Computational Metal Oxide Growth Model For Hydrogen Fuel Container

Srikanta Kumar Mohapatra, Susanta Kumar Mohapatra, Sushanta Kumar Kamilla

Abstract: Liquid hydrogen may be the right one to use as a future alternative for petroleum oil. Though there are several advantages of liquid hydrogen, the major challenge confronted is the storage and carrier of this fuel. Developing compact, reliable, safe and cost effective hydrogen container is needed so that it can be used as a fuel to fulfill our day-to-day needs. Besides storage certain other problems associated with liquid hydrogen are its liquefaction and compression. These problems also requires to be addressed effectively. In this paper, effort has been given to design an efficient computational model using programming that can predict a suitable material which can bring improvements in the existing hydrogen fuel storage container. From the current study, the most suitable material proposed by our computational model is Titanium (Ti). On comparing computational modelling result with experimental result on thickness of TiO2 on Ti sheet (Ti-TiO2), it was found nearly similar. In both the case the preparation condition was taken same.

Index Terms: Hydrogen Fuel, Titanium Dioxide, Oxidation Model, Oxidation Growth, Hydrogen Storage, Alternative Fuel, Petroleum

1. INTRODUCTION

Hydrogen is gaining a great deal of attention as an energy carrier as well as an alternative fuel. However, in order to fully implement the so called ‘Hydrogen Economy’, significant technical challenges need to be overcome in the fields of production and storage of hydrogen, and its point of use especially in fuel cells for the automotive industry. There are a number of challenges inherent to the development of a hydrogen economy that need to be represented within the modeling approach, in order to analyze of the possible pathways for hydrogen development. The main challenge is the storage and carrier of the fuel. The main problem is the make a container for the storage of the hydrogen element as this element’s nature undergoes several problems. The basic problems are:-

a) Hydrogen can leak from any container whether it is insulated or not insulated [1].

b) Very low temperature is required to store it due to its inflammable nature.

c) Due to its reactive nature whenever it comes in contact with any metal surface, it alters the structural properties.

d) It requires high volume of container, therefore transportation problem comes into the picture.

Considering the above mentioned problems along with certain other problems like liquefaction [2], compression etc. attempts have been made by us to make a model to choose the appropriate material which may be suitable for the improvement of current existing hydrogen fuel container. Recent scientific literatures have increased interest on the Ti–TiO2 nanotube [3],[4] and its alloys are considered as promising materials for Hydrogen storage application.

Particularly, TiO2 nano-tubes grown on Ti substrates (Ti–TiO2) by Anodization may successfully be used for Hydrogen storage [5]. Titanium dioxide (TiO2) layer is formed on the surface of a titanium plate by high temperature thermal oxidation in the presence of oxygen which is called dry oxidation [6]. This type of oxidation reaction is similar to the diffusion process. The thickness of the oxide layer depends on the temperature, time and the flow rate of oxygen. Similarly the oxidation rate can be enhanced by electrochemical process which is called wet oxidation [7]. Both dry and wet oxidation needed high temperature for growth, but kinetics is different. In this case also the time and temperature required to produce a particular layer thickness are obtained. The wet oxidation has always been faster than dry oxidation and cost effective [8],[9],[10]. For that reason, prior to growth of wet oxidation, simulation is extensively required to avoid wastage of time and expenditure. Beside this selection of appropriate material is also necessary for the storage of hydrogen fuel.

2. OXIDATION MODEL

2.1 Model Overview

Both dry and wet oxidation needed high temperature for growth, but kinetics is different. Since from the top layer of the metal surface is consumed, the metal-metal oxide moves deeper into the plate. In this process, due to different densities of metal-oxide layer and metal the volume expansion is also different [11]. The ratio of the thickness is inversely proportional to the densities and directly proportional to the atomic/ molecular weights. So the fraction of metal-oxide inner layer thickness with respect to total oxide thickness is given by: i.e.

\[ \frac{X_\text{Metal}}{X_\text{Oxide}} = \frac{X_\text{Oxide}}{X_\text{Metal}} \]

\[ X_\text{Metal} = X_\text{Oxide} \frac{W_\text{Oxide}}{W_\text{Metal}} \]

2.2 Model Formulation Principle

Oxidation is a process when oxygen reacts with metal to form metal - oxides. Thus, in atmospheric condition, on the surface of metals like Aluminium or iron get converted to their oxides. Technically, this process is depending upon the concentration of oxygen molecules per unit volume on the surface and also number of oxygen molecules passing per unit time per unit area or diffusion flux [12],[13]. As for the
assumption the oxidation process is generally involved with
the inward movement of the oxidant species [14]. So the
transported oxidant species, i.e. rate of oxidation must
consider the following three steps shown in Figure 1.
(1) The rate at which oxidizing molecules absorb at
the outer surface.
(2) The rate at which oxide molecules diffuse across
the oxide film towards metal.
(3) The rate at which the reaction occurs at the
interface between metal and form a new layer of
metal oxide.

