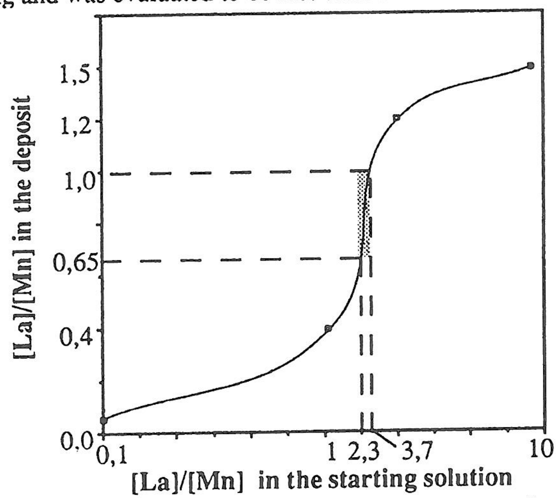
Solutions containing the precursors (La, Mn), were analyzed before and after the plasma deposition. The starting solutions used as precursors for deposition were ICP standard solutions of lanthanum and manganese with a very low rate of impurities. The original concentration of these solutions was 10000 µg/ml dissolved in 5% HNO_3 and 94% H_2O (Alpha company). The impurity rate of these solutions was less than 1 ppm. For some experiments, these solutions were diluted by distillated water which was analyzed by the same techniques.

ICP-OES analysis of the solutions (after the deposition) shows that lanthanum concentration is determined with a shift of about 20% comparatively to the starting solutions, while manganese concentration shift is only about 4%. Because of these errors it is not possible to know exactly whether one of the elements is preferentially introduced to the low pressure reactor. The deposition time has also no significant influence in such an enrichissement of one of the elements. The impurity rate is also less than 1 ppm.

IV - THIN FILM ANALYSISf

The stoichiometry of the deposits were determined by ICP-MS for different concentrations of the main elements in the starting solutions. Figure 2 plots the ratio of La and Mn concentrations in the deposits as a function of this ratio in the starting solutions. This curve shows the importance of a very precise concentration of these elements in the starting solution in order to obtain a stoechiometric deposit ($LaMnO_3$). The concentration ratio of La/Mn in this case is about 2.3, showing a preferential deposition of Mn. The highest impurity rate was found for Fe, Ca and Mg and was evaluated to be less than 1 w%.

Figure 2 : Concentration of the deposits (EDX-ray analysis) as a function of the concentration in the starting solutions.



These deposits made on quartz and YSZ were characterized by conventional XRD and TEM-XRD. Figure 3 shows the XRD spectra of some of these samples. For a low concentration of manganese (La/Mn = 50) in the starting solution, La_2O_3 phase is identified, while for a lowest concentration of lanthanum (La/Mn = 1-10) $LaMnO_3$ perovskite with a low amount of Mn_3O_4 are present in the deposit.

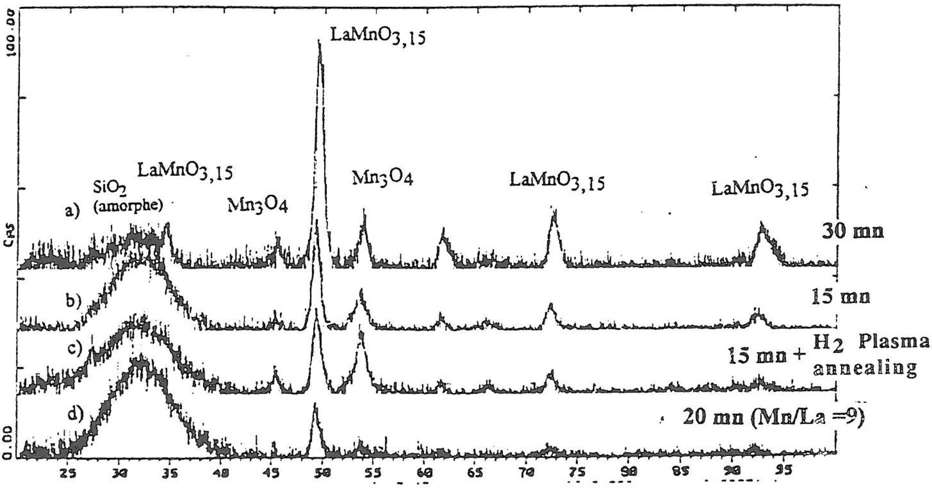


Figure 3 : XRD patterns of some deposits showing a perovskite phase of LaMnO3 with a low amount of Mn3O4

Figure 4 shows the TEM-XRD diffraction pattern of a thin film obtained after 5 minutes deposition. The diffraction pattern (Ewald's spheres) of this deposit shows a microcrystalline structure in which small crystals of a hundred of nanometer are randomly oriented. The size of this particle agglomeration was about 100 nm suggesting the possibility of cluster formation in the plasma stream prior to the deposition. The calculation of four plane distances from this pattern led to the identification of a LaMnO3 perovskite structure.

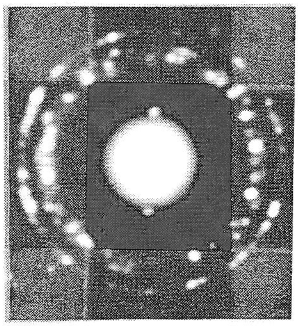


Figure 4 : TEM-XRD pattern of a deposit with a short time deposition. The Ewald's spheres indicate the presence of randomly oriented LaMnO3 microcrystals.

