Innovative Reuse of Agricultural Wastes as Industrial Raw Materials to Form Magnesium Composites

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Innovative reuse process of rice husks (RH), being one of the representative agricultural wastes, has been developed to fabricate magnesium composites by solid-state reaction to form magnesium silicide (Mg₂Si) reinforcements, having high hardness and Young’s modulus. From a view point of the biomass energy, rice husks, including about 70 mass% organics, could be effectively used as environmentally benign fuels to supply electric power or biomass ethanol. Considering that the most of the rice husk wastes after absorbing organics is SiO₂, the solid-state synthesis of Mg₂Si compounds by reaction of SiO₂ with magnesium was suggested in this study. First of all, the effect of the acid washing treatment to remove organics of rice husks on the crystallization of amorphous SiO₂ was evaluated by TG-DTA and XRD analysis. The carbon content of 0.05% in the wastes was drastically reduced by using acid-washed rice husks, compared to that of non-acid-washed ones (0.19%).

When employing the wastes with and without the acid washing treatment, the crystallization temperature is about 1273 and 1073 K, respectively. The latter showed the lower crystallization temperature because the reaction of the alkaline contents, such as K, P, and Ca, with SiO₂ content of 0.05% in the wastes was drastically reduced by using acid-washed rice husks, compared to that of non-acid-washed ones (0.19%).

1. Introduction

The total weight of rice husks (RH) in the world in 2003 is about 100 million tons, and 70% of them come from the Southeast Asia countries, Thailand, Cambodia, Laos etc.¹ In general, rice husks are burned in the open air, and their ashes are scattered to the rice field as fertilizers. However, it causes 0.15 kg CO₂ gas in burning 1 ton RH. On the other hand, 0.09 kg methane gas comes from the rotted rice husks of 1 ton. A new reuse process of rice husks should be established as soon as possible because these gases are very environmental burdens. When considering that 70% organic contents, such as cellulose, hemi-cellulose and lignin are contained in rice husks, and the rest consisting of 20% SiO₂ and 10% absorbed water,² rice husks are significantly important and environmentally friendly fuels to produce the biomass energies; the electric power by burning and the liquid ethanol by fermentation. In particular, they are carbon neutral renewable energy resources because CO₂ discharge from power plant in burning rice husks are comparable to that in being absorbed during the rice plant growth. In promoting the biomass energy technologies, however, it is also important to establish the environmentally benign process to dispose or reuse the wastes of rice husks after absorbing organics, such as rice husk ashes (RHA), including the main content of SiO₂, come from the power plant. The previous works showed the possibilities in applying them to produce metallic silicon (Si), silicon carbide (SiC), Silicon nitride (Si₃N₄), etc.³⁻⁵ It is, however, clarified that a poor purity and expensive processing cost cause difficult to employ rice husk wastes as the practically reusable materials. They are mostly thrown away to the river and rice field. A few of them are employed as sheep raw materials for the reinforcement of the concrete. SiO₂ could be employed as industrial raw materials to synthesize magnesium silicide (Mg₂Si) via a deoxidization reaction of SiO₂ by magnesium in solid-state.⁶ Mg₂Si intermetallics are suitable reinforcements of magnesium alloys because of their superior characteristics, such as high hardness of 350–450 Hv and high Young’s modulus of 120 GPa.³ In particular, magnesium composite alloys with Mg₂Si dispersoids fabricated by powder metallurgy (P/M) process in solid-state show high mechanical properties and a good wear resistance due to the uniform distribution of fine Mg₂Si particles in the matrix.⁸ In this study, the burning conditions of rice husks are optimized to produce their reactive ashes with magnesium alloy powder. In particular, the effect of the acid washing treatment before burning and heating temperature in burning on the purity and structures of the ashes are discussed in detail. The solid-state reaction between high purity rice husk wastes and AZ31 magnesium alloy powder are also investigated to form magnesium composites with Mg₂Si dispersoids. XRD and optical microstructure analysis on the composites are carried out.

