Sintered steels as interconnectors in polymer electrolyte membrane fuel cells

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Abstract

This paper presents opportunities for application of sintered stainless steels for interconnectors used in polymer electrolyte membrane fuel cells. Mechanical properties and corrosion resistance were compared in steels sintered with the pressures of 400MPa and 700MPa. In order to determine the effectiveness of the employed method of sinter preparation, the evaluation of microstructural and mechanical properties was carried out. A fundamental criterion for application of materials for fuel cell interconnectors is corrosion resistance under operating conditions of fuel cells. In order to determine the impact of sintering parameters on corrosion resistance in materials, potentiokinetic curves were recorded in the solution which simulated anode and cathode environments i.e. solution of \( 0.1 \text{ mol dm}^{-3} \ \text{H}_2\text{SO}_4 + 2 \text{ ppmF}^{-} \), saturated with hydrogen and oxygen at the temperature of \( T=80^\circ\text{C} \).

Keywords: fuel cells, interconnectors, sintered materials, microstructure, corrosion resistance

1. Introduction

In consideration of intensive search for modern solutions for electricity production today, fuel cells constitute generators which produce electricity and heat with high efficiency and without emission of pollutants [1-2]. Electricity is produced as a result of electrochemical reactions which occur on the surface of electrodes. Polymer electrolyte membrane fuel cells (PEMFC) belong to the group of low-temperature fuel cells. In fuel cells, the fuel (hydrogen, carbon, methanol, hydrazines etc.) is oxidized on the anode (negative electrode), whereas reduction of the oxidizer occurs on the cathode (positive electrode). Through electrochemical processes, energy production can occur virtually continuously and the only limitation is the size of fuel container. Equations for the reactions that occur are given by:

Anode: \( 2\text{H}_2 \rightarrow 4\text{H}^{+} + 4\text{e}^{-} \)  \hspace{1cm} (1)

Cathode: \( \text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O} \)  \hspace{1cm} (2)

Water constitutes a by-product. Individual cell in hydrogen fuel cell is composed of a membrane closed between electrode (Membrane Electrode Assembly MEA) and bipolar plates/interconnectors at both sides of the electrodes (Fig. 1) [3].

Fig. 1. Simplified view of polymer electrolyte membrane fuel cell

Due to the exposure of hydrogen fuel cells to aggressive operating conditions, materials they are made of must be characterized by a suitable corrosion resistance [4]. Bipolar plates in fuel cells based on metallic materials must be also characterized by particular porosity, hydrophobicity and improved
heat and electricity conduction [5]. Application of materials resistant to corrosion i.e. titanium or gold for bipolar plates in fuel cells considerably increase costs of production. Therefore, proposal of application of stainless steel for these components in fuel cells seems to be attractive for several reasons [6].

The subject of investigations within this study is to present opportunities for application of sintered stainless steel for bipolar plates in fuel cells. In order to achieve this goal, microstructural and mechanical properties and corrosion resistance in sintered materials were compared.

2. Experimental

Bipolar plates in fuel cells were obtained through application of powder metallurgy and covered the following stages in manufacturing process:

- powder preparation,
- cold moulding of the powder,
- sintering.

Water-atomized 304L and 434L stainless steels were used for the investigations. Chemical composition of individual powders is presented in Table 1.

Table 1. Chemical composition of the powders used for sintering

<table>
<thead>
<tr>
<th>Powder</th>
<th>C [%]</th>
<th>Mo [%]</th>
<th>Ni [%]</th>
<th>Cr [%]</th>
<th>Si [%]</th>
<th>Mn [%]</th>
<th>Fe [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>0.013</td>
<td>0.98</td>
<td>11.2</td>
<td>18.9</td>
<td>0.9</td>
<td>0.1</td>
<td>balance</td>
</tr>
<tr>
<td>434L</td>
<td>0.015</td>
<td>0.98</td>
<td>16.2</td>
<td>8.0</td>
<td>0.1</td>
<td>balance</td>
<td></td>
</tr>
</tbody>
</table>