Combining these results with the FTIR specta of some deposits, we can assume that the oxidation is the most dominant phenomenon in the plasma stream. FTIR spectra of the deposits show actually a very low rate of nitrates (nitrate bands are at least 100 times more sensitive than the oxide bands) and the same bands than the reference oxide perovskite LaMnO3 bands (608, 490, 388 cm^{-1}). In this case, the deposit seems to be composed of a mixture of Mn_3O_4 and $LaMnO_3$.

V - PROFILOMETRY & DEPOSITION RATE

The profile of the deposits were measured with a dynamic focalisation profilometer. The deposition rate is higher on the axis of the reactor and leads preferentialy to a high deposition rate in the center of the substrate. This deposition rate was near to 1µm/mn. The real deposition rate for the current configuration of the reactor was evaluated by the measurement of the weight of the substrates before and after deposition, leading to a deposition rate of 130 µg/mn for a solution flow rate of about 0,12 sccm/mn.

A deposit made on YSZ was investigated by optical microscopy after a metallographic preparation, and confirme the profile of the deposit and its good porosity.

VI - PARTICULE SIZES & AGGLOMERATIONS

The particule size distribution is one of the most important parameters for the ceramic characterization. This distribution was evaluated by Image analyzing of some SEM micrographs. A narrow particle size distribution was obtained around a mean value of about 0.2 µm. The calculation of the mean value of the droplet sizes for the nebulized solution was estimated to be about 2 µm prior to their introduction into the plasma reactor. The evaporation of these droplets is one of the possible phenomenon, leading to the precipitation of the solute and the shrinking of the particles. The shape factor estimation shows that most of these particles are slightly changed to the elliptic shape (mean shape factor = 0.7). The input power between 1000 and 2400 Watts seems also to have no real influence on the shape and size of the particles. SEM micrographs showed also that the number of the particles is higher in the center of the substrate. However, the particles has the same mean diameter and shape factor in the edge and in the center of the substrate. Figures 5 shows one of these micrographs with a good porosity. The porosity of one of the deposit was also investigated after a metallographic preparation, comparatively to the porosity of the electrolyte (YSZ).

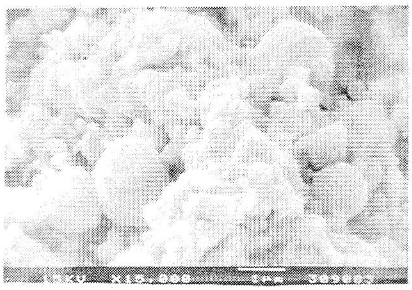


Figure 5 : SEM micrograph of one deposit showing its good porosity.

VII - DEPOSITION PHENOMENA

These results suggest a nucleation phenomenon leading to the agglomeration of clusters in the plasma stream. In view of the fact that the thermal transfer is extremely low at low pressure, the influence of the input power on the shrinking of the particles is not significant and oxide formation takes place mainly in the plasma stream before deposition. The OES identification of MnO and LaO bands during the deposition confirme as well this fact. The different stages of the deposition process are schematically represented in figure 6.

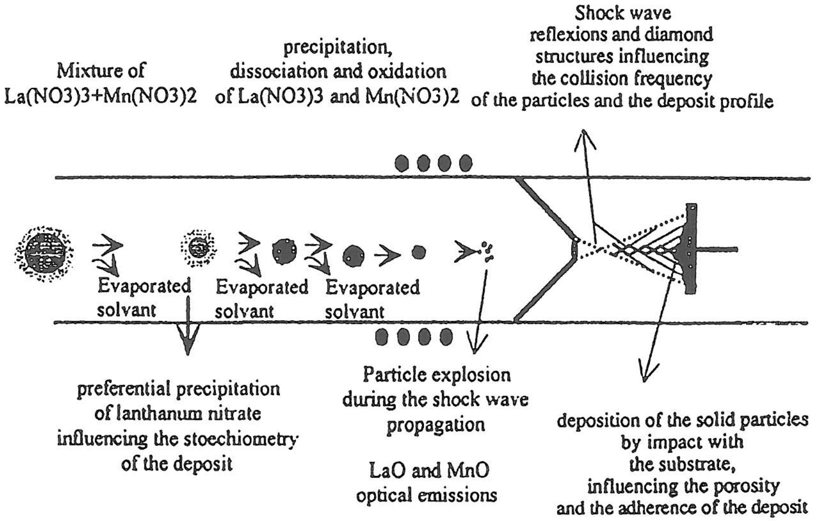


Figure 6 : Cluster formation and deposition process.

CONCLUSIONS

The XRD analysis led to the identification of different oxides. For a low concentration rate of Mn, lathanum oxide (La_2O_3) was identified, while for a low concentration rate of lanthanum, manganese oxide (Mn_3O_4) diffraction pattern was observed. For a suitable concentration ratio of La/Mn, $LaMnO_3$ perovskite oxide was present in the deposits as microcrystals being randomly oriented, according to XRD-TEM patterns obtained for particle agglomerations in the range of hundreds of nanometers. Particle agglomerations used for this purpose were obtained during a short time deposition (5 mn). That led to the conclusion that clusters are formed and transformed in the plasma stream prior to the deposition. FTIR analysis confirmed that nitrates were completly transformed to oxides in the deposits during the plasma deposition. The crystallinity of some deposits was improved by a H_2-Ar post plasma annealing at 650°C.

SEM and Image analysis investigations showed a submicronique distribution of the particle sizes through the deposits. The profil of the deposits was inhomogeneous over the surface of the substrate. The deposition rate evaluated at the center of the substrate was about 1μm/mn for the current configuration of the reactor. The profil of the deposits was also determined by a dynamique focalisation profilometer, and optical microscopy of metallographic preparated deposit on YSZ, leading to the confirmation of a preferantial agglomeration in the center of the substrate (reactor's axis). SEM investigation of the metallographic specimen confirmed also its good porosity.

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