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Preparation of Perovskite Powders and Coatings by Radio Frequency Suspension Plasma Spraying

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Perovskite-type $LaMnO_3$ powders and coatings have been prepared by a novel technique: reactive suspension plasma spraying (SPS) using an inductively coupled plasma of approximately 40 kW plate power and an oxygen plasma sheath gas. Suitable precursor mixtures were found on the basis of solid state reactions, solubility, and the phases obtained during the spray process. Best results were achieved by spraying a suspension of fine MnO_2 powder in a saturated ethanol solution of $LaCl_3$ with a 1 to 1 molar ratio of lanthanum and manganese. A low reactor pressure was helpful in diminishing the amount of corrosive chlorine compounds in the reactor. As-sprayed coatings and collected powders showed perovskite contents of 70 to 90%. After a posttreatment with an 80% oxygen plasma, an almost pure $LaMnO_3$ deposit was achieved in the center of the incident plasma jet.

Keywords induction plasma spraying, perovskite, radio frequency plasma synthesis, solid oxide fuel cell, suspension plasma spraying

1. Introduction

Radio frequency (rf) inductively coupled plasma with its intrinsic properties offers a high potential for the development of new applications. The plasma is generated in the high frequency field of an induction plasma torch. Figure 1 shows the scheme of an induction plasma torch; the principle of rf plasma spraying is explained elsewhere (Ref 1).

Compared to the more conventional direct current (dc) plasma, rf plasma has a slow but large volume plasma jet resulting in a long residence time of the particles in the plasma. Therefore, the possibility of plasma chemical reactions increases. Further advantages of rf plasma technology are the axial injection of raw materials and the electrodeless plasma generation, which enables operation under a wide range of conditions including reducing or oxidizing atmospheres.

Recently a novel technology, called suspension plasma spraying (SPS), was developed for the production of ceramic powders (Ref 2). This technique avoids the time and energy consuming successive steps of conventionally used production routes such as precipitation, calcination, sintering, crushing, and screening in sintering techniques or concentration, atomization, and consolidation in spray pyrolysis processes (Ref 3). In SPS technology, a suspension of fine powder or precursor components is fed to an rf plasma torch and directly gas atomized into the plasma through an atomization probe. The whole in-flight process (atomization, drying, and melting associated with or without chemical reactions) occurs in approximately 10 ms. Finally, the powder is either collected for further application or directly deposited onto a substrate. The SPS process has already been applied for the preparation of hydroxyapatite, cobalt spinel, and Al-Ni-Mo intermetallics (Ref 4, 5).

An interesting new application of SPS might be the preparation of perovskite powders or deposits to be used for cathodes in solid oxide fuel cells (SOFC). Solid oxide fuel cells convert chemical energy directly into electrical energy; they exhibit high efficiency and a high temperature level of waste heat.