2. Materials Flow in Reuse of Si–O Wastes

The chemical compositions of Thailand and Japanese rice husks by ICP (Inductively Couple Plasma) analysis and ESCA (Electron Spectroscopy for Chemical Analysis) results on them are shown in Table 1 and Fig. 1, respectively. The main elements are carbon and oxygen, contained in organics, and silicon. The other elements, such as very few of K, Ca, P, Al are also contained. The difference of compositions

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
<th>N1s</th>
<th>Si2p</th>
</tr>
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<tbody>
<tr>
<td>Thai</td>
<td>70.5</td>
<td>23.9</td>
<td>1.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Japan</td>
<td>69.7</td>
<td>24.9</td>
<td>1.0</td>
<td>4.4</td>
</tr>
</tbody>
</table>
between them is very little, and the peak binding energy of Si2p is 103.4–103.6 eV. It means silicon elements exist as SiO$_2$ structures in both rice husks. Figure 2 shows XRD results of as-received rice husks before burning. Both indicate the amorphous structures with a broad pattern, that is, SiO$_2$ element is also amorphous. Accordingly, the wastes after removing organics include the main content of SiO$_2$, and their crystal structure strongly depends on the removing conditions.

The innovative reuse process of rice husk wastes proposed in this study is schematically illustrated in Fig. 3. Two routes to employ the wastes including SiO$_2$ to fabricate the magnesium composite alloys with Mg$_2$Si dispersoids synthesized by the deoxidization reaction (4Mg+SiO$_2$ → Mg$_2$Si+2MgO) are introduced. One is a material flow in reusing the rice husk ashes put out from the biomass power plant, and another is that in employing rice husk wastes after absorbing organics by the fermentation to produce the liquid ethanol. In the former route (Route A), for example, 300 tons of rice husks are employed as fuels per day in 10 MW power plant in Thailand. Their ashes of 15 tons are discharged by air-burning them at 1273 K in the plant. ICP analysis result on them indicates that 88% SiO$_2$ and 6.7 mass% carbon, coming out from organics, and some of P, Ca, Al and K elements are contained. XRD result shows SiO$_2$ with crystalline structures, in particular, α-Cristobalite or Tridymite. On the other hand, the latter route (Route B) supplies high purity wastes, that is, a very few carbon are contained because most of organics are consumed to produce methanol by fermentation at 353–393 K. It also means the amorphous structures could be maintained in the rice husk wastes after fermentation. Such wastes with a high purity are reactive, and suitable for...
the lower temperature reaction with magnesium alloys to form Mg$_2$Si compounds.

3. Preparation of Rice Husk Wastes in Laboratory

Specimens of rice husk wastes via Route A are prepared by burning as-received rice husks in the electric furnace at 873, 1073 and 1273 K for 600 s in air. The remarkable difference of the burning conditions used in the laboratory furnace with the power plant is a heating ratio in burning. Rice husks are gradually heated from room temperature to 1273 K in the small furnace. In power plant, however, they are thrown in the combustion furnace controlled at 1273 K and rapidly heated in air. In the Route B, the organic contents of rice husks are chemically resolved by yeasts during fermentation. In the laboratory, the acid treatment with 0.5% HCl solution is adopted as an easy way to remove the organics from rice husks, and the wastes after water washing are burned at 873, 1073 and 1273 K for 600 s in air. The color and morphology changes before and after burning are observed. The behavior of resolving the organics of rice husks are investigated by using TG-DTA (Thermogravimetric-Differential Thermal Analysis) equipment. It is measured in air with a heating ratio of 10 K/min. ICP and XRD analysis on each rice husk waste are carried out to quantify the content of each element and identify the structure phases. The crystallization temperature of the amorphous SiO$_2$ contained in rice husks is also investigated by using XRD analysis when heat treated up to 1423 K after acid treatment.

4. Results and Discussions

4.1 Characteristics of rice husks and their wastes after burning

Table 2 shows ICP analysis results on Thailand rice husk wastes with and without acid washing treatment burned at 1273 K, compared to ashes come out from power plant, measured by ICP analysis.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>P</th>
<th>Ca</th>
<th>K</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>With A.T.</td>
<td>43.8</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Without A.T.</td>
<td>40.9</td>
<td>0.2</td>
<td>0.4</td>
<td>0.5</td>
<td>0.19</td>
</tr>
<tr>
<td>RHA from</td>
<td>35.2</td>
<td>0.4</td>
<td>0.9</td>
<td>1.2</td>
<td>6.73</td>
</tr>
<tr>
<td>power plant</td>
<td></td>
<td></td>
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</tr>
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</table>

*A.T.; Acid washing treatment

Table 2 Chemical compositions of Thailand rice husk wastes with and without acid washing treatment burned at 1273 K, compared to ashes come out from power plant, measured by ICP analysis.