In order to reveal impact of the parameters which accompany the process of alloy steels on functional properties of the manufactured plates, different compaction pressures and sintering atmospheres were used. The following types of sintered materials were obtained during the investigations (DA - dissociated ammonia):

- 304L powder, compaction pressure of 400 MPa, T=1250°C for 30 min. in ammonia medium, 304L/400/DA,
- 304L powder, compaction pressure of 700 MPa, T=1250°C for 30 min. in ammonia medium, 304L/700/DA,
- 434L powder, compaction pressure of 400 MPa, T=1250°C for 30 min. in hydrogen medium, 434L/400/H2,
- 434L powder, compaction pressure of 700 MPa, T=1250°C for 30 min. in ammonia medium, 434L/700/DA.

Properties of the powders used for sintering and properties of the obtained sinters are presented in Table 2.

Table 2. Properties of powders and sinters

<table>
<thead>
<tr>
<th>Powder</th>
<th>Powder density [g cm⁻³]</th>
<th>Sinter density [g cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>400MPa 2.62</td>
<td>6.16</td>
</tr>
<tr>
<td></td>
<td>700MPa 6.60</td>
<td></td>
</tr>
<tr>
<td>434L</td>
<td>400MPa 2.87</td>
<td>5.98</td>
</tr>
<tr>
<td></td>
<td>700MPa 6.60</td>
<td></td>
</tr>
</tbody>
</table>

Sintered materials in question are designed for components of fuel cells. Due to aggressive operating conditions of fuel cells, these type of elements are required enhanced corrosion resistance. In order to optimize mechanical properties of the material with corrosion resistance, ferritic 434L steel sinters were sintered in hydrogen medium. The employed procedure allowed for increasing corrosion resistance, however, at the expense of reduction in mechanical properties.

Microstructural tests were carried out using Axiovert optical microscope and JOEL Model JSM-5400 scanning microscope. In order to determine mechanical properties in sintered materials, static tensile test was performed using MTS servo-hydraulic testing machine and measurement of hardness in the studied sinters by means of Rockwell method.

Electrochemical tests were conducted in three-electrode arrangement, using CH Instrument measurement unit. Reference electrode was formed by the saturated calomel electrode (SCE) while auxiliary electrode was platinum wire. Working electrode was formed by the sintered material. Electrochemical measurements were taken in solution of 0.1 mol dm⁻³ H₂SO₄ + 2ppm F⁻ at T=80 °C [7]. In consideration of electrochemical reactions which occur at the surface of electrodes, the environment inside fuel cell is always acidized, which causes destruction of the materials. Furthermore, ions from membrane, i.e. F⁻, SO₃⁻, SO₄²⁻, intensify the processes of corrosion [8]. In order to fully reproduce the operating conditions of fuel cells, the solution was saturated with H₂ (operating conditions in fuel cell on the anode side) and O₂ (operating conditions in fuel cell on the cathode side).

Before electrochemical measurements, metallic samples were polished with sandpapers 250, 600, 800 and 1200. Potentiokinetic curves were registered within the range of potentials from -0.8 to 1.6 V vs. SCE (saturated calomel electrode), scan rate 5 mV s⁻¹. Based on the obtained polarization curves, the parameters which determine corrosion resistance of the material were determined i.e. corrosion potential Ecorr, corrosion current density icorr, and polarization resistance Rp [8]. Corrosion potential and corrosion current densities were determined based on extrapolation of the tangent to the potentiokinetic curves in both anode and cathode range. Based on the slope value, ΔE=f(Δi) polarization resistance was determined (Rp). Higher values of polarization resistance correspond to higher corrosion in the given environment presented by the studied material.

