Retention of amorphous silica in rice hulls at high temperatures

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Abstract

Rice hulls contain around 20 wt% amorphous silica (rice hull silica). Rice hull silica containing no potassium impurity crystallized from amorphous silica to cristobalite at 1300°C. When a small amount of MgO or α-Fe_2O_3 or Al_2O_3 were added to the rice hull silica, the rice hull silica crystallized to cristobalite at 1500°C. MgO, α-Fe_2O_3 and Al_2O_3 diffused to silica as Mg^{2+}, Fe^{3+} and Al^{3+} at high temperatures. These ions broke the SiO_4 tetrahedron network, so that the amorphous state of rice hull silica was maintained. As sintering occurred at 1500°C in rice hull silica mixed with additives such as MgO, the melting of the silica particle surface by sintering made the SiO_4 tetrahedrons to move easily, so that the rearrangement of SiO_4 tetrahedrons occurred and amorphous silica in the rice hull silica crystallized to cristobalite at 1500°C.

1. Introduction

Silica is very useful raw materials for ceramics, semiconductors, silicones and so on. Silica includes polymorphs such as quartz, cristobalite and tridymite, and amorphous silica. The basic crystalline structure of silica is a SiO_4 tetrahedron network in which oxygen ions of a SiO_4 tetrahedron are shared by different tetrahedra and are linked in a three-dimensional network. Crystalline and amorphous silica are determined by the crystalline structure of whether these SiO_4 tetrahedra are regularly or randomly arranged.

Some kind of plant has silica to keep sunshine receiving posture or to protect mechanically by its hardness [1]. The plants are rice, wheat, barley, bamboo, corn, sugar cane and so on. They are so-called siliceous plants. Rice plant has the most silica content in siliceous plants, 18.8-22.3 wt% in rice hulls and 11-15 wt% in rice straw [2]. The accumulation mechanism of silica in rice hulls is follows; Very few soluble silicate ions are absorbed via the root of a rice plant from irrigation water and soil. Silicate ions are carried through the trachea and accumulate in the cuticle on the cell wall of the epidermis of rice hulls. Silicate ions change to amorphous silica by transpiration. The silica is close to the cell wall of the outer epidermis. Silica in rice hulls is obtained by combustion easily, because organic constituents of rice hulls such as cellulose and lignin burn. Natarajan et al. reported that a heating value of rice hulls was 15MJ·kg⁻¹ [3]. There have been several reports on the formation of silica by combustion of rice hulls [4-10]. The average chemical composition of rice hull ashes, varying from 86.9 to 97.3 wt% SiO_2, 0.58 to 2.5 wt% K_2O, 0 to 1.75 wt% Na_2O, 0.2 to 1.5 wt% CaO, 0.12 to 1.96wt % MgO, trace to 0.54wt% Fe_2O_3, 0.2 to 2.85 wt% P_2O_5 and trace to 0.42wt% Cl, was reported by Houston [11]. To obtain pure silica from rice hulls, rice hulls were leached by acid solutions such as HCl, H_2SO_4 and HNO_3 to remove the impurities such as K_2O, Na_2O and CaO before combustion [4,6,12,13]. Real et al. reported that the pure silica of approximately 99.5% was obtained from the rice hulls leached with HCl solution before combustion at 600°C [6]. Since rice hulls contain about 20 wt% silica, research on high purity silica was conducted eagerly regardless of the crystallinity of silica. Recently, it has been reported that the dust of polymorphs of silica such as cristobalite, tridymite and quartz is possibly carcinogenic to humans [14,15], while that of amorphous silica is safe [14,16]. The rice hull silica is originally amorphous state and changes to cristobalite and/or tridymite depending on the combustion temperatures and impurities such as K^+ [4,5,6,7,8,13].

The amorphous silica dispersing at a molecular level in the cuticle has high reactivity and large specific surface of more than 300 m^2·g^{-1} [17]. The amorphous silica crystallized to cristobalite and a small amount of tridymite at the combustion temperature above 900°C due to K_2O containing 0.4 wt% in the combustion ash [5]. In the rice hull silica containing 3.2 wt% K_2O, amorphous silica crystallized to cristobalite at the temperature above 800°C [18]. K^+ ions are thought to break the SiO_4 tetrahedron network and thus prevent crystallization of silica, but they tend to react with silicate ions to form compounds such as poly potassium silicate $(K_2Si_nO_{2n+1})$. $K_2Si_nO_{2n+1}$ melt at 800 to 900°C, so the SiO_4 tetrahedra are easy to move and the SiO_4 tetrahedron network is arranged and the amorphous silica crystallizes to cristobalite and a small amount of tridymite. By washing the rice hulls with hydrochloric acid, the rice hulls containing no K^+ was obtained. The rice hull silica obtained by burning the rice hulls containing no K^+ crystallized from amorphous to cristobalite at 1300°C [18].