Figure 4 shows the morphology changes of Thailand rice husks by the acid washing treatment and their wastes after burning at 873 and 1273 K with and without acid washing treatment, which are burned at 1273 K for 600 s in air by using a small muffle electric furnace, compared to the ashes come out from Roi-et power plant in Thailand. The carbon content of rice husk wastes via the acid washing treatment is 0.05%. It is remarkably smaller than that in burning as-received rice husks (0.19% carbon content). It also indicates that the content of the other elements of the former, such as P, Ca, K, is also smaller. That is, the acid washing treatment is effective to reduce or remove organics and other impurities contained in rice husks, except for silicon. On the other hand, the remained carbon of 6.7% in the ashes come out from the power plant is much larger than that of the wastes prepared in the small furnace without the acid treatment. The difference strongly depends on the heating ratio in burning rice husks. That is, the carbon elements of the cellulose are taken in the melting area due to the reaction of K$_2$O and SiO$_2$, when rapidly heating rice husks in air. Such carbon elements are obstructed to contact oxygen during burning, and remain in the ashes. Based on the above chemical compositions, their calculated purity of SiO$_2$ is 99.3, 95.4 and 88.7%, respectively.

Figure 4 shows the morphology changes of as-received rice husk and their wastes burned at 873 and 1273 K with and without acid washing treatment, compared to rice husk ashes in power plant.
burned wastes without the acid treatment indicate the stick-like morphology, being similar to as-received rice husks.

TG-DTA measurement is carried out to investigate the resolution behavior of the organics contained in rice husks. As shown in Fig. 5, the weight reduction until 373 K in TG curves corresponds to the vaporization of absorbed water on the rice husks. The remarkable decrease means the resolution of the organics such as cellulose, hemi-cellulose or lignin. There is no clear difference in TG curves. However, as shown in Fig. 5(a), DTA curve in using as-received rice husks is extremely different from that of acid-washed ones shown in Fig. 5(b). The first exothermic heat at 606 K corresponds to the pyrolyzed organics containing low molecule substances. The second one at 733 K is due to the combustion of fixed carbon with a high molecular weight. The total exothermic heat of DTA curve in using rice husks with and without the acid washing treatment is 20.4 and 35.8 kJ/g, respectively. The TG-DTA results indicate that the acid washing treatment is effective to remove 40% organics of rice husks, in particular the thermally stable fixed carbon contents, which causes the carbon compound impurities of wastes or ashes after burning.

Figure 6 shows XRD patterns of as-received rice husks and their wastes burned at 873 and 1273 K (a) and (b), compared to the ashes in power plant (c). When processing the rice husks by the acid washing as shown in Fig. 6(a), the wastes burned at 873 and 1273 K indicate a broad peak. That is, amorphous SiO$_2$ completely remains in the wastes by employing the acid washing treatment on rice husks. On the other hand, as shown in Fig. 6(b), some peaks of crystalline SiO$_2$ ($\bigcirc$) and carbon compounds ($\triangle$) are detected in that burned at 1273 K, not 873 K, when applying no pre-treatment. The crystallization occurred by heating at 1273 K because of the decrease of the melting point of SiO$_2$ via reaction with a few impurities of alkali elements such as K, P, Ca remained in rice husks. The ashes also crystalline SiO$_2$ peaks. Furthermore, it is clarified that the crystallization of amorphous SiO$_2$ occurs in heating over 1073 K. This corresponds to the previous result on the structure changes of rice husks in air-burning.$^{10}$ The dependence of the crystallization of amorphous SiO$_2$ on the burning temperature of rice husks is shown in Fig. 7. In employing the acid washing treatment, Fig. 7(a) indicates that very small peaks of crystalline SiO$_2$ are detected at 1373 K, and they become strong in heating at 1423 K. The limited burning temperature to form amorphous SiO$_2$ is 1273 K when using the acid-
washed rice husks. On the other hand, there is no remarkable change in the XRD pattern, having Cristobalite SiO$_2$ peaks, of the wastes without the acid washing treatment in burning at 1423 K as shown in Fig. 7(b). That is, no grain growth or melting phenomenon of the crystalline SiO$_2$ contained in the wastes occurs.

