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Development of Ca-doped LaCrO3 feed material and its plasma coating for SOFC applications

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Abstract. In order to realize SOFC as power generating devices, multiple cells are connected in series through an interconnect material to accumulate the voltage output. The interconnect should have very low permeability for the gases used. A novel solution combustion process has been developed for producing the phase pure, well-sinterable powders of Ca-doped LaCrO3 interconnect material. A process has been developed to produce the coarse granules as a feed material using combustion-synthesized powder for plasma spray through (a) preparation of granules through cold iso-static pressing followed by breaking and sieving (b) sintering of the green granules followed by sieving. The flow ability and deposition efficiency studies on +45-75 and 75-125 μm powders suggested that +45-75 powder is more suitable for the plasma spray coating. The plasma process parameters; plasma power, flow rate of carrier gases and distance between substrate and plasma gun have been optimized to achieve required coating characteristics. The as-produced coating using 20 kW power plasma gun on the porous Sr-doped LaMnO3 cathode substrates has been examined by SEM. An adherent coating of about 100 μm has been observed in the micrographs. No large cracks were observed throughout the coating. However, the coating was not found to be impervious in nature. Also the micrographs showed incomplete melting of the plasma-coated material. The similar experiments were performed using a higher power (~60 Kw) plasma gun. The coated coupons were tested for leakage by checking water penetration. It was found that water did not penetrate for quite a long time. Therefore, the coupon was further tested for leakage by keeping it over a port connected to vacuum pump. The vacuum attained was 7x10-3 mbar and it was maintained for four consecutive days. The SEM studies on the coated sample showed a quite dense coating along with a very few small local pores.

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1. Introduction
High temperature solid oxide fuel cells (SOFC) have been extensively investigated for the last two decades because of their potential use as clean and efficient power generating devices. SOFC is an all-ceramic energy conversion device that generates power by way of electrochemical reaction of fuel and oxidant across an oxygen ion-conducting electrolyte [1-3]. In order to realize SOFC as power generating devices, multiple cells are connected in series through an interconnect material to
accumulate the voltage output. The interconnect should have a good electrical conductivity, very low permeability for the gases used and thermo-chemical compatibility with other cell components under the operating conditions. Since alkaline earth metal doped LaCrO$_3$ ceramics fulfill the basic requirement for stack development, they are widely used as interconnect materials in SOFC. Alkaline earth metal doped LaCrO$_3$ are also of interest due to their application as heating element for high temperature furnaces and electrode materials for electrochemical gas sensors [4-6]. The thermal expansion of 30% Ca-doped LaCrO$_3$ matches well with YSZ and hence, it is a preferred as an interconnect material for tubular SOFC. In the recent years, combustion process has attracted a considerable attention because of its capability to deliver phase-pure, ultrafine powders at low calcinations temperature, which can be readily sintered to high density at a comparatively lower temperature [7-9]. The process involves an exothermic decomposition of a homogeneous fuel-oxidant precursor (mostly in the form of a gel).

Various processes such as thermal spray, electro-phoretic deposition and slurry coating are used for the deposition of dense, thin layer of interconnect material [10-13]. Plasma coating is widely accepted technique by which LCR interconnect material is deposited on porous LSM cathode [14-15]. Plasma spraying has the advantage that it can spray very high melting point LCR material Plasma sprayed LCR coatings are generally much denser, stronger and cleaner than the other thermal spray processes.

The present paper reports the bulk preparation of sinter-active powder of Ca-doped LaCrO$_3$ (LCR) interconnect material and producing the sintered aggregates (granules) as a feed material for plasma spray using the same. The LCR powder and granules were characterized for their particle characteristics where as quality of plasma coating was characterized for its imperviousness through water penetration technique and vacuum leak testing.

2. Experimental

The ultrafine, well-sinterable LCR powder was prepared in bulk through the glycine-nitrate solution combustion process as described in our previous publication [16]. The powders and sintered samples were characterized in terms of phase purity using X-ray diffraction (XRD), particle size using transmission electron microscopy (TEM) and particle size analyzer based on laser scattering, sintering characteristics using scanning electron microscopy and density measurements and conducting behavior using a standard four-probe technique [16].

In order to prepare LCR granules (with better flow-ability) as a feed material for plasma coating, the powder at 700 °C was mixed with 1 weight % poly vinyl alcohol (PVA) solution to make a thick paste. PVA act as a binder for granulation. It was then dried completely and crushed with a mortar and pestle. The crushed powder was pressed in cold isostatic press (CIP) in the form of cylindrical blocks at a pressure of 15 KPsi and broken. This pressing and breaking process was repeated twice. Finally, the granulated powder was sieved to obtain a size fraction of +75-125 μm. These green granules were sintered at 1250 °C. The sintered granules were grounded lightly in a mortar and pestle to break the locally bonded clusters and sieved to obtain the target size fraction of -75+37 μm suitable for plasma spray. The as-produced granules of LCR were characterized in terms of their bulk density, particle size and spray deposition efficiency. These LCR granules were used to make plasma spray coating over porous LSM. The plasma gun operating at about 60 kV was used for this purpose. The developed coating was characterized in terms of its microstructure and vacuum leak testing.