Flux equation: All three steps can be independently treated as
flux equation. In oxidation growth calculation, we have divided
total flux into 3 categories
i) Initial adsorption flux
ii) Oxidation diffusion flux
iii) Reaction flux

\[ \text{Flux equation: } \text{All three steps can be independently treated as flux equation.} \]

In the oxidation process reaction flux is directly proportional to
interface concentration.
\[ R_{\text{flux}} \propto IO_{\text{con}} \] (4)
Where
\[ R_{\text{coeff}} = \text{Reaction rate coefficient} \]

3 OXIDATION MODEL SIMULATION

3.1 MODEL DEPENDENCY FACTORS

The model depends upon the following three factors
i) Initial oxidation growth
ii) Time for initial oxidation
iii) Total time for oxidation
iv) Variable temperature

The oxidation growth can be affected by two
fundamental physical factors, i.e. pressure, Temperature. The
growth at inner side and outer side is calculated by observing
above two factors with corresponds to time.

3.2 DETERMINATION METAL OXIDE GROWTH FROM FLOW MODEL

The total oxidation process is varied out through the following
steps

1. Calculation of initial adsorption oxidation concentration
   on the metal surface:
   In the first case initial adsorption of oxidation concentration
   on the metal surface (IA_{\text{flux}}) which is defined as number of oxidant
   molecules on the surface area of metal. This express as
   \[ I_{\text{A flux}} = h(EO_{\text{con}} - SO_{\text{con}}) \] (1)
   Where
   \[ h = \text{Gas phase transport coefficient} \]
   \[ EO_{\text{con}} = \text{Concentration of oxidant molecules in equilibrium} \]
   \[ SO_{\text{con}} = \text{Surface oxidation concentration} \]
   Solubility limit for wet oxidation varies more than dry oxidation
   was reported in literature. Practically in both wet and dry
   oxidation, it is observed that only a small difference occurs
   between concentration of oxidant molecules in equilibrium and
   surface oxidation concentration i.e
   \[ (EO_{con} - SO_{con}). \]

2) Calculation of oxidant diffusion across surface area:
Oxidant diffusion flux can be calculated as
\[ OD_{\text{flux}} = \frac{D_{\text{coeff}}}{O_t} (SD_{\text{con}} - IO_{\text{con}}) \] (2)
where
\[ OD_{\text{flux}} = \text{Oxidant diffusion flux} \]
\[ D_{\text{coeff}} = \text{Diffusion coefficient} \]
\[ O_t = \text{Oxide thickness} \]
\[ SO_{\text{con}} = \text{Surface oxidation concentration} \]

But after sometime oxidant diffusion flux becomes constant. It
can be calculated by applying Arrhenious equation
\[ D_{\text{coeff}} = A_t e^{\frac{-E_a}{k_b T}} \] (3)

Where
\[ D_{\text{coeff}} = \text{Diffusion coefficient} \]
\[ A_t = \text{Arrhenious coefficient} \]
\[ E_a = \text{Acivation energy} \]
\[ K_b = \text{Boltzman constant} \]
\[ T = \text{Temperature} \]

\[ IO_{\text{con}} = \text{Interface oxidant concentration} \]

\section*{Figure 1 One-dimensional oxidation model metal (Titanium)}
3.3 Oxidation Growth Determination Flow Diagram

Figure 3: Oxidation growth determinations flow chart

3.4 Simulation Algorithm

```matlab
str = 'Enter an Oxidation state (wet/dry):';
// oxidation state to be entered between dry and wet
oxd_state = input(str,'s'); // it will display current oxidation state
material_type = input('Choose Material Type T','s');
// material to be chosen for the oxidation
switch material_type
    case 'Ti'
        material_parameters(); // different known and unknown parameters to be inputted
    end
Temperatue = input('Enter the Temperature:');
// input temperature
RRC = input('Enter the reaction rate constant:');
P = calculate_RC(c1, E1, K, Temperature);
//Rate constant calculation
Q = 2 * P;
Pc = Q/N;
S = Q/RRC;
LC = PC/S;
Xg = calculate_Oxi_Growth(LC, PC);
// oxidation growth to be calculated
if strcmp(Xg, 'funtbl')
    fprintf('Oxidation Growth = %f
', Xg);
else
    disp('Wrong input, Run Again')
end
end
```

