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Preparation and characterization of glass-like carbon/silica composites from rice hull and phenolic resin

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Abstract Glass-like carbon/silica composites were prepared from rice hull and phenolic resin. Monolithic composites were prepared by carbonizing green bodies made from phenolic resin and rice hull in nitrogen atmosphere at temperatures raging from 1173 K to 1773 K. The resultant composites consisted of approximately 70 mass% of glass-like carbon and 30 mass% of silica, the latter being originated from rice hull. The highest compressive strength, bending strength, and fracture toughness were 227 MPa, 50 MPa, and 0.80 MPam$^{1/2}$, respectively. The composites did not show any detectable hygroscopic expansion upon immersing in water. The mechanical properties were not deteriorated up to 1573 K, as long as the silica maintained its amorphousness.

Introduction

Iizuka et al. [1, 2] proposed a composite material which was prepared by carbonizing mixtures of rice bran and phenolic resin, and named the composite RBC (rice bran ceramics). Due to its high mechanical strengths and high solid lubrication property, RBC has been industrially used in oil-free bearings and other applications. The preparation procedure of RBC is as follows; (i) a mixture of rice bran powder and a Na-containing resole type phenolic resin is pyrolyzed in a nitrogen atmosphere to prepare powdered product (RBC powder), (2) the RBC powder is then mixed with phenolic resin again to be formed into monolithic green bodies by either uniaxial pressing or injection molding, (3) and the green bodies are carbonized in a nitrogen atmosphere at 1173 K. Since rice bran contains phosphates of magnesium and potassium as inorganic constituents and sodium is incorporated from the first phenolic resin, the resultant monolithic RBC contains approximately 40 mass% of inorganic constituents of phosphates and carbonates of magnesium, potassium and sodium, the rest 60 mass % being glass-like carbon.

The mechanical properties of RBC depend on the method of the forming; the mean compressive strengths of uniaxially formed and injection-molded RBC's are 132 and 264 MPa, respectively. The difference in the compressive strength is attributed to the difference in the porosity; bulk densities of uniaxially formed and injection-molded RBC's are approximately 1.3 and 1.4 g/cm^3, respectively. High mechanical strength accompanied with low density makes RBC a promising structural material.

One of the shortcomings, however, is that RBC shows hygroscopic expansion. That is most likely due to the presence of hygroscopic or water-soluble phosphates and carbonates as inorganic constituent. Therefore, in order to

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eliminate hygroscopicity of RBC, these salts have to be replaced with other chemically stable substances.

Compared to phosphates and carbonates, silica and silicates have higher chemical stability, higher mechanical strength, higher refractoriness, and lower thermal expansion. Therefore, we expect that better materials than RBC may be produced if the phosphates and carbonates are replaced with silica or silicates.

Rice hull has been known to contain highly pure amorphous silica as its major inorganic constituent. Numerous studies have been conducted to utilize rice hull as ‘‘ubiquitous’’ silica source [3–5]. Typically, approximately 20 mass% of rice hull is inorganic constituent, more than 96 mass% of which being silica, and the rest of which being K_2O, CaO, MgO and others. In spite of the high potentiality of rice hull-originated silica and numerous works, however, industrial utilization of rice hull-originated silica has never been commercially established. For example, in Japan, out of 2.6 million tons of rice hull produced per year, about one third of it is just combusted as agricultural waste and the rest is returned to soil.

As an attempt to propose better material than RBC, we prepared composite materials through carbonizing mixtures of rice hull and phenolic resin, which will be denoted as RHC (rice hull ceramics). In this paper, chemical, structural and mechanical aspects of RHC were investigated as a function of the carbonization temperature.

Experimental

Preparation of RHC powder

Rice hull was taken from rice harvested in Yamagata prefecture, which consisted of about 80 mass% of organic and 20 mass% of inorganic constituents. A resol type, Na-free phenolic resin (Code ST-611-LV, Dainippon Ink and Chemicals Inc., Japan) was mixed with the raw rice hull. The mixing ratio of the phenolic resin to the rice hull was 1 to 3 by weight [1, 2]. The mixture was pyrolyzed in a flow of nitrogen gas at 1173 K for 3 h. During the pyrolysis, the carbonaceous matter contained in the rice hull and the phenolic resin was decomposed to volatile species and glass-like carbon. Then, the pyrolysis product was pulverized into powder smaller than 106 μm in diameter, which will be referred to as RHC powder in this paper.

