Formation mechanism of island CoO in La-Sr-Co-Fe oxygen transport membrane deposited by low pressure plasma spraying-thin film technology

Shaopeng Niu, Kesong Zhou, Chunming Deng, Liping Xu, Min Liu, Wei Zeng, Zhikun Chen
Guangdong Institute of New Materials, National Engineering Laboratory for Modern Materials Surface Engineering Technology & The Key Lab of Guangdong for Modern Surface Engineering Technology, Guangzhou 510651, China

Abstract: Dense oxygen transport membranes (OTMs) made from mixed oxygen ionic and electronic conductors (MIEC) have attracted intense research interest owing to their unmatched advantages on pure oxygen production, oxygen-fuel combustion and oxygen-related catalytic processes over traditional techniques. As one kind of the most-studied membranes, cobalt-containing membranes have unsatisfied thermal stability, though the oxygen permeability of these membranes is generally excellent due to the existence of cobalt. However, in situ forming CoO phase which were observed in the cobalt-containing membranes prepared by low pressure plasma spraying-thin film technology (LPPS-TF), were found to exhibit a remarkable stabilizing effect in the preliminary work. As one of the main premises to reveal the stabilization mechanism of these island CoO phase, their formation mechanism were studied in the first place in the paper.

1. Introduction
As one of the ceramic functional films, OTMs can realize continuous oxygen transfer process in a high temperature (always more than 700 °C) and oxygen partial pressure gradient environment. These membranes can separate other gas molecules, but only allow oxygen to pass through in the form of oxygen ions diffusion. No external circuitry is necessary for charge compensation, because electrons will migrate in the opposite direction of the oxygen transfer. Therefore, the selectivity of the OTMs is theoretically infinite [1-3].

Pervoskite-type oxides with the formula ABO3 were thought to be candidate materials for application of OTMs since the study began. ABO3 structure is flexible in its elemental composition, slight modifications of A/B-site elements or contents can significantly affect the oxygen permeability and the thermal stability of the membranes, and hence the performance control can be easy to implement [4]. However, the pervoskite has frail crystals due to its very limited slips and ionic bond like combination of A-site cations and oxygen ions. As a result, the pervoskite materials commonly have low strength, high brittleness and poor ductility [5]. This natural defect has always been one of the core factors which restrict the industrial application of OTMs. To solve the problem, asymmetric membrane comprising a dense thin film on a porous support with sufficient strength has been proposed [6]. Owing to its potential in reducing the thickness and increasing the mechanical strength, two vital ingredients that should be acquired for an applicable OTM, asymmetric membrane has become one of the current research focus. Because of the advantages over conversional wet chemical methods in preparation efficiency and non-sintering, atmospheric plasma spraying (APS) technique has already been tried to fabricate the
asymmetric membrane in the early 20th century [7]. However, preparing a gas-tight membrane by APS is quite a challenge at that time. Until recent years, the situation has started to be changed with the development of LPPS-TF, also named as plasma spraying-physical vapor deposition (PS-PVD), which now is well-known in producing thermal barrier coatings with columnar structure for high temperature parts in aero-engines and gas turbines [8, 9]. The LPPS-TF process provides an effective avenue for membrane preparation. By means of high-powered plasma gun (180kW) and operating pressures down to 200Pa and below, the process leads to the formation of a laminar plasma plume with extended dimensions (length >2m) and produces a hot (>6000 °C) supersonic gas stream. So that, a thin, gas-tight and well-adherent ceramic coating can be deposited rapidly. And successful preparation has already been reported by researchers [10-13].

In these studies, most found that there were CoO phase appearing in the LPPS-TF made Co-containing membranes by X-ray diffraction (XRD) analysis [12, 13]. But these CoO phase were normally ignored, as they were generally thought to be only the impurities due to the perovskite decomposition in the low oxygen preparation environment. However, an unexpected stabilizing indication of the CoO phase was detected in the preliminary work [14]. As such, the effect of the CoO phase should be reframed, but before that, the formation of CoO phase should be figure out initially. So in the paper, a general forming process was given by studying the influence of the torch power, particle size of the powder and spray distance on the formation of CoO phase.

2. Experimental

2.1. Powders and Substrates
Classical La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF-6428) perovskite material was chose to study. The substitution of divalent Sr for trivalent La in the A-site increases the oxygen vacancy whereas the substitution of Fe for high valence Co in the B-site preserves the perovskite structure, which makes the LSCF materials more balanced in performance [15].

In the work, two kinds of plasma spray powders with different particle size, LSCFA (15-45μm) and LSCFB (5-25μm) were used as the feedstock material supplied by Oerlikon Metco company. The element contents of the two powders were determined by titration. As shown in Table 1, the actual chemical compositions of the both powders are close to the calculated value.

| Element contents in two kinds of LSCF powders |
|---------------------------------------------|
| Element contents (wt.%)                     |
| La  | Sr  | Co  | Fe  | O   |
| Calculated. | 37.4 | 15.7 | 5.3 | 20.0 | the rest |
| LSCFA | 36.0 | 16.5 | 4.3 | 21.0 | the rest |
| LSCFB | 35.3 | 16.0 | 4.5 | 21.4 | the rest |

Porous AISI 316L stainless steel discs with porosity of 35% were used as the substrates. Mirror polished bulk stainless steel samples were used for collecting the LSCF droplets.

2.2. Membrane preparation and particles collection
LPPS-TF preparation works were carried out in an LPPS-hybrid facility using a current-controlled O3CP gun. Argon and helium were used as plasma gases. By using two kinds of powders, five experiments were performed under different process parameters containing current, argon-helium mixture ratio which could be set to adjust the torch power. The experimental conditions are listed in Table 2. The same spray distance (1000mm) and chamber pressure (150Pa) were used in the five experiments.

The particles collection process can be described in figure 1. Mirror polished samples were placed at three different spray distances (600, 800, 1000mm) from the nozzle. The plasma jet should complete a very fast move from the top sample to the bottom so that a certain number of independent particles would be deposited on the surface of the samples in a flat shape.
Table 2 Five experimental conditions

| No. | Parameters                  | Torch power /kW | Powders |
|-----|-----------------------------|-----------------|---------|
| 1#  | 2400 Current /A 100-20 Ar-He flow rate /L/min | 51.2            | LSCFA   |
| 2#  | 100-20 57.0                |                 |         |
| 3#  | 2600 90-30 60.6            |                 |         |
| 4#  | 80-40 63.2                 |                 |         |
| 5#  | 80-40 63.0                 |                 | LSCFB   |

Figure 1. The schematic diagram of particles collection

Only LSCFA powder was used in particles collection. The 4# parameter was selected to use for the particles deposition.

2.3. Microstructure and composition analysis
The morphologies of the membranes and the collected particles were observed by the scanner electron microscope (SEM, FEI nano 450). The Co contents in the membranes and particles were detected by the energy dispersive spectrometer (EDS).

3. Results and discussion

3.1. Microstructure and Co contents

Figure 2. The cross-sectional morphologies of the LPPS-TF membranes prepared under 1-5# experimental conditions(a-e); Co atom percent in 1-5# membranes and the two powders (f)
Figure 2a to 2e shows the cross-sectional morphologies of the LPPS-TF membranes prepared under 1-5# experimental conditions. A corresponding growing of density can be observed from 1# to 4# membrane with the increasing torch power which leads to an improving melting degree of powders. The 5# membrane has denser microstructure compare to the others due to the use of smaller size LSCFB powder, which is more likely to be melted in the plasma jet. The membrane deposition principally follows the liquid solidification way, which means the well melted powders are sufficient to make up the membrane with high density. The density trend of the above membranes just reflects such regularity.

Similar to the density change, the Co content is also growing from 1# to 5# membrane as shown in figure 2f. In the magnification morphology of the 5# membrane shown in figure 3a, lots of punctate Co-rich phase can be found existing in the interlaminer interfaces. These Co-rich phase are proved to be the CoO according to the preliminary research. It reveals that the formation of CoO makes the 5# membrane have a significant increase in the Co content. Moreover, it’s also a sign that the formation of CoO is bound up with the melting degree of the powders.

![Figure 3](image)

**Figure 3.** The magnification back scattering morphology of the 5# membrane (a), the EDS pattern of the punctate phase (b)

### 3.2. Particles collection

![Figure 4](image)

**Figure 4.** The morphologies of the collected particles at the spray distances of 600, 800 and 1000 mm (a-c), the magnification morphology of the particle at the spray distance of 1000 mm (d), the EDS pattern of the island CoO (e)
As mentioned above, the powders with higher melting degree will form more CoO phase, so the collected particles with small diameters range from 5 to 15μm were chose to study in this part of work. As shown in figure 4, these observed particles have nearly round shape and smooth edge, meaning the droplets had well spreading at the moment they impacted the substrates. Nearly no quenching cracks were generated in these particles, and that is the key factor to form highly dense ceramic coatings.

According to the results of the EDS mapping, both surfaces of the particles collected at the spray distances of 600 and 800mm have uniform elements distribution and none obvious Co content increase. By contrast, some island CoO phase with an average size of 200nm are found to appear on the surface of the particle collected at the distance of 1000mm (Figure 4c, d). The difference reflects that the growth of CoO phase correlate with the flight time of the droplets. Relatively longer time heating in the plasma jet for the droplets seem to help the CoO phase growing.

3.3. Formation mechanism of the island CoO phase
Based on the above tested results, the formation mechanism of island CoO is given briefly in figure 5. As shown, once the particle with suitable size fed into the high temperature plasma jet which is composed of lots of Ar+, He+ and electrons, it will be quickly melted to form a droplet which has melt interior and a gas-liquid critical outer shell. The random motion of the ions is ongoing from the interior to the outer shell. Among these ions, high valence Co ions (Co3+/4+) have priority of gaining the electrons and fulfilling the valence downgrade. As a result, located in the outer shell, the electrons in the plasma would preferentially combine with the more reactive Co3+/4+ and the surrounding O2- to form the CoO clusters. These clusters keep growing and accumulating along with the flight, also a continuous heating process of the droplet. When the droplet finally hits on the substrate, the CoO phase will be the first to solidify in a punctate shape at the surface of the flat particle, owing to its higher melting point (1935℃) than that of the LSCF materials, which is normally less than 1565℃.

![Diagram of formation mechanism of island CoO](image)

**Figure 5.** The formation mechanism diagram of the island CoO

4. Conclusions
To sum up, the experimental results show that the initial formation or not of the CoO is depend on the melting degree of the powder particles. Besides, the growth of the CoO phase is depend on the flight time, or heating time to be precisely, of the droplets. Based on the two conclusions, the formation mechanism of island CoO is given briefly. It is thought the formation place is located on the gas-liquid critical outer shell of the flying droplet. In this case, the electrons in the plasma would preferentially combine with the more reactive Co3+/4+ and the surrounding O2- to form the CoO clusters. Along with the growth and accumulation of these clusters, the more stable CoO phase finally generate.
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