Thermal Degradation of Woodceramics under Different Oxygen Concentration

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Woodceramics have been studied as an Ecomaterial, and is expected to have applications in a wide variety of fields. In this report, thermogravimetry and differential thermal analysis of Woodceramics with changing concentration of oxygen was conducted. Experiments in chemical reaction kinetics were also performed in order to clarify the thermo-physical and thermo-chemical properties of Woodceramics in the presence of oxygen. The experimental results show that both mass loss curves and differential heat curves are dependent on the concentration of oxygen. In addition, the reaction rate law of the thermal degradation of Woodceramics with change in concentration of oxygen is reported to verify the suitability of the method.

Keywords: woodceramics, ecomaterials, oxygen, thermo gravimetry, differential thermal analysis, chemical kinetics

1. Introduction

Woodceramics is a composite material of wood or woody material into which phenolic resin has been injected, imparting the promising characteristics of an Ecomaterial. There have been many studies involving the physical properties¹⁻⁵ of this material, and practical uses have been suggested in various fields. Hokkirigawa and others⁶) have reported potential uses such as a wear-resistant material or a heat insulator. In addition, we⁷) reported the far infrared radiation properties of Woodceramics to be about 80% of that of a black body, and consequently Woodceramics have been considered as infrared radiators. In such uses, it is important to know the thermal stability and change of state of the Woodceramics while being heated. We⁷) also conducted thermo gravimetry (TG) and differential thermal analysis (DTA) of Woodceramics in a nitrogen atmosphere. However, a kinetic analysis under these conditions has not yet been carried out. For understanding of the effect of oxygen on the thermo-physical and thermo-chemical properties of Woodceramics under elevated temperatures, it is needed when practical use in air. In this report, experiments in thermo gravimetry differential thermal analysis performed on Woodceramics are reported in which the concentration of oxygen was controlled. A kinetic analysis was attempted and values of the apparent activation energy, order of reaction and pre-exponential factor were obtained.

2. Experimental

2.1 Apparatus

The mass loss and differential heat of the specimen were measured simultaneously by a differential heat balance (Rigaku-denki Co, Ltd TG-DTA TAS-200). The reference material used for the differential thermal analysis was a 0.3μm α-Al₂O₃ powder. The Pt-PtRh thermocouples were used to measure the temperatures of the specimen and the reference material.

2.2 Specimen

The specimen¹¹) was a medium density fiberboard (MDF) Woodceramics powder (Tohokukagaku Co, Ltd) which had been injected with a phenolic resin and heated at 1073 K. The mass ratio of board to resin was 1 : 1. The particle diameter of the specimen was 75 to 150μm and the powder had been preserved in a desiccator for more than 72 hours at room temperature prior to use.

2.3 Measurements

About 10mg of specimen and reference material were each placed in separate Pt–Rh alloy pans. A mixed nitrogen and oxygen gas was allowed to flow into the apparatus in which the oxygen concentration was regulated at 5, 8, 12, 16 and 20% by volume. The total flow was maintained constant at 100ml/min. The mass loss and temperature difference of the specimen were measured at heating rates of 2, 3, 5, 10 and 15K/min. Repeatability of these measurements were confirmed under the same experimental conditions.

3. Results

Figure 1 shows the TG curves plotted against temperature for 5, 8, 12, 16 and 20% oxygen concentration at a heating rate of 2 K/min. A slight mass loss occurred between room temperature and 373 K because of desorption from the specimen. We neglected this mass loss in the kinetic analysis. From Fig. 1, it can be seen that a slight mass loss occurred below 573 K, but this was unrelated to the change in concentration of oxygen. Also, an abrupt mass loss by oxidation occurred above 673 K followed by completion of thermal degradation of the specimen around 773 K. When the concentration of oxygen was increased, thermal degradation occurred more rapidly, and the rate of mass loss increased.

Figure 2 shows the corresponding differential thermogravimetry (DTG) curves in Figs. 1 and 3 shows the DTA curves for the 5, 8, 12, 16 and 20% of oxygen concentrations...
at heating rate of 2 K/min. The locations, heights of the peaks, and peak temperatures in the DTA curves correlate well with the DTG curves. The areas under the DTG and DTA peaks remained the same with increasing concentrations of oxygen and the average enthalpy change obtained from the DTA curves was 10.5 KJ/g at a heating rate of 2 K/min.

Results similar to Figs. 1, 2 and 3 were obtained at the others heating rates. It can be said that the same thermal degradation is occurring independent of the concentration of oxygen.