Preparation of monolithic RHC

RHC powder was mixed with another Na-free phenol resin to form monolithic green bodies. The mixing ratio of the resin to the RHC powder was 1 to 3 by weight [1, 2]. Green bodies were formed by either uniaxial pressing under 45 MPa at 423 K into sheets 6 mm × 78 mm × 155 mm or injection molding under 14 MPa at 443 K into bars 3 mm × 12 mm × 64 mm in size.

The green bodies were carbonized in a nitrogen atmosphere at temperatures ranging from 1173 K to 1773 K for 3 h. During the carbonization, the phenolic resin decomposed to glass-like carbon and volatile species. The resultant monoliths will be referred to as p-RHC (short for pressed RHC) and i-RHC (short for injection-molded RHC), depending on the forming method of the green bodies.

Characterization

Carbon contents in p-RHC samples were calculated from the weight losses observed in thermogravimetric analyses up to 1273 K in air. Chemical compositions of the inorganic constituents in raw rice hull and RHC powder were analyzed for Si, K, Na, Ca, Mg, Fe and Al with an inductively coupled plasma spectrometer (ICP, Model ICPS-7000, Shimadzu, Japan). Before the analyses with ICP, raw rice hull and RHC powder were calcined at 1073 K in air to eliminate carbonaceous matter, and the inorganic residues were decomposed with a HF/HCl mixed acid following the method developed by Endo et al. [6]. The inorganic residues were also subjected to X-ray diffraction analysis (XRD, Miniflex, Rigaku Corp., Japan) to investigate the crystallinity. Bulk density of p- and i-RHC samples was measured by the Archimedes method using water as substituting liquid. Compressive strength was measured for p-RHC samples cut into 5 mm × 5 mm × 10 mm in size and for i-RHC samples cut into 3 mm × 3 mm × 6 mm in size with a Shimadzu autograph under a crosshead speed of 0.5 mm/min. Bending strength and fracture toughness of i-RHC samples were measured according to JIS R 1601 and JIS R 1607, respectively. Microstructures of i-RHC samples were observed with a scanning electron microscope (SEM) under an acceleration voltage of 15kV (Model JSM-T330A, JEOL, Japan). For the measurement of hygroscopic expansion during immersion in water, a p-RHC sample carbonized at 1573 K and an RBC sample, which were cut into bars 5 mm × 5 mm × 50 mm in size and thoroughly dried beforehand, were immersed in water at room temperature. Linear expansion was continuously monitored with a laser displacement gauge as a function of the immersion time.

Results and discussion

Chemical and structural aspects

Figure 1 shows inorganic contents in p- and i-RHC samples carbonized at various temperatures. For the samples carbonized at 1573 K or lower temperatures, the inorganic

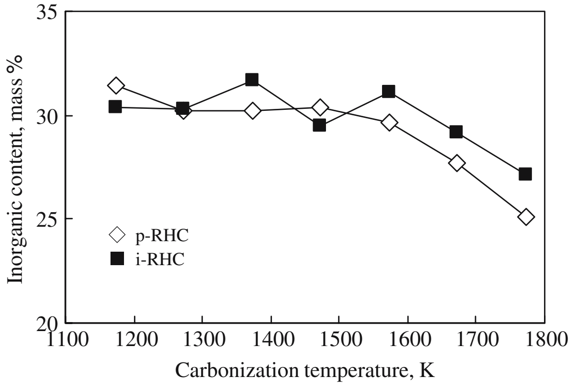

Fig. 1 Inorganic contents in p- and i-RHC carbonized at various temperatures

contents are approximately 30 to 32 mass% regardless of the forming method. When the carbonization temperature exceeded 1573 K, however, inorganic content decreased to ca. 25 mass%. The decrease in the inorganic content may be due to the loss of SiO_2 by the reaction with carbon to form volative SiO as expressed in Eq. (1).

$$SiO_2 + C \rightarrow SiO + CO \tag{1}$$

Table 1 shows the chemical compositions of the inorganic constituents in raw rice hull and RHC powder. In both samples, silica is the major component. It was also confirmed that the chemical composition of the inorganic constituent did not vary very much by the processing of RHC.