3.5 Experimental Growth of Metal Oxide

The model simulates different metals by taking the associated parameters to calculate the oxidation growth. The result of oxidation growth in different metal is:

<table>
<thead>
<tr>
<th>METAL</th>
<th>Total Oxidation Growth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>36</td>
</tr>
<tr>
<td>Ti</td>
<td>42</td>
</tr>
<tr>
<td>Zr</td>
<td>38</td>
</tr>
<tr>
<td>Al</td>
<td>34</td>
</tr>
</tbody>
</table>

The Figure 4 clearly indicates that the oxidation growth to the inner layer is higher than the outer layer which proves the Ti plate may be the best material as compared to the oxidation factor.

Table 2 TiO₂ Simulation with Different Temperatures & Time

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Oxidation Growth (1 hour)</th>
<th>Oxidation Growth (4 hour)</th>
<th>Oxidation Growth (6 hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>12 µm</td>
<td>17 µm</td>
<td>36 µm</td>
</tr>
<tr>
<td>200</td>
<td>11 µm</td>
<td>15 µm</td>
<td>37 µm</td>
</tr>
<tr>
<td>300</td>
<td>15 µm</td>
<td>15 µm</td>
<td>38 µm</td>
</tr>
<tr>
<td>400</td>
<td>16 µm</td>
<td>19 µm</td>
<td>40 µm</td>
</tr>
<tr>
<td>500</td>
<td>16 µm</td>
<td>20 µm</td>
<td>42 µm</td>
</tr>
</tbody>
</table>
According to literatures the promising materials for Hydrogen storage application is Ti–TiO₂. Particularly, TiO₂ grown on Ti foil (Ti-TiO₂) by anodization (wet oxidation) may successfully be used [16]. The oxidation reaction is similar to the diffusion process. The thickness of the oxide layer depends on the temperature and time, and the flow rate of oxygen. In wet oxidation case the time and temperature required to produce a particular layer thickness are obtained [9]. For that reason, prior to fabrication and selection of appropriate materials, simulation is extensively required to avoid wastage of time and expenditure. In our model we have taken different temperature with respect to the time interval. The Table 2 shows the oxidation growth at different time and different temperature. It is observed that at time 6 hour and at the temperature 500 ℃ the model shows the best growth result.

4. PRACTICAL IMPLEMENTATION AND DISCUSSION

The Ti sheets are cut into specific size and shape. Then these pieces were cleaned in acetone, dried and then processed for anodization. The anodization is carried out using ultrasonic waves (100 W, 42 kHz, Branson 2510R-MT) by immersing a part of the Ti foil (total geometrical area 4 and 12.5 cm) in the electrolytic solution (1000 ml). Water (5 vol%), 0.5 M NH 4 F, 0.25 M Na 2 [ H₂ EDTA ] and ethylene glycol were mixed together thoroughly and used as the electrolytic solution (pH = 6.4–6.5). Ti sheet acts as the anode and platinum (Pt) as the cathode. The anodization has been carried out for 1 h at an applied potential of 80V DC using a rectifier (Xantrex, XFR 600-2). The schematic diagram of electrochemical anodization method is shown in Figure 5. The anodized grown sample was dried in a hot air oven. Then anodized sample was annealed under an oxygen (O₂) atmosphere in a furnace at 500 ℃ for 6 h to yield crystalline Ti-TiO₂ film. [17]

The cross-sectional view of the Ti-TiO₂ film is shown in Figure 7 which reveals that the Ti-TiO₂ film thickness is 41.1 μm but in our prediction algorithm by considering experimental parameter like 6 hours annealing at effective temperature of 500℃, it is found 42 μm, which is nearly same.

5.CONCLUSIONS

It is found that Ti as compared to other metals inner layer oxidation growth is more than other metal. This indicates that the diffusion of the gas from the container due to the oxidation, takes more time rather than other metals. Hydrogen gas may sustain within the container without penetrating it. Above all the practical implementation is more important rather than the theoretical aspect which has discussed in this work. So the simulation model can be used before the practical implementation to calculate the growth of oxidation for any temperature.

REFERENCES:


