INDUCTION PLASMA SYNTHESIS OF NANOSIZED COMPOSITE OXIDES

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Abstract

The induction plasma system has been used for the synthesis of nanosized particulate composite oxides. The process is based on the high temperature oxidation (combustion) of vapourized metallic (Ni + Cr) powders, followed by a rapid quenching of the products by water spray. The input powdered metals of identical elemental composition (Ni-Cr ratio) were introduced as three different forms: pure physical mixture of the metals, agglomerated powders or intermetallics. The very finely divided products (d_p < 100 nm) so obtained were subjected to extensive physico-chemical analyses including those provided by SEM, TEM and XRD. Particle size analysis was effected by both the analysis of microscope images and the use of a superfine particle analyser. The influences of the chosen processing parameters on the final products particle size distribution, including applied plasma power, processing pressure and the oxygen presence in a carrier gas are presented.

1. Introduction

The extensive use of solid oxide fuel cells (SOFC) as electrical energy sources requires among other characteristics the use of very efficient electrode materials, especially for the fuel electrode (anode). The interfaces between the electrolyte and the electrode, particularly the triple phase boundaries (TPB), are important parts of the reaction zone of such cells [xvi]. Optimization of cell performance is based on, among other variables, making the TPB as extensive as possible by adjustment of the electrode material grain size, pore size and overall porosity [xxvii]. The presence of nanosized particles is very desirable for extending the triple phase boundary length. In general, nanomaterial synthesis processes such as vapour deposition and sol-gel processing require expensive, complex and specialized equipment and they are also time consuming. Plasma treatment of metal salt solutions [xx, xxv, xxvi, xxvii] yields very interesting results but it is limited to soluble chemical compounds and provides for relatively low throughput rates due to the high energy consumption for solvent evaporation and particle calcination. Direct oxidation of metallic single-component feeds in a transferred arc [xxviii] or DC plasma torch [xxvii] has already been reported. Induction plasma processing of commercial metal powders to synthesize nanosized composite oxides in a single step process has also been recently proposed [xxvii]. This process is based on the introduction of mixed metallic powders into the oxygen-rich, high frequency plasma, followed by a water spray quench to prevent grain growth. The present paper deals with a more systematic study of the plasma induced combustion process, whereby commercial powdered nickel and chromium metals are employed as the raw materials for the production of nanosized composite oxide. These metals, whose oxides are
often used as SOFC anode material [xxxv, xxxvi], are characterized by their relatively high melting points, 1455°C and 1890°C, and boiling points, 2900°C and 2200°C, which make them good candidates for the evaluation of this process.

2 Experimental

2.1 Analytical Methods Used
XRD analysis - identification of elements and phases in powdered samples was performed by X-ray diffraction (XRD, Rigaku GeigerFlex), using Cu-Kα radiation with a nickel filter. The XRD was equipped with Jade 6.0 analytical software. The powders were lightly milled and the samples were placed in an appropriate sample holder.

SEM and TEM analysis - powder morphology and particle size estimations were made using:
1) a field emission gun scanning electron microscope (FEGSEM, Leo 1530 with GEMINI field emission column) in the secondary electron mode, with the sample powders dispersed in acetone and deposited on a wafer, and
2) a transmission electron microscope (TEM, Hitachi H-7500), samples also being dispersed in acetone and deposited on a copper grid (400 mesh) covered with formvar/carbon film.

Particle size measurements were performed using a Submicron Particle Size Analyzer (Brookhaven Instruments Corp., model 90 Plus). Powdered samples were treated with a dispersing agent in a strong ultra-sound bath to disintegrate agglomerates.

2.2 Raw Materials

The input metal particles used were either a mix of nickel (Novamet SP 400, dp ≤ 10 μm) and chromium (pulverized, 20 μm < dp < 60 μm), or a 50:50 wt% nickel-chromium alloy (Amdry, 44 μm < dp < 125 μm).

2.3 Apparatus

The apparatus (Fig. 1) was comprised of a radio-frequency induction plasma torch (TEKNA Plasma Systems, model P1-50), coupled with a water-cooled reactor chamber, a Venturi scrubber and an exhaust demister. Powdered raw materials were fed by a screw type powder feeder (Sylvestor model Mark 1X) through a water-cooled injection probe directed into the plasma torch center. Argon or oxygen was alternately used as the powder carrier gas. After vapourisation and oxidation in the oxygen-rich plasma, the reaction products were quenched in the fine mist of a hollow cone water spray and collected in the scrubber as a water suspension. This suspension was then filtered, using glass-fibre paper, and dried at ambient temperature to recover the powdered products.

Table 1. Plasma torch processing parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma central gas</td>
<td>Argon - 24.3 lpm</td>
<td></td>
</tr>
<tr>
<td>Plasma sheath gas</td>
<td>Oxygen - 75 lpm</td>
<td></td>
</tr>
<tr>
<td>Powder carrier gas</td>
<td>Argon or Oxygen 5 or 7 lpm</td>
<td></td>
</tr>
<tr>
<td>Powder federate</td>
<td>5 - 10 g/min</td>
<td></td>
</tr>
<tr>
<td>Generator plate power</td>
<td>40 kW and 60 kW</td>
<td></td>
</tr>
<tr>
<td>Processing pressure</td>
<td>400 Torr and 750 Torr</td>
<td></td>
</tr>
</tbody>
</table>

The processing parameters as set out in Table 1 were used for the preliminary series of experiments. Later experimental series were conducted employing those tabulated parameters...
marked in bold type, and varied according to a $2^{4-1}$ factorial design. Only the effects resulting from choosing the initial powder type are presented in this paper, the complete analysis of this project will be presented soon.