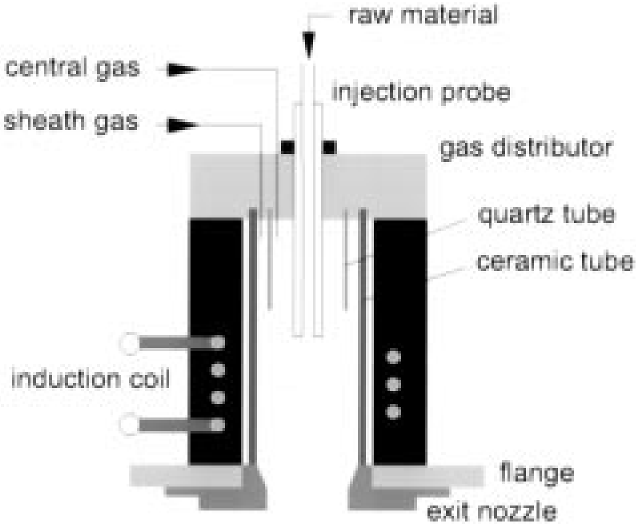

Fig. 1 Scheme of an rf plasma torch

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Future applications include topping stages in central power plants as well as small combined heat and power supply systems (Ref 6). In both cases there is a strong need for economical production methods of SOFC components using low cost materials to meet the very strict economic requirements for a wide-spread future application of SOFC systems. Perovskite-type oxides $LaMO_3$ (M = cobalt, iron, manganese, chromium) doped with alkaline earth metals on lanthanum sites for improved conductivity have been studied to be used as the cathode material on the air side on which oxygen molecules are reduced to oxygen ions to be incorporated into the electrolyte. At present, the main cathode material is $(LaSr)MnO_3$, while other lanthanum-site doped perovskites are applied as functional layers in SOFC (Ref 7). The requirements concerning grain size distribution, morphology, phase composition, etc., of the powders processed by sintering techniques (Ref 8) as well as thermal deposition methods (Ref 9) are extremely high. This results in very high costs for powder production using conventional methods. Against this background, SPS was tested for the production of perovskite powders or for the deposition of layers that could considerably diminish the production costs of SOFC components. In this article the results of perovskite powder and coating preparation for SOFC applications are presented.

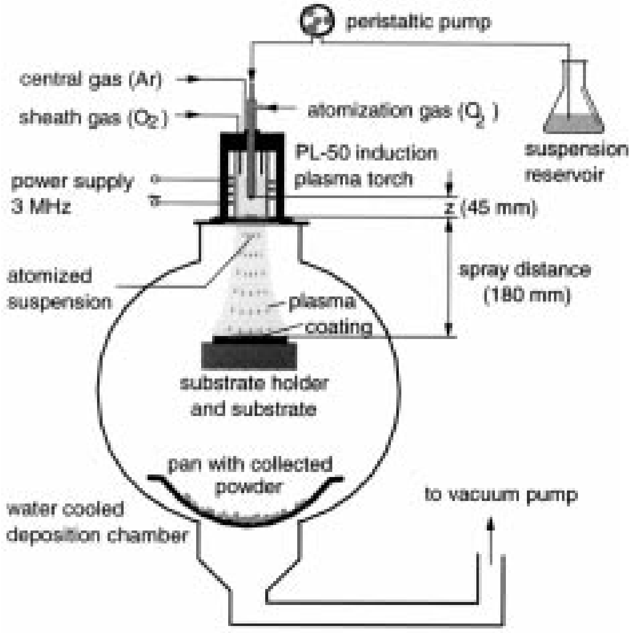

Fig. 2 Experimental setup of the suspension plasma spraying experiments

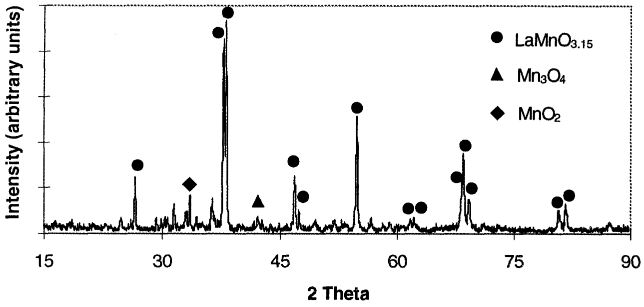

Fig. 3 X-ray diffractogram of perovskite powder obtained in a solid state reaction at 1100 °C

2. Experimental Procedure

Powders and coatings of $LaMnO_3$ have been produced by SPS. A suspension of fine MnO_2 powder (grain size <50 µm) in saturated aqueous and ethanol solution of $LaCl_3$ with a 1 to 1 molar ratio was applied.

Figure 2 shows the experimental setup used for rf plasma synthesis/densification and deposition. The plasma is generated using a PL50 induction plasma torch (Tekna Plasma Systems Inc., Sherbrooke, Canada), operating at a frequency of 3 MHz. The suspension is fed by a peristaltic pump to the injection probe that is built as an airblast atomizer. The powders produced by the SPS process were either collected in a vessel situated on the reactor bottom or directly deposited onto nickel plates (3.1 mm thickness). Table 1 summarizes the conditions for both rf plasma synthesis/densification and rf plasma deposition.