Amorphous silica is safe and generally has a large specific area and high reactivity, which is advantageous for ceramics synthesis, purification processes, etc. For example, in the chlorination of the mixture of silica and carbon,

the conversion of amorphous silica to $SiCl_4$ at 900°C for 1 h was 49.2% and that of quartz (α-SiO_2) was 8.7% [19]. The reactivity of amorphous silica was much higher than that of α-SiO_2. In some ceramic synthesis, the temperature may be over 1300°C. If silica is amorphous even at the temperature above 1300°C, it is suitable for reactions involving silica. Dust generated when handling amorphous silica powder is safe because it is not a carcinogen, but care must be taken with general dust health hazards. When MgO, α-Fe_2O_3 or Al_2O_3 is added to rice hull silica, these oxides diffuse in the SiO_4 tetrahedron network as Mg^{2+}, Fe^{3+} and Al^{3+} ions.

Since the voids of SiO_2 are large (The void radius of β-cristobalite at normal pressure above 250°C is 0.175 nm [20]. Amorphous silica has larger voids than cristobalite.), Mg^{2+}, Fe^{3+} and Al^{3+} having ionic radius of 0.089, 0.078 and 0.054 nm [21] can easily diffuse through the SiO_4 tetrahedron network. As these ions break the SiO_4 tetrahedron network, the SiO_2 is thought to remain amorphous. In this paper, the crystallization behavior of amorphous rice hull silica was reported when a small amount of MgO, α-Fe_2O_3 or Al_2O_3 was mixed with amorphous rice hull silica.

2. Experimental

Rice hulls used in this report were collected in Naganuma, Hokkaido, Japan. The preparation method of rice hull silica was the same as previous report [22]. The rice hulls were washed thoroughly with distilled water to remove adhering soil and dust and then dried in air at 100°C in an oven for 24 h. Then, the rice hulls were leached with dilute HCl solution to decrease the impurities 25 g of the rice hulls were refluxed with 0.5 L of 3 %v/v HCl solution at 100°C for 2 h to leach impurities such as K_2O and CaO. After refluxing, the rice hulls containing HCl were rinsed with distilled water to pH 7.0 and were dried at 80°C for 1 h in vacuo. The HCl-leached rice hulls were heated at 600°C for 1 h in flowing N_2, and then were combusted at 600°C for 1 h to obtain the rice hull silica (amorphous). The chemical composition of the rice hull silica was shown in Table 1. The chemical composition of rice hull silica without the HCl-leaching was as follows; SiO_2: 92.36 wt%, Al_2O_3: 0.01 wt%, CaO: 0.56 wt%, Fe_2O_3: 0.12 wt%, K_2O: 0.98 wt%, MgO: 0.03 wt%, MnO: 0.06 wt%, Na_2: 0.01 wt%. The rice hull silica contained 99.5 wt% silica, was completely free of K_2O and Na_2O, and was greatly reduced CaO and Fe_2O_3 as shown in Table 1.

In order to investigate the behavior of crystallization of rice hull silica, each 5 wt% of MgO (97% purity, MERCK), α-Fe_2O_3 (100 % purity, Kanto Chemical), α-Al_2O_3 (99% purity, Kanto Chemical) and α-Al_2O_3 (97% purity, Stem Chemicals) was added to the rice hull silica. These additives and rice hull silica were pulverized and mixed in an agate mortar for 30 min. The rice hull silica mixed with each of the additives was heated in air at the temperature of 600 to 1500°C at a rate of 10°C·min^{-1} and held for 1 h. The crystalline phases in rice hull silica before and after the heating were identified by an X-ray diffractometer (Rigaku, RINT2000/PC) with CuKα ray and a graphite monochrometer. The morphology of rice hull silica was observed by SEM (Scanning Electron Microscopy, JSM-5200, JEOL).

Table 1. Chemical composition of rice hull ashes (wt%).

SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O
99.48	0.04	0.02	0.03	0.00	0.01	0.01	0.00