Figure 2 shows XRD profiles of the inorganic constituents in p-RHC samples carbonized at various temperatures. Amorphous silica is the major inorganic constituent in the samples carbonized at 1573 K or lower temperatures, while it crystallizes to cristobalite and α-SiC after the carbonization at 1673 and 1773 K, respectively. Since it has been ascertained that the carbonization of the present phenolic resins gives glass-like carbon, RHC samples carbonized at 1673 K or lower temperatures are regarded as glass-like carbon/silica composites.

Table 1 Chemical compositions of the inorganic constituents in raw rice hull and RHC powder (in mass%)

Component	Rice hull	RHC powder
SiO_2	96.5	96.2
K_2O	3.7	3
Na_2O	0.3	0.3
CaO	0.9	0.5
MgO	0.2	0.2
Fe_2O_3	0.1	0.5
Al_2O_3	0	0
Total*	101.1	100.7

*The total exceed 100% within the range of experimental error

Figure 3 shows the variation of bulk density of p- and i-RHC samples as a function of the carbonization temperature. The bulk densities lie in a range from 1.1 mg/cm^3 to 1.5 mg/cm^3. As a whole, i-RHC samples have higher bulk densities than p-RHC samples, reflecting the difference in the forming method. It should be noted that the bulk densities decrease as the carbonization temperature exceeds 1573 K. The decrease in the bulk density may be mainly due to the loss of SiO_2 as expressed in Eq. (1). If we estimate the theoretical density of RHC to be 1.66 g/cm^3 by roughly assuming that RHC consists of 30 mass% fused silica (2.20 g/cm^3) and 70 mass% of glass-like carbon (1.50 g/cm^3), the porosity of RHC samples would lie in a range from 10% to 40% depending on the forming method and the carbonization temperature.

Figure 4 shows the change of microstructure of i-RHC with carbonization temperature. The i-RHC samples carbonized at 1173 through 1573 K have a smooth texture consisting of almost uniform-sized grains and small pores. On the other hand, those carbonized at 1673 K or 1773 K have remarkably large pores. These pores were probably generated by the volatilization of SiO. The change of the

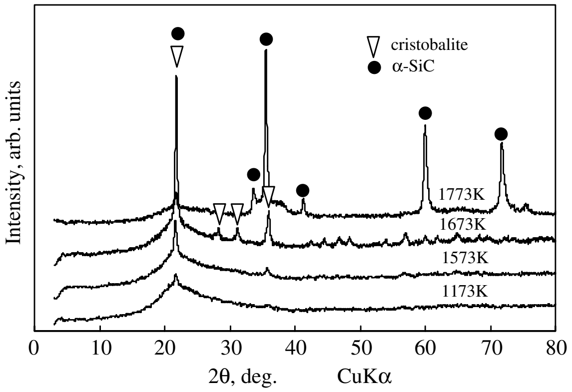

Fig. 2 X-ray diffraction profiles of inorganic constituents in p-RHC samples carbonized at various temperatures

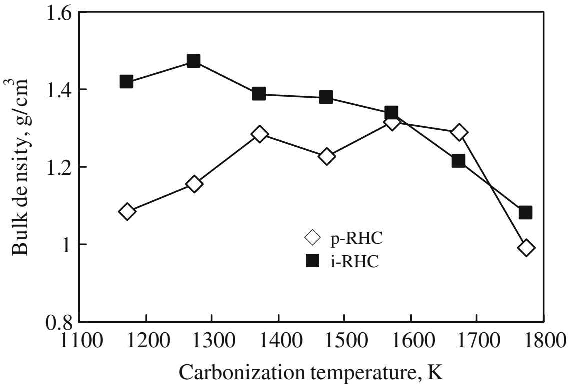

Fig. 3 Variation of bulk density of p- and i-RHC as a function of carbonization temperature