For analysis of the powders and the deposited layers, x-ray diffraction (XRD) (Rigaku D2max Geigerflex, Danvers, MA; and STOE Stadi P, Darmstadt, Germany) and scanning electron microscopy/electron dispersive analysis by x-ray (EDX) measurements (JEOL JSM840A/Link AN 10000, Peabody, MA; and

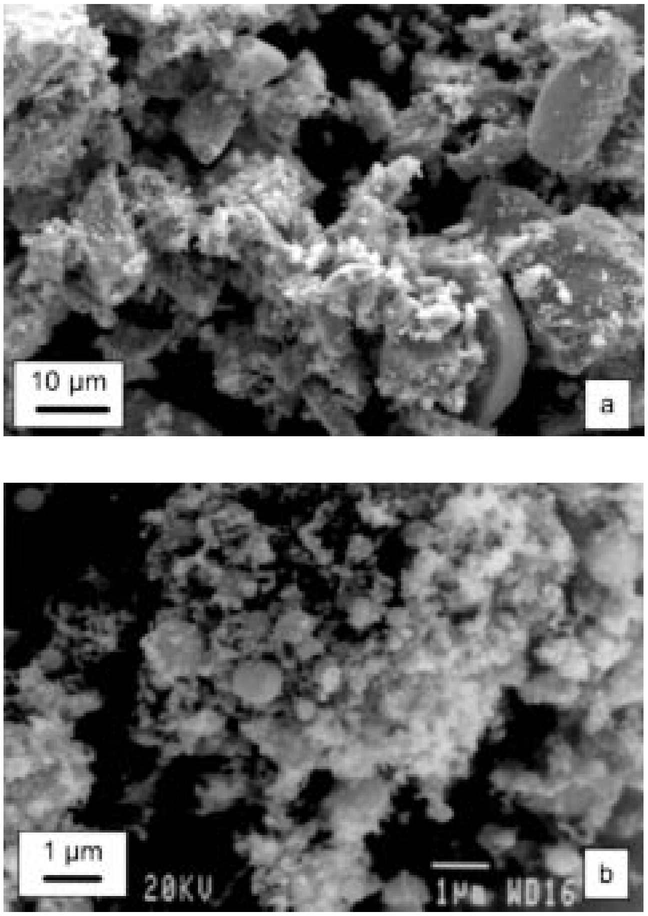

Fig. 4 Scanning electron micrographs of MnO_2 (a) raw powder and (b) powder obtained from suspension plasma using a suspension of MnO_2 in a saturated aqueous $LaCl_3$ solution

TOPCON ISI-DS 130, Elektroneu Optik Sevice, Dortmund, Germany) were completed.

3. Results and Discussion

The chemical reaction and stoichiometry of the perovskite formation was determined using $LaCl_3/MnO_2$ and $La(NO_3)_3/MnO_2$ mixtures (1 to 1 molar ratio) by carrying out a solid state reaction at 1100 °C in an oven for 12 h. Using $LaCl_3$ as the starting material, a nearly pure $LaMnO_{3.15}$ (ASTM 32-484) (Ref 10) perovskite phase was detected by XRD (Fig. 3).

Much lower purity was achieved with $La(NO_3)_3/MnO_2$ mixtures. Thus, the first spray experiments used a suspension of MnO_2 powder (<50 μm) in a saturated aqueous $LaCl_3$ solution with a 1 to 1 molar ratio. Applying the parameters given in Table 1 (70 kPa reactor pressure), the powders obtained were collected in the reactor bottom for SEM and XRD analysis.

The scanning electron micrograph shown in Fig. 4 revealed that very fine grains smaller than 2 μm were produced. This indicates that the raw powder particles of the suspension completely melted in the plasma.