Using the Arrhenius equation, the reaction rate law\(^8\) for thermal degradation was introduced. It was assumed Woodceramics as a reaction matter, and oxygen as an atmosphere for the experimental condition.

\[
\beta \left( \frac{d\alpha}{dT} \right) = A \exp \left( -\frac{E}{RT} \right) (1 - \alpha)^n
\]  \hspace{1cm} (1)

Where the symbols are as follows;

- \(\beta\): heating rate in K/s
- \(\alpha\): fractional mass loss of specimen
- \(T\): temperature of specimen in K
- \(A\): pre-exponential factor
- \(E\): activation energy in J/mol
- \(R\): gas constant in J/(mol·K)
- \(n\): order of reaction.

To evaluate the kinetic parameters, we used the Ozawa method\(^9\) which uses the data obtained from the measurements at more than three heating rates to get the apparent activation energy \(E\). We used the data obtained at heating rates of 2, 3, 5, 10 and 15 K/min. This method uses the equation below.

\[
\log \beta + 0.4567 \frac{E}{RT} = \text{const.}
\]  \hspace{1cm} (2)

The apparent activation energy \(E\) can therefore be obtained from the slope of the fitting line into plots of \(\log \beta\) against \(1/T\) for the fixed degree of conversion. Figure 4 shows plots of \(\log \beta\) against \(1/T\) at 20% oxygen concentration. Table 1 shows calculated apparent activation energies by using this method.

<table>
<thead>
<tr>
<th>Degree of conversion</th>
<th>Concentration of oxygen</th>
<th>Activation energy in kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>5%</td>
<td>89.7 97.5 85.0 102.2 98.5</td>
</tr>
<tr>
<td>0.3</td>
<td>8%</td>
<td>84.7 95.8 81.2 99.8 97.7</td>
</tr>
<tr>
<td>0.4</td>
<td>12%</td>
<td>77.7 90.9 75.9 97.8 95.6</td>
</tr>
<tr>
<td>0.5</td>
<td>16%</td>
<td>71.4 85.6 70.7 94.8 92.8</td>
</tr>
<tr>
<td>0.6</td>
<td>20%</td>
<td>66.1 80.7 65.6 91.6 88.7</td>
</tr>
<tr>
<td>0.7</td>
<td>20%</td>
<td>61.1 75.8 60.8 87.6 84.2</td>
</tr>
<tr>
<td>0.8</td>
<td>20%</td>
<td>56.8 71.4 56.3 83.9 79.6</td>
</tr>
</tbody>
</table>
method. It seems that when the concentration of oxygen was increased, the value of activation energy increased.

Next, we used Coats-Redfern method\(^{(10)}\) to estimate the order of reaction \(n\). This method uses the equations below.

\[
\ln \left( \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} \right) = \ln \left( \frac{AR}{BE} \left( 1 - \frac{2RT}{E} \right) \right) - \frac{E}{RT} \tag{3}
\]

(when \( n \neq 1 \))

\[
\ln \left( \frac{\ln(1 - \alpha)}{T} \right) = \ln \left( \frac{AR}{BE} \left( 1 - \frac{2RT}{E} \right) \right) - \frac{E}{RT} \tag{3}
\]

(when \( n = 1 \))

We can therefore obtain the straight line from a plot of the left side of eq. (3) against \(1/T\) if the value of order of reaction \(n\) is true. Then, we plotted left side of eq. (3) against \(1/T\) assuming that the value of \(n\) is 0 and 1 to conclude which value of \(n\) gives the better straight line in the different experimental condition. We assumed \(n = 0\) as \(n \neq 1\), because Woodceramics react well with oxygen on the surface like the zero-order reaction when the temperature change is low and the oxygen concentration is high.\(^{(11)}\) Figure 5 shows the plot at heating rate of 2 K/min and 20% oxygen concentration, and Fig. 6 at heating rate of 15 K/min and 5% oxygen concentration. Table 2 shows the correlation coefficient of the fitting line of the plots of left side of eq. (3) against \(1/T\).