3. Results and discussion

The developed glycine-nitrate solution combustion process gave rise to well-sinterable, ultrafine LCR powder [16]. The four probe DC conductivity measurement on the sintered bar sample as a function
of temperature exhibited the expected Arrhenius behavior, as shown in Fig. 1. The conductivity value obtained at 1000 °C was found to be 57 S cm⁻¹.

Fig. 1: D. C. conductivity of sintered La₀.₇Ca₀.₃CrO₃ as a function of temperature.

The feed powder for plasma spray process is required to have sufficient flow-ability, a feature typically not possessed by very fine size powders.

Fig. 2: Optical micrographs of +45-75 μm and +75-125 μm LCR granules developed for plasma spray

On the other hand, coarse powders are difficult to melt and good coating becomes difficult. In order to balance these competing phenomena, aggregates of fine particles can be prepared. In order to check the suitability of LCR powders as a feed material for plasma, two grades of granules: (a) +45-75 μm and (b) +75-125 μm were prepared and tested for the required characteristics.
Fig. 2 shows the morphology of the developed sintered aggregates observed under optical microscope. The micrographs confirm the targeted size of the granules. The flow-ability test was done as per ASTMB-213. The 50 gm of each +45-75 μm and +75-125 μm granules were found to flow in 32.6 seconds and 18.17 seconds, respectively. The tap density of the 45-75 μm and 75-125 μm powder sample was found to be 2.73 g/cc and 3.08 g/cc, respectively. Table 1 shows the plasma spray deposition efficiency at different powers.

Table 1. Deposition efficiency LCR granules at different powers

| Power in put(kW) | Sample: +45-75 μm (% efficiency of deposition) | Sample: +75-125 μm (% efficiency of deposition) |
|------------------|-----------------------------------------------|-----------------------------------------------|
| 12               | 5.00                                          | 0.93                                          |
| 16               | 18.49                                         | 2.09                                          |
| 20               | 24.12                                         | 3.33                                          |
| 28               | -                                             | 14.39                                         |

Fig. 3 shows the variation in the deposition efficiency of the developed LCR granules as a function of the plasma powder used. The results shows that sample +75-125 μm require higher power to get reasonably good efficiency which is not suited to coat on ceramic substrates. Based on the above-described comparative study between the +45-75 μm and +75-125 μm LCR granules, +45-75 μm granules were used for plasma coating experiments.

A lot of factors, such as plasma power, the feed rate of powder, the spraying distance, and the pressure of carrier gas influenced the deposition by means of plasma spraying. These parameters have been optimized before developing the plasma coating of LCR over porous LSM substrates. The Fig. 4 shows SEM micrograph of the plasma coated surface obtained using the 25 kV plasma power gun.
The micrographs show a porous coating with the presence of a wide range of pores with size distribution of about 5-75 μm. The porous nature of the coating was confirmed by water penetration technique which showed an almost instantaneous penetration of the water through the coating. This also indicates the presence of an open porosity throughout the coating. The micrograph also shows that the LCR granules could not be melted completely resulting in such a large pores. Hence, the coating was not further tested for the vacuum leak testing. The possible reason for such porous coating is the combination of poor thermal conductivity of the LCR granules and insufficient plasma power used.

Based on the observations related to the LCR plasma coating using a 25 kW plasma coating, the experiments were performed using a 60 kW plasma gun. Fig. 5 shows the corresponding plasma coated LCR surface. The micrograph reflects an almost complete melting of the LCR granules resulting in fine microstructure. The micrograph also indicates a highly dense microstructure with a small amount of very fine local pores. There were no large pores/cracks observed through out the coating. The coating was initially tested through water penetration technique. Drops of water were kept over the coating and the time taken for penetration of water was visually noticed. It was found that water did not penetrate for quite a long time. Hence, the coupons were further tested for vacuum leakage. The vacuum attained was 7x10⁻³ mbar and it was maintained for four consecutive days.

Fig. 6 shows the SEM micrograph reflecting the crossection of plasma coated LCR over porous LSM cathode. About 100 μm thick dense coating could be achieved. The micrograph also reflects a good bonding of the plasma coated LCR with the porous LSM substrate. Such kind of dense, adherent coating is a primary requirement for SOFC applications.
Fig. 5: SEM micrograph showing plasma coated LCR surface using 60 kW power plasma gun

Fig. 6: SEM micrograph showing crosssection of LCR coating over porous LSM cathode

Fig. 7 shows XRD pattern of the plasma coated LCR coating. All the peaks could be indexed to mono-phasic $\text{La}_0.7\text{Ca}_{0.3}\text{CrO}_3$. This shows that there is no phase change during the plasma processing of LCR.
Fig. 7: XRD pattern of plasma coated LCR

4. Conclusions
A solution combustion process has been used to produce well-sinterable, ultrafine powder of Ca-doped LaCrO$_3$ interconnect material in bulk. A process has been developed to produce the coarse granules for plasma spray through powder metallurgy route using the combustion-synthesized powder. The developed granules were qualified successfully for their suitability to plasma spray. The experiments have been performed for the plasma spray coating of LCR granules on the porous Sr-doped LaMnO$_3$ cathode substrates. It was found that by using a 60 kW power plasma gun, a dense, adherent coating could be achieved as confirmed by microstructural and leak testing studies. The developed plasma coating may find its applications in high temperature SOFC.

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