With EDX analysis a large amount of residual chlorine was found and indicates that the reaction was not fully completed in the plasma. X-ray diffraction analysis (Fig. 5a) showed that perovskite was the main product, along with some phases of LaOCl, La_2O_3, and Mn_3O_4. The subsequent annealing of the powder at 1100 °C showed the formation of almost pure perovskite phase (Fig. 5b), indicating the proper ratio of lanthanum and manganese in the primary suspension as well as the absence of preferential evaporation of one of the elements. However, it also points out that the temperature or the reaction time during the plasma synthesis was not sufficient for complete perovskite formation.

The decrease of the reactor pressure to 30 kPa resulted in a diminished amount of chlorine compounds, which has beneficial consequences with respect to the corrosive atmosphere in the reactor. For this reason the following experiments were performed at 30 kPa pressure, although the purity of the resulting powder has not changed significantly. Possible parameter variations for an improved chemical reaction in the plasma are (a) increase of the plasma power, (b) increase of the residence time of the material in the plasma, (c) reduction of the suspension feed rate, and (d) the replacement of water by another liquid phase, which should ensure a higher temperature of the plasma. Using alcohol as the suspension liquid in a plasma that mainly consists of oxygen should raise the plasma enthalpy due to the contribution of the combustion heat to the total plasma enthalpy. The EDX analysis of the powder obtained from a suspension of MnO_2 in a saturated ethanol $LaCl_3$ solution revealed a much smaller content of chlorine. The XRD measurement showed mainly the perovskite phase $LaMnO_{3.15}$, with only a relatively small amount of additional phases such as LaOCl and La_2O_3 (Fig. 6).

Coating experiments were performed (Table 1) by applying the optimized parameters of the powder preparation. Nickel plates of 60 by 60 by 3.1 mm^3 were used as substrates, and the spray distance was 180 mm. The substrates were fixed in the axis of the plasma jet without any movement during the coating experiment. Thus, a high growth rate of the deposit of approximately 100 μm thickness in each run of 90 s was achieved. The layers obtained were quite dense and, hence, are not suited in this state for the SOFC application as cathode layers (Fig. 7). Some more development work with the objective of achieving a considerably enhanced layer porosity must be carried out in further experiments.

The phase composition of the as-sprayed layers determined by XRD revealed an amount of undesired La_2O_3 in the range of

Table 1 Experimental conditions for $LaMnO_3$ powder and layer production by suspension plasma spraying

Central plasma gas, slpm	Ar, 30
Sheath plasma gas, slpm	O_2, 120
Atomization gas, slpm	O_2, 5
Plate power, kW	41
Suspension feed rate, mL/min	10
Reactor pressure, kPa	30-70
Spray distance (a), mm	180

(a) During the coating experiments

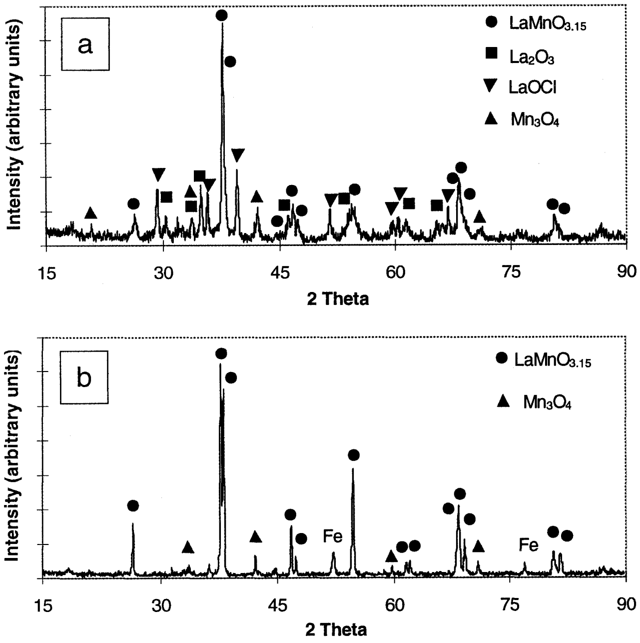

Fig. 5 (a) X-ray diffractogram of powder obtained from suspension plasma spraying. (b) X-ray diffractogram of annealed powder from the same sample proving the proper stoichiometry (iron from sample holder)