4.2 Magnesium Composite Alloys with Mg$_2$Si by Using Rice Husk Wastes

Magnesium composite alloys dispersed with Mg$_2$Si particles are fabricated in using the elemental mixture of Thailand rice husk wastes and AZ31 alloy powder. Four kinds of them are employed after grinding less than 50 μm; 1) burned at 1273 K after acid washing treatment (A.T.), 2) as-received after A.T., 3) burned at 1273 K without A.T., and 4) as-received without A.T. Each elemental mixture of AZ31 powder and 4 mass% rice husk wastes are compacted at room temperature by applying a pressure of 600 MPa. The compacts show no crack and delamination, that is, a good compactability even including rice husk wastes. After heating them at 723 K for 300 s in nitrogen gas atmosphere to synthesize Mg$_2$Si, they are immediately consolidated by hot extrusion in air. The extrusion ration is 15, and the die temperature is 573 K. Figure 8 shows XRD patterns of hot extruded AZ31 alloys in using each mixture powder. Mg$_2$Si peaks are detected in employing the wastes 1) and 3). The other ones, however, indicate no Mg$_2$Si compound, that is, the solid-state reaction between the wastes including amorphous SiO$_2$ and magnesium powder does not occurred at 723 K. All indicate MgO peak due to the originally contained oxides as the surface films of raw AZ31 magnesium alloy powder. Mg$_2$Si peak intensity in using wastes 1) is higher than that of wastes 3). A small peak of SiO$_2$ is detected in the wastes 3). It means that rice husk wastes burned at 1273 K after the acid washing treatment are much reactive with AZ31 magnesium alloy powder because they include completely amorphous SiO$_2$ structures and a very few impurities as mentioned above. Crystalline SiO$_2$ of those without the pre-treatment do not completely react with AZ31 powder. In the case of wastes 2) and 4), the organics such as cellulose and semi-cellulose are chemically resolved during heating and hot extrusion process, and the generated gases and remained resolution elements obstruct the reaction of SiO$_2$ in rice husks with magnesium alloy powder. Figure 9 indicates the optical microstructures of hot extruded AZ31 composite alloys with in-situ formed Mg$_2$Si dispersoids when using rice husk wastes burned at 1273 K as raw materials. As shown in Fig. 9(a), only Mg$_2$Si with a mean size of 50 μm, not SiO$_2$ particles, are uniformly observed in the matrix. It also means that the rice husk wastes were consumed to synthesize Mg$_2$Si via the reaction with magnesium alloy powder. Figure 9(b), however, reveals some SiO$_2$ particles locally remained without reacting beside Mg$_2$Si compounds. This result also corresponds to the XRD pattern as shown in Fig. 8. In both materials, the segregation of Mg$_2$Si particles is observed at the primary AZ31 powder boundaries, and should be obstructed to improve the decrease of the mechanical properties of the composites.
5. Conclusions

(1) The acid washing treatment on rice husks is effective to fabricate amorphous SiO$_2$ with a high purity of about 98–99% because it resolves and remove organics, such as cellulose, hemi-cellulose and lignin, and some alkali oxides. The reduction ratio of the total weight of the pre-treated rice husks is about 40%, compared to that of non acid-washed ones.

(2) The crystallization temperature of amorphous SiO$_2$ is about 1273 K in employing the acid-washed wastes. Non acid-washed wastes show that of about 1073 K because of the decrease of the melting point of SiO$_2$ due to the reaction with alkali elements such as K, P, Ca during burning.

(3) Rice husk wastes burned at 1273 K after the acid treatment are more suitable to synthesize Mg$_2$Si via reaction with magnesium alloy powder, compared to those without pre-treatment. This is because a high purity and amorphous structure of SiO$_2$ are finer and more reactive.

Acknowledgements

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