![Experimental set-up](image)

**Figure 1. Experimental set-up**

3. Results and discussion

Table 2 summarizes the main processing parameters in addition to the principal results of the preliminary runs.

<table>
<thead>
<tr>
<th>Run no</th>
<th>Powdered Feed</th>
<th>Processing</th>
<th>Products Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type &amp; Ni/Cr ratio</td>
<td>Rate [g/min]</td>
<td>Carrier [lpm]</td>
</tr>
<tr>
<td>5</td>
<td>Alloy 50/50</td>
<td>10</td>
<td>Ar - 5</td>
</tr>
<tr>
<td>6</td>
<td>Aggl 50/50</td>
<td>10</td>
<td>Ar - 5</td>
</tr>
<tr>
<td>7</td>
<td>Mix 50/50</td>
<td>10</td>
<td>Ar - 5</td>
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<tr>
<td>8</td>
<td>Mix 50/50</td>
<td>5</td>
<td>Ar - 5</td>
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<tr>
<td>9</td>
<td>Alloy 50/50</td>
<td>5</td>
<td>Ar - 5</td>
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<tr>
<td>10</td>
<td>Alloy 50/50</td>
<td>5</td>
<td>Ar - 5</td>
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<tr>
<td>11</td>
<td>Alloy 50/50</td>
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<td>Ar - 5</td>
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<tr>
<td>12</td>
<td>Mix 33/67</td>
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<td>Ar - 5</td>
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<td>Alloy 50/50</td>
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<td>Ar - 5</td>
</tr>
<tr>
<td>14</td>
<td>Alloy 50/50</td>
<td>5</td>
<td>O$_2$ - 5</td>
</tr>
<tr>
<td>15</td>
<td>Alloy 50/50</td>
<td>5</td>
<td>O$_2$ - 7</td>
</tr>
</tbody>
</table>
The XRD analysis of the synthesised product (Fig. 2) indicates that the nichromite compound (NiCr$_2$O$_4$) was readily produced by this method in all the experiments performed, with no detectable traces of unreacted metallic Ni or Cr. The presence of excess NiO in the products is explained by the non-stochiometry of the Ni/Cr 50:50 w/w% input mixture ratio. A 50:50 w/w ratio corresponds to a 47% Ni, 53% Cr molar ratio. Hence, there is too much Ni in a 50:50 w/w ratio for the quantity of Cr available to produce only the NiCr$_2$O$_4$ phase since it has a molar ratio of 2 Cr for 1 Ni.

Also, it can be seen that the eskolite phase (Cr$_2$O$_3$) is present only when mixed or agglomerated Ni and Cr powders are used, indicating that the contact achieved between metallic particles is not intimate enough to subsequently produce the binary composite oxide.

Figure 2. XRD spectra of the synthesis products obtained by the combustion of alloyed and mixed Ni and Cr powders as raw materials

The FEGSEM and TEM micrographs show that the nichromite particles form large agglomerates (size often over 1 μm), but much smaller sub-structures can be seen, ranging
from less than 10 nm to more than 100 nm (Fig. 3). The observed shapes of these particles are very diverse, some being spherical, some exhibiting a crystal-like shape.

*Figure 3. FEGSEM (left) and TEM (right) micrographs of the NiCr2O4 agglomerates obtained by combustion of alloyed initial powder*

The image analysis of all product samples that were part of the $2^{4+1}$ factorial design shows that particles produced from the original alloyed powder have much smaller sizes than those produced with the Ni/Cr powder mixes. Particles produced from the alloy have average sizes below 100 nm, while many particles produced from the powders mixes are above 100 nm (Fig. 4). The other processing parameters (total pressure, $O_2$ partial pressure and power input) do not seem to be significant, but further analysis is required to confirm this hypothesis.

*Figure 4. TEM micrographs of NiCr2O4 powders obtained by plasma induced combustion of (a) alloyed initial powder and (b) Ni and Cr powders mix*
4. Conclusion

Following the conduct of a series of some twenty five experiments, the following conclusions are made:

- Inductively coupled plasma is successfully used for the synthesis of composite oxides by the oxygen combustion of powdered metallic feeds;
- High quench rates associated with the post-synthesis process suppress grain growth, resulting in the ultrafine particle product;
- Using metallic nickel and chromium as process testing material, it is possible to readily produce both single component NiO and Cr₂O₃ phases, as well as the binary nicknichrome (Ni(Cr₂O₄) phase, without any XRD detectable traces of residual metallic Ni or Cr being present;
- The formation process for the binary Ni(Cr₂O₄) phase is enhanced by the use of pre-alloyed Ni-Cr particles as the synthesis raw material;
- The particle size of products obtained from pre-alloyed powders are much smaller (10 nm < dₚ< 100 nm) than those obtained from mixtures of Ni and Cr powders, which were as large as many hundredths of nanometers for comparable processing conditions;

Further analysis will be necessary to assess the effect of generator plate power, the total pressure within the reactor and the oxygen partial pressure on the products properties.

Future work will include the synthesis of ternary oxide phases, including those compositions that are closer to currently identified SOFC anode materials.

References