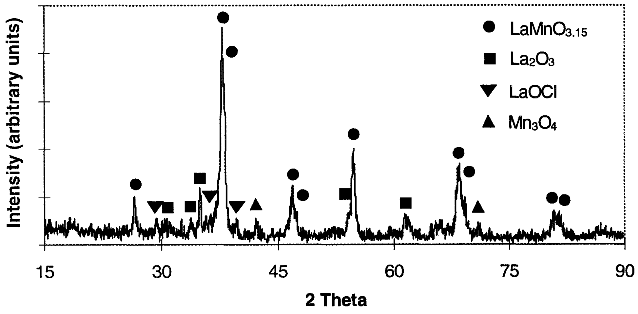

Fig. 6 X-ray diffractogram of powder suspension plasma spraying synthesized with ethanol as the suspension liquid phase

20 to 30% (Fig. 8a). Therefore, in further experiments the as-sprayed layers were immediately posttreated with a plasma that consisted of 80% oxygen. After five minutes the amount of La_2O_3 was reduced to approximately 10%. A longer posttreatment of 12 min (Fig. 8c) led to the formation of almost pure $LaMnO_{3.0}$ perovskite phase (ASTM 35-1353). It is worth mentioning that this complete transformation occurred only in the axis zone of the plasma jet. Further toward the margin of the deposit the impurity content of the layers was still in the range of 10 to 20%.

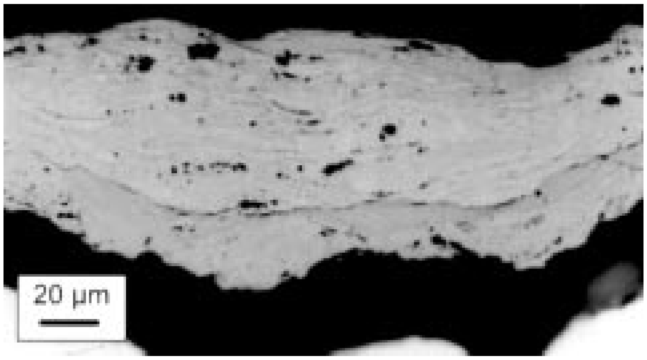

Fig. 7 Optical micrograph of a cross section of a suspension plasma sprayed perovskite layer

