Experimental design applied to improving the effect of bismuth oxide as a sintering aid for tin oxide

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A B S T R A C T
Tin oxide has been extensively studied due to its wide variety of applications. However, its poor sinter ability requires the use of sintering aids for its processing. The sintering behaviour of three different SnO2-based powder mixtures, containing Bi2O3 in amounts between 1 and 2 mol%, has been analyzed. The effects of thermal treatment parameters (heating rate, maximum temperature and soaking time) on the densification were obtained by a factorial experimental design 23. Bi2O3 adequate proportion (around 1.5%) combined with a fast heating (15 °C/min) and a high maximum temperature (1300 °C), allows reaching densifications around 45%. However, soaking time has no significant effect over densification. An interpretation of the significant effects has been proposed based on thermodynamic behaviour of Bi-containing compounds and the mass transport mechanisms.

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Diseño experimental aplicado a la mejora del efecto del óxido de bismuto como promotor de sinterización del óxido de estano

R E S U M E N
El óxido de estano es un material ampliamente estudiado dada su gran variedad de aplicaciones. Sin embargo, debido a que sinteriza sin densificarse, su proceso requiere la incorporación de promotores de la sinterización. Se ha estudiado el comportamiento de 3 mezclas a base de óxido de estano que contenían óxido de bismuto como promotor de la sinterización, en proporciones 1-2% mol. A través de un diseño factorial de experimentos 23, se han evaluado los efectos de los parámetros del tratamiento térmico (velocidad de calentamiento, temperatura máxima y tiempo de permanencia) sobre la densificación. La combinación de una adecuada proporción de Bi2O3 (alrededor del 1,5%), una velocidad de

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Introduction

Tin oxide exhibits many attractive physical and chemical properties, such as high conductivity (n-type semiconductor) and corrosion resistance. Traditionally, SnO₂ has been used as raw material for some pigments [1] and as opacifier in ceramic glazes [2]. Nowadays, it is broadly used in the production of gas sensors [3,4], as well as components requiring high chemical corrosion resistance in chemical industry applications [5]. In the last field, an important application is obtaining electrodes for the processing of aluminium by electrolysis [6,7] and electric glass melting furnaces [8].

One of the main drawbacks of SnO₂ is its poor sinter ability since hinders its use [9,10]. According to Kimura et al. [11], two different phenomena can occur during the sintering process in ceramic bodies: densification and particle coarsening. High densification is obtained when bulk transport mechanisms, as grain-boundary diffusion, are predominant. By contrast, surface transport mechanisms, as surface diffusion or evaporation-condensation, generates a non-densified body because of the particle coarsening. In the case of pure tin oxide, the studies describe a decomposition of SnO₂ in SnO and O₂ at temperatures above 1100 °C. In consequence, the evaporation-condensation mechanism predominates during sintering, whereby the electrodes obtained from this material showed a very low densification [12,13].

Different approaches have been used to improve densification, namely, hot isostatic pressing [14], Field Activated Sintering Technique (FAST) [15] or the addition of other metallic oxides as “sintering aids” [16,17], those promote the formation of a eutectic liquid between SnO₂ and the “sintering aid” at low temperature favouring a liquid-phase sintering [18,19]. Between the oxides proposed as “sintering aids” for tin oxide, bismuth oxide has been proposed as a non-toxic alternative. The Bi₂O₃–SnO₂ phase diagram contains three stable solid phases: bismuth oxide (m.p. 840 °C), tin oxide (m.p. 1800 °C) and Bi₂Sn₃O₇ (melts incongruently near 1400 °C and decomposes to solid SnO₂ and a Bi₂O₃-rich liquid). In addition, a low-temperature eutectic was present for a 2 mol% SnO₂ and 98 mol% Bi₂O₃ (825 °C). In addition, the presence of Bi₂O₃ suppresses SnO₂ sublimation owing to the high pressure of oxygen resulting from Bi₂O₃ or Bi₂Sn₃O₇ sublimation [20]. In consequence, the sintering mechanism of SnO₂ through the gas phase is partially blocked.

In this work, a factorial experimental design 2³ has been used to analyze the effect of thermal cycle parameters (heating rate, maximum temperature and soaking time) over the performance of bismuth oxide as sintering aid for tin oxide. Thermodynamic data have been used to interpret the obtained results.

Experimental procedure

Raw materials were SnO₂ (purity 99.85%, Quimiamel S.A., Spain), and Bi₂O₃ as sintering aid (purity 98%, Fluka AG, Germany). Three different compositions were formulated to evaluate the effect of bismuth oxide proportion over the sintering behaviour of tin oxide (Table 1). 0.8% in weight of polivinylalcohol (Mowiol 8-88, Clariant Iberica S.A. Spain), was added to each composition as a ligand.

Firstly, raw materials were mixed in a planetary mill (Pulverisette 5, Fritsch GmbH, Germany), at 230 rpm during an hour using water as a fluid and the suspension was dried at 110 °C for 24 h. Secondly, the dried powder was sieved trough a 600 μm mesh and was moistened to 5% (kg water/kg dry solid). Thirdly, disc specimens of 2 cm diameter and 0.5 cm thickness were dry-pressed at 450 kg cm⁻² in a laboratory uniaxial press (Nannetti Spa, Italy). Finally, eight different thermal treatments were carried out in a laboratory furnace in air atmosphere (RHF1600, Carbolute Furnaces, UK) with the experimental design showed in Table 2. Bulk density of green and sintered specimens was measured by mercury immersion (Archimedes’ method), and densification (change in bulk density due to sintering divided by the change needed to attain a pore-free solid), was calculated according to German [21].