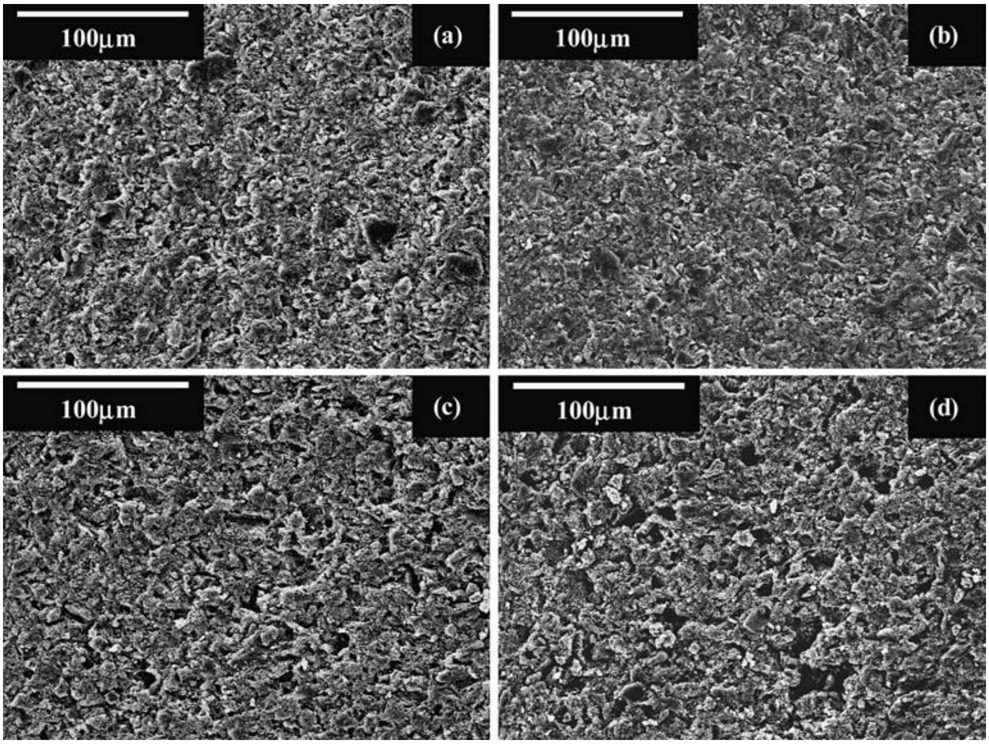

Fig. 4 Scanning electron micrographs (×500) of i-RHC carbonized at (a) 1173 K, (b) 1573 K, (c) 1673 K, and (d) 1773 K

microstructure with the carbonization temperature corresponds to the change of the bulk density.

Mechanical properties

Figure 5 shows the effect of carbonization temperature on compressive strength of p- and i-RHC. For p-RHC, the compressive strength was not affected very much by carbonization temperature as long as the temperature did not exceed 1573 K. The average compressive strength of p-RHC carbonized at 1473 K was 128 MPa. The compressive strength, however, decreased drastically as the carbonization temperature exceeded 1673 K.

The compressive strength of i-RHC was always higher than that of p-RHC, reflecting higher bulk density. It increased with increasing carbonization temperature up to 1473 K, and then decreased with a further increase in the carbonization temperature. The average compressive strength of i-RHC carbonized at 1473 K was 227 MPa. Considering that RHC retains its compressive strength up to ca. 1573 K while RBC stands only up to 1273 K [2], RHC has comparable compressive strength superior thermal durability to RBC.

Figures 6 and 7 show the effect of carbonization temperature on bending strength and fracture toughness of