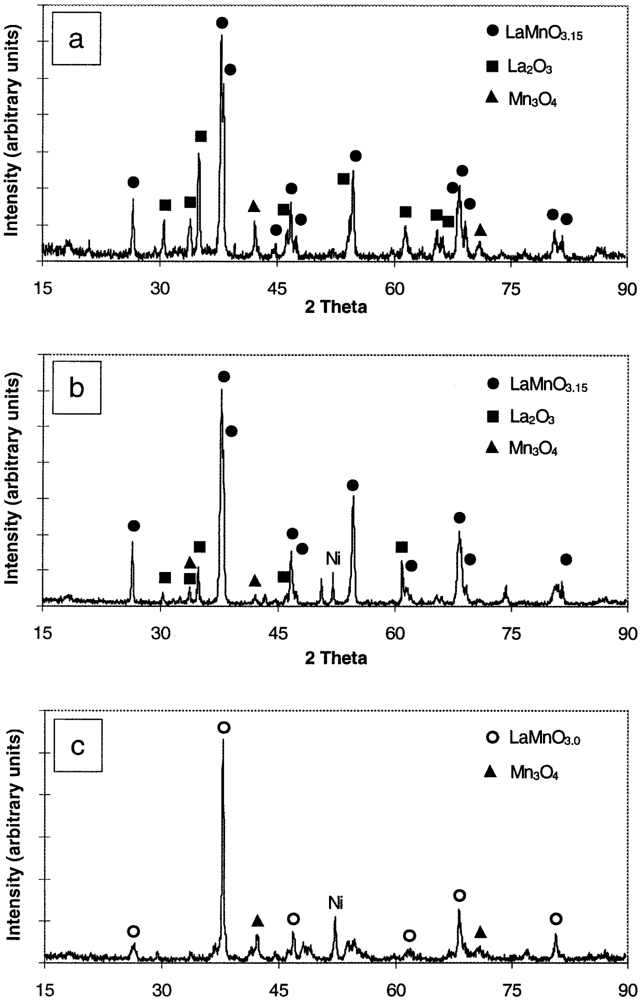

Fig. 8 Influence of the oxygen plasma posttreatment. X-ray diffractograms of (a) as-sprayed coating, (b) coating treated with an oxygen plasma for 5 min, and (c) coating treated with an oxygen plasma for 12 min (nickel sawdust from sample preparation)

4. Conclusion and Outlook

Perovskite powders and coatings were prepared in an rf inductively coupled plasma using a precursor suspension of MnO_2 powder in an ethanol solution of $LaCl_3$. The powder completely melted in the plasma and formed the $LaMnO_3$ perovskite phase as the primary phase. A certain amount of additional phases such as mainly La_2O_3 were also present. The phase purity of the perovskite coatings could be further enhanced through a posttreatment with an 80% oxygen plasma.

To achieve the requested long-term stability of the $LaMnO_3$ cathode layer in the solid oxide fuel cell application, the formation of La_2O_3 must be totally suppressed. Additionally, the porosity of the layers must be further improved because the low porosity obtained will not ensure gas transport to the cathode-electrolyte interface. For improved electrical conductivity of the cathode layer a suitable precursor and the appropriate process parameters must be found for the doping of the $LaMnO_3$ with strontium. Eventually the cathode layers must be electrochemically characterized for comparison of the electrode performance with conventionally fabricated SOFC cathodes.

References

1. T.B. Reed, Induction Coupled Plasma Torch, *J. Appl. Phys.*, Vol 32, 1961, p 821-824
2. F. Gitzhofer, E. Bouyer, and M.I. Boulos, Suspension Plasma Spraying, U.S. Patent 5,609,921, 1997
3. L. Pawlowski, Materials Used for Spraying, *The Science and Engineering of Thermal Spray Coatings*, John Wiley & Sons, Inc., 1993, p 1-20
4. E. Bouyer, F. Gitzhofer, and M.I. Boulos, Parametric Study of Suspension Plasma Sprayed Hydroxyapatite, *Thermal Spray: Practical Solutions for Engineering Problems*, C.C. Berndt, Ed., ASM International, 1996, p 683-691
5. E. Bouyer, M. Müller, N. Dignard, F. Gitzhofer, and M.I. Boulos, Suspension Plasma Spraying for Powder Preparation, *Progress in Plasma Processing of Materials 1997: Proc. of the Fourth Int. Thermal Spray Conf. 1996* (Athens, Greece), P. Fauchais, Ed., Begell House, Inc., New York, 1997, p 751-759
6. N.Q. Minh and T. Takahashi, System and Application, *Science and Technology of Ceramic Fuel Cells*, Elsevier, Amsterdam, 1995, p 331-349
7. E. Fendler, R. Henne, R. Ruckdäschel, and H. Schmidt, Protecting Layers for the Bipolar Plates of Planar Solid Oxide Fuel Cells Produced by Vacuum Plasma Spraying, *Proc. Second European Solid Oxide Fuel Cell Forum* (Oslo, Norway), Vol 2, B. Thorstensen, Ed., 1996, p 269-278
8. L.-W. Tai and P.A. Lessing, Tape Casting and Sintering of Strontium-Doped Lanthanum Chromite for a Planar Solid Oxide Fuel Cell Bipolar Plate, *J. Am. Ceram. Soc.*, Vol 74, (No. 1), 1991, p 155-160
9. E. Fendler, R. Henne, and M. Lang, The Production of Porous Layers for the Solid Oxide Fuel Cell by Vacuum Plasma Spraying, *Thermal Spray Science and Technology*, C.C. Berndt and S. Sampath, Ed., ASM International, 1995, p 533-537
10. A. Cooper, Bell Laboratories, Murray Hill, New Jersey, private communication, 1976