Characterization of crystalline structures present on some specimens was performed using an X-ray diffractometer (Theta-Theta D8 Advance, Bruker, Germany), with CuK α radiation (λ = 1.54183 Å). The generator applied an intensity light source of 45 kV and 40 mA. XRD data were collected by means of a VÁNTÉC-1 detector in a 2θ from 5 to 90° with a step width of 0.015° and a counting time of 1.2 s/step. SEM images were taken with a FEG-SEM (QUANTA 200F, FEI Co, USA) from polished sections of some samples.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>99.0</td>
<td>98.5</td>
<td>98.0</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>Heating rate ( °C min⁻¹)</th>
<th>Tmax ( °C)</th>
<th>Soaking time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–1</td>
<td>5</td>
<td>1100</td>
<td>1</td>
</tr>
<tr>
<td>+1</td>
<td>15</td>
<td>1300</td>
<td>4</td>
</tr>
</tbody>
</table>
Experimental results and discussion

Results showed that the addition of bismuth oxide allows to reach densifications of 45% (corresponding to a relative density of 73.8% with respect to pore-free SnO₂). However, sintering aid was only effective at temperatures around 1300 °C and its proportion is limited to 1.5% because higher contents of Bi₂O₃ tend to decrease maximum densification values (Fig. 1). In addition, the faster heating rate seems to increase densification, but an effect of soaking time was not appreciable.

The main effects and interactions (Table 3), as well as their standard deviation σ, were obtained according to Box et al. [22]. It was considered as significant the effects higher than 3σ. Maximum temperature has the greatest effect on densification followed by heating rate and the interaction \( T \times r \). However, densification seems not to be influenced by soaking time and the other interactions.

XRD of samples of composition B treated with the 15/1300/4 cycle identified a small proportion of a pyrochlore-type compound Bi₂Sn₂O₇, being cassiterite the main phase (Fig. 2). This pyrochlore showed an inhomogeneous spatial distribution as SEM images demonstrate (Fig. 3). It was concentrated in the centre of the sample and the volume near the surface was practically free of this phase. In consequence, there is a loss of bismuth oxide during the thermal treatment, which mainly comes from the vicinity of the sample surface. In the other hand, the Bi₂SnO₇ was present in discrete agglomerates, showing interphases with the tin oxide particles which points to a wetting by a liquid phase at high temperature.

It can be proposed that Bi₂O₃ reacts with SnO₂ to generate Bi₂SnO₇ at \( T > 850 \, ^\circ C \) [23], and consequently very small densification is obtained at 1100 °C. This fact is due to the absence of any liquid phase and the predominant surface mass transport mechanisms characteristic of pure SnO₂ sintering. Surface transport which masks any volumetric mass transport mechanism. By contrast, the presence of a bismuth-rich liquid phase at 1300 °C is the way for a volumetric mass transport mechanism which allows densifications around 45%. In parallel, the high oxygen partial pressure generated by Bi-containing compounds reduces the gas-phase transport of SnO₂. Accordingly, it is advisable to add bismuth oxide to promote SnO₂ densification at 1300 °C. By contrast, Bi₂O₃ effect is negligible at 1100 °C.

The effect of heating rate can be related with bismuth oxide losses, because the weight loss of samples treated at 1300 °C and the faster heating rate was slightly lower than their counterparts obtained with the slower heating rate (the mean values were 4.18% and 4.00% respectively). By contrast, the weight losses of samples treated at 1100 °C were around a mean value of 0.96%, slightly higher to the 0.8% content of PVA, meaning that the bismuth oxide losses were clearly inferior. According to this hypothesis, the lower heating rate

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Effects and interactions of thermal treatment on densification</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( r \times T )</td>
<td>( r \times t )</td>
</tr>
<tr>
<td>A</td>
<td>4.96</td>
<td>38.89</td>
</tr>
<tr>
<td>B</td>
<td>5.14</td>
<td>38.70</td>
</tr>
<tr>
<td>C</td>
<td>3.96</td>
<td>34.21</td>
</tr>
</tbody>
</table>
allows the diffusion out of the sample of a bigger fraction of the
gaseous species generated by Bi₂Sn₂O₇ sublimation. In conse-
quence, the blocking effect over the gas-phase transport of
SnO₂ is less intense. On the other hand, the loss of bismuth
could also be related to the lack of a measurable effect of soaking
time over densification. As a bigger volume fraction of the
sample loses the bismuth, the densification mechanism is
stopped in those zones, and the effect of larger soaking times is
lower. Probably with shorter soaking times the significance of this
effect could be evaluated. Further research is needed to
confirm this point.

Conclusions

Bismuth oxide promotes tin oxide densification combined with
an adequate thermal cycle. The experimental design has shown that the highest densifications (around 47%) are
obtained with proportions of Bi₂O₃ between 1.0 and 1.5% molar combined with a fast heating rate (15 °C min⁻¹) and a
maximum temperature of 1300 °C. Heating rate, maximum temperature and their interaction are the parameters with a
significant effect over densification. However, soaking time has no significant effect over densification, at least in the range
of values investigated.

Bi₂O₃ reacts to generate Bi₂Sn₂O₇, which is found in the
central volume of the most densified samples but not near
their surfaces. In addition, higher densifications are linked with higher mass losses during the thermal treatment due to
bismuth compounds volatilization.

The evolution of densification in the presence of bismuth
oxide has been interpreted considering the thermochemical
behaviour of Bi-containing compounds, and their effect over the
mass transport mechanisms.

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