3. Results and Discussion

Figure 1 showed the XRD patterns of rice hull silica and rice hull silica mixed with MgO, α-Fe_2O_3 and α-Al_2O_3 heated at 600 to 1500°C for 1 h. Table 2 listed the crystalline phases of rice hull silica mixed with MgO, α-Fe_2O_3, α-Al_2O_3 or γ-Al_2O_3, and rice hull silica without additives heated in air at 600 to 1500°C for 1 h. Since γ-Al_2O_3 transformed to α-Al_2O_3 at 1300°C as shown in Table 2, the XRD peaks of rice hull silica mixed with γ-Al_2O_3 at the temperature more than 1400°C was the same as the XRD peaks of rice hull silica mixed with α-Al_2O_3 as shown in Figure 1(d), and the morphology of rice hull silica mixed with γ-Al_2O_3 was the same as that mixed with α-Al_2O_3. Amorphous silica in rice hulls containing no potassium component crystallized to cristobalite at the temperatures above 1300°C [18], but the crystallization temperature was increased by 200°C due to additives such as MgO. The peak detection limit of one component of the mixture was 0.1 to 10 wt% in the powder XRD method, but the XRD peaks of MgO added at 5 wt% to the rice hull SiO_2 was detected at the temperature at 600 to 1000°C. The XRD peaks of MgO became smaller as the temperature was increased and disappeared at 1400°C. Kaneyasu et al. reported that MgO and SiO_2 reacted at 1400°C to form Mg_2SiO_4 [23]. Although no XRD peaks of the reaction product of SiO_2 with MgO were observed in Figure 1(b), it was considered that Mg^{2+} diffused in the SiO_4 tetrahedron network to react. The XRD patterns of the rice hull silica added a-Fe_2O_3 heated at 600 to 1500°C in Figure 1 showed that the XRD peaks of α-Fe_2O_3 became smaller as the temperature increased, and disappeared at 1000°C. Quartz glass, which is amorphous silica, reacts with Fe_2O_3 at 950°C [24]. It was considered that Fe^{3+} diffused in the SiO_4 tetrahedron network in the case of α-Fe_2O_3 as well as MgO. The XRD patterns of the rice hull silica added α-Al_2O_3 heated at 600 to 1500°C in Figure 1 showed that the XRD peaks of α-Al_2O_3 appeared to decrease as the temperature increased,

though the XRD peaks of α-Al_2O_3 was observed up to 1500°C. Hamano et al. reported that a spinel phase, a precursor of mullite, began to form at 980°C in the Al_2O_3-SiO_2 system [25]. In the case of α-Al_2O_3, it was considered that Al^{3+} diffused in the SiO_4 tetrahedron network like the other two additives. MgO, α-Fe_2O_3 and Al_2O_3 diffuse in the SiO_4 tetrahedron network at high temperatures as Mg^{2+}, Fe^{3+} and Al^{3+} to react with SiO_2. Since the voids of silica are large (The void radius of β-cristobalite at normal pressure above 250°C is 0.175 nm [20]. Amorphous silica has larger voids than cristobalite.), Mg^{2+}, Fe^{3+} and Al^{3+} having ionic radii of 0.089, 0.078 and 0.054 nm [21] diffuse easily. Mg^{2+}, Fe^{3+} and Al^{3+} ions diffused in the SiO_4 tetrahedron network reacted with the SiO_4 tetrahedra at high temperatures, and the network was broken, resulting in the maintenance of the amorphous state.
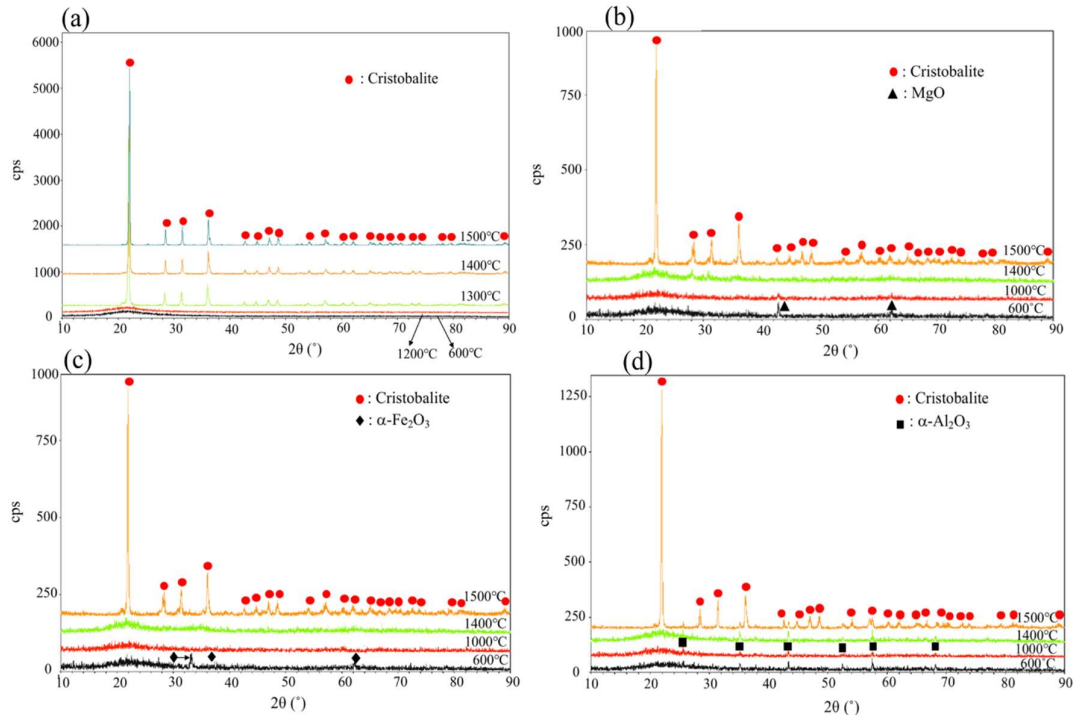