![Fig. 5 Plots of left side of eq. (3) against 1/T at heating rate of 2 K/min and 20% oxygen concentration.](image)

![Fig. 6 Plots of left side of eq. (3) against 1/T at heating rate of 15 K/min and 5% oxygen concentration.](image)

### Table 2 Correlation coefficient of the fitting line of the plots of left side of eq. (3) against 1/T.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Order of reaction</th>
<th>Concentration of oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 K/min</td>
<td>(n = 0)</td>
<td>0.999 1.000 1.000 0.999 0.998</td>
</tr>
<tr>
<td></td>
<td>(n = 1)</td>
<td>0.995 0.991 0.988 0.985 0.983</td>
</tr>
<tr>
<td>3 K/min</td>
<td>(n = 0)</td>
<td>0.999 0.999 0.996 0.999 0.996</td>
</tr>
<tr>
<td></td>
<td>(n = 1)</td>
<td>0.993 0.987 0.980 0.986 0.977</td>
</tr>
<tr>
<td>5 K/min</td>
<td>(n = 0)</td>
<td>0.995 0.999 0.999 0.991 0.974</td>
</tr>
<tr>
<td></td>
<td>(n = 1)</td>
<td>0.999 0.995 0.986 0.966 0.939</td>
</tr>
<tr>
<td>10 K/min</td>
<td>(n = 0)</td>
<td>0.982 0.991 0.997 0.999 0.999</td>
</tr>
<tr>
<td></td>
<td>(n = 1)</td>
<td>1.000 1.000 0.998 0.996 0.999</td>
</tr>
<tr>
<td>15 K/min</td>
<td>(n = 0)</td>
<td>0.974 0.986 0.981 0.997 0.994</td>
</tr>
<tr>
<td></td>
<td>(n = 1)</td>
<td>0.999 1.000 1.000 0.997 0.999</td>
</tr>
</tbody>
</table>

### Table 3 Pre-exponential factor of thermal degradation of Woodceramics.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Concentration of oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 K/min</td>
<td>382 694 \times 10 758 877 \times 10^2 374 \times 10^2</td>
</tr>
<tr>
<td>3 K/min</td>
<td>138 243 \times 10 434 437 \times 10^2 312 \times 10^2</td>
</tr>
<tr>
<td>5 K/min</td>
<td>116 \times 10 415 233 510 \times 10^2 386 \times 10^2</td>
</tr>
<tr>
<td>10 K/min</td>
<td>191 489 \times 10 802 136 \times 10^2 124 \times 10^2</td>
</tr>
<tr>
<td>15 K/min</td>
<td>136 205 \times 10 244 193 \times 10^3 438 \times 10^2</td>
</tr>
</tbody>
</table>

and oxygen concentration is high, it is apparently zero-order reaction. It can be said that concentration of oxygen affects the reaction at high heating rate and low oxygen concentration.

To get the value of pre-exponential factor, we substituted the value of activation energy and order of reaction at which the value of correlation coefficient is high for eq. (1). Table 3 shows the result of the calculation.

### 4. Discussion

The practical use of Woodceramics as a heat insulating material has been proposed. From Fig. 1, it can be said that it is thermally stable until about 623 K for use in air. The flash point is about 673 K. There is a slight mass loss below 623 K, because of thermal degradation of non-carbonized ingredients of the specimen. The slight mass loss is unrelated to the concentration of oxygen.

From Figs. 2 and 3, the peak temperature converges on a specific value when its concentration of oxygen becomes high. We think because this contact area between the specimen and oxygen is limited. Similar results were obtained at all the heating rates.

The values of kinetic parameters changed with changing concentration of oxygen from Tables 1 and 2. The value of apparent activation energy is high at the initial stage of the reaction. We think that there is the affections of the energy required at flashing point, the increase of the area which contacts to the specimen and oxygen when the reaction
progressed, and the enhancement of the reaction by the exothermic energy that occurred formerly.

The incineration or the use for the fuel of Woodceramics in the case of a waste can also be considered. The reaction at heating rate of 15 K/min and 5% oxygen concentration was completed until below 1023 K, and little ash remained. The calorific value obtained from the peak area of the DTA curve increased with increasing the heating rate, but was unrelated to the concentration of oxygen. By the above mentioned, we can expect that the burning process would be regulated by changing concentration of oxygen because the reaction rate depends on concentration of oxygen.

We will report the further studies at the other heating condition concerning with the reaction which depends on the surface and inner structure of specimen.12,13)

5. Conclusions

The oxidation reaction of Woodceramics at various concentration of oxygen was analyzed.

(1) In the high oxygen concentration atmosphere, the oxidation reaction is not dependent on the quantity of the sample, and order of reaction becomes 0.

(2) In oxygen atmosphere of the low concentration, it was proven that the rate equation depended on the quantity of the sample as the first order.

(3) The value of activation energy is high in the reaction initial stage, and it decreases with the progress of the reaction.

(4) Pre-exponential factor and activation energy increase with the increase in the oxygen concentration.

Acknowledgements

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