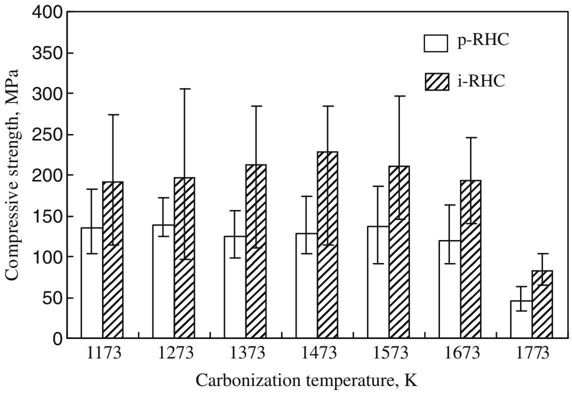

Fig. 5 Effect of carbonization temperature on compressive strength of RHC

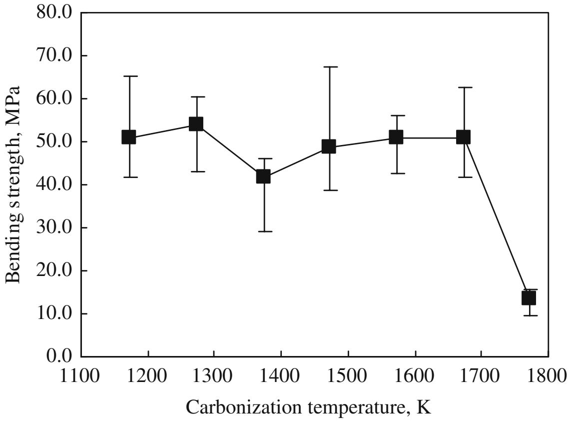

Fig. 6 Effect of carbonization temperature on bending strength of i-RHC

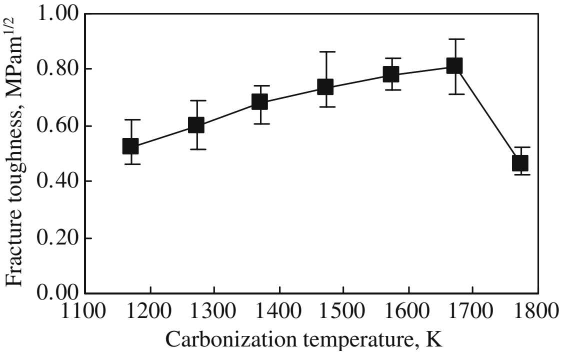

Fig. 7 Effect of carbonization temperature on fracture toughness of i-RHC

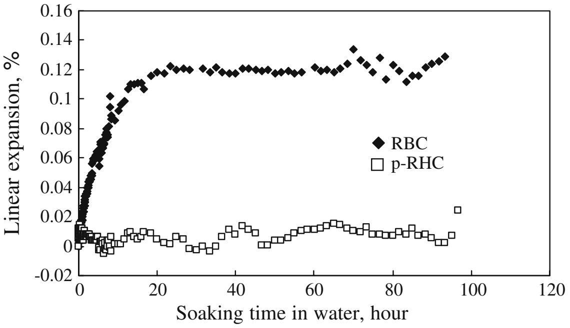

Fig. 8 Hygroscopic expansion behavior of p-RHC carbonized at 1573 K as compared with RBC

i-RHC, respectively. Typical bending strength is approximately 50 MPa and fracture toughness is in a range from 0.50 MPam$^{1/2}$ to 0.80 MPam$^{1/2}$ as long as the carbonization temperature did not exceed 1673 K.

The drastic decreases in compressive strength, bending strength and fracture toughness upon carbonizing at 1773 K should correspond to the generation of large pores in the microstructure accompanied with the decrease in the bulk density.

Figure 8 compares the hygroscopic expansion behavior of p-RHC with RBC. The linear expansion of the conventional RBC upon immersing in water exceeded 0.1% in the first 20 h while p-RHC carbonized at 1573 K did not show any detectable expansion during the immersion for 100 h. The better dimensional stability of RHC should be attributed to the inertness of silica to water.

Consequently, it has been demonstrated that RHC has superior thermal and water durability and comparable mechanical properties to the conventional RBC.

Summary

Composite materials consisting of approximately 70 mass% of glass-like carbon and 30 mass% of silica have been prepared by carbonizing green bodies made from rice hull and phenolic resin in nitrogen atmosphere at temperatures raging from 1173 K to 1573 K. The highest compressive strength, bending strength, and fracture toughness of the material were 227 MPa, 50 MPa, and 0.80 MPam$^{1/2}$, respectively. The present composite did not show any detectable hygroscopic expansion when it was immersed in water for 100 h. The optimum carbonization temperature of the composite lied in a range from 1473 K to 1573 K. Compared with the conventional composite material made from rice bran and phenolic resin, the present composite has higher thermal and water durability and comparable mechanical properties.

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