3. Results and discussion

Analysis of morphologies for the used powders revealed that they were characterized by a comparable mean diameter of 50 μm
and density of ca. 2.6 g/cm$^3$. Morphology of the used powders is presented in Fig. 2.

![Fig. 2. Morphology of: a) 304L powder; b) 434L powder](image)

Structures in the studied sintered materials 304L and 434L are presented in Fig. 3. After sintering of 304LHD steels, sinters revealed austenitic structure with distinctive deformation twins. Structure of 434 LHC steel was a mixture of ferrite and martensitic phases. Arrows in the microstructures in Fig. 3 point to the pores in sintered materials.

![Fig. 3. Microstructure of sintered materials: a) 304L/400/DA; b) 304L/700/DA; c) 434L/400/H2; d) 434L/700/DA](image)

In order to determine the effect of compaction parameters on corrosion resistance, potentiokinetic curves were registered in the abovementioned corrosion environments and then their courses were compared.

![Fig. 4. Force-displacement dependence curve for the investigated stainless steel sinters](image)

### Table 3. Properties of sintered materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>TS [MPa]</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L/400/DA</td>
<td>359</td>
<td>64 HRF</td>
</tr>
<tr>
<td>304L/700/DA</td>
<td>504</td>
<td>99 HRF</td>
</tr>
<tr>
<td>434L/400/H2</td>
<td>162</td>
<td>60 HRF</td>
</tr>
<tr>
<td>434L/700/DA</td>
<td>479</td>
<td>100 HRF</td>
</tr>
</tbody>
</table>

In polymer electrolyte membrane fuel cells, the fuel (hydrogen) is fed to the anode, whereas the oxidant (oxygen) is transported to the cathode. In order to study corrosion properties in sintered steels, potentiokinetic curves were registered in anode and cathode environment. The investigations were conducted in water environment saturated with oxygen and hydrogen. Fig. 5 and 6 present potentiokinetic curves registered for austenitic 304L steel and ferritic 434L steel. For each of the registered polarization curves, one can point to the area of active solubilization, passivation and transpassivation. Values of corrosion potentials and densities of corrosion currents registered for 304L steel are comparable in both cases i.e. in the solution saturated with O$_2$ and H$_2$. In the area of transpassivation, polarization curves are almost identical. As results from the course of potentiokinetic curves, application of lower values of compaction pressure in austenitic steel sinters beneficially affects corrosion resistance in the studied environment. Corrosion potential in 304L/400/DA sinter is moved towards positive values as compared to 304L/700/DA steels, both in the solution saturated with H$_2$ and O$_2$. Corrosion current densities in 304L/400/DA steel also show higher values as compared to the values of $i_{corr}$ recorded for 304L/700/DA steel (Table 4 and 5).

In the case of ferritic steel, reduction in compaction pressure and application of hydrogen atmosphere at lower compaction pressure did not positively affect corrosion resistance of the material in the studied corrosion environment (Fig. 6). Profiles of potentiokinetic curves reveal that corrosion potential in 434L/400/H2 sinters is moved towards lower values ($E_{corr}$ for 434L/700/DA amounts to -0.316V vs. SCE, whereas for 434L/400/H2 $E_{corr}=-0.551V$ vs. SCE; see Table 4, 5).
4. Conclusions

Based on the investigations, the following conclusions can be drawn:

- Changes in compaction pressure in materials causes changes in sinter densities (with lower compaction pressure, sinters with lower densities are obtained),
- Austenitic and ferritic powders sintered under the same conditions (compaction pressure and sintering atmosphere) show comparable mechanical properties (tensile strength and hardness),
- Mechanical properties of sintered materials in hydrogen atmosphere are subject to considerable reduction as compared to the materials sintered in ammonia medium,
- In the case of the sinter with austenitic 304L austenitic structure, lower compaction pressure ensures obtaining of enhanced corrosion resistance,
- Sintering of materials in hydrogen atmosphere reduces resistance to material corrosion, both under anode and cathode conditions.

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References