Figure 1. XRD patterns of rice hull silica (a) rice hull silica mixed with MgO (b) α-Fe_2O_3 (c) α-Al_2O_3 and (d) heated at various temperatures for 1 h.

Table 2. Crystalline phases of rice hull ash mixed various additives heated at 600 to 1500°C for 1 h with heating rate of 10°C·min^{-1} in air.

Temp. (°C)	No	Additive			
		MgO (5 wt% for SiO_2)	α-Fe_2O_3 (5 wt% for SiO_2)	α-Al_2O_3 (5 wt% for SiO_2)	γ-Al_2O_3 (5 wt% for SiO_2)
1500	C	C	C	C, α-Al_2O_3	C, α-Al_2O_3
1400	C	A	A	A, α-Al_2O_3	A, α-Al_2O_3
1300	C	A	A	A, α-Al_2O_3	A, α-Al_2O_3(t)
1200	A	A	A	A, α-Al_2O_3	A
1100	A	A	A	A, α-Al_2O_3	A
1000	A	A, MgO(t)	A	A, α-Al_2O_3	A
900	A	A, MgO	A, α-Fe_2O_3	A, α-Al_2O_3	A
800	A	A, MgO	A, α-Fe_2O_3	A, α-Al_2O_3	A
700	A	A, MgO	A, α-Fe_2O_3	A, α-Al_2O_3	A
600	A	A, MgO	A, α-Fe_2O_3	A, α-Al_2O_3	A

A: Amorphous silica, C: cristobalite.
(t): Small XRD peaks were detected.

Rice hull silica heated at 1200°C

Rice hull silica heated at 1300°C

Rice hull silica mixed with MgO heated at 1400°C for 1 h

Rice hull silica mixed with MgO heated at 1500°C for 1 h

Rice hull silica mixed with α-Fe$_2$O$_3$ heated at 1400°C for 1 h

Rice hull silica mixed with α-Fe$_2$O$_3$ heated at 1500°C for 1 h

Rice hull silica mixed with α-Al$_2$O$_3$ heated at 1400°C for 1 h

Rice hull silica mixed with α-Al$_2$O$_3$ heated at 1500°C for 1 h

Figure 2. SEM photographs of rice hull silica and rice hull silica mixed with MgO, α-Fe$_2$O$_3$ and α-Al$_2$O$_3$ before and after crystallization.

Figure 2 presented the SEM photographs of rice hull silica heated at 1200°C and 1300°C, and rice hull silicas mixed with MgO, α-Fe$_2$O$_3$ and α-Al$_2$O$_3$ heated at 1400°C and 1500°C. These SEM images showed the morphology of rice hull silica before and after the crystallization. On the SEM images before the crystallization, the rice hull silica was isolated particles, but the rice hull silicas mixed with the additives were in compact particles because these were ground and mixed in a mortar. On the SEM photographs after crystallization to cristobalite of rice hull silica and rice hull silica mixed with MgO and α-Al$_2$O$_3$, the silica particle surfaces were melted and the particles were stuck together. On the SEM photograph of the rice hull silica mixed with α-Fe$_2$O$_3$, the entire particles were melted.

When K$^+$ ions are added to the rice hull silica having a very disordered void-rich structure (i.e. amorphous silica), K$^+$ ions with ion radii of 0.16 nm [21] (since K$^+$ ions exist in the voids of amorphous silica, K$^+$ ions are considered to take the maximum coordination number of 12) diffuse easily into amorphous silica having the structure similar to silica glass having voids with radius of 0.25 nm [26], and react with silicate ions to form compounds such as poly potassium silicate (K$_2$Si$_n$O$_{2n+1}$) [5,18]. K$^+$ ions tend to break the SiO$_4$ tetrahedron network of silica and inhibit the growth of crystalline phases, but the compounds such as K$_2$Si$_n$O$_{2n+1}$ melt at 800°C, so the SiO$_4$ is easy to move and the SiO$_4$ tetrahedrons is rearranged and amorphous silica crystallizes to cristobalite and a small amount of tridymite [18].

Amorphous silica without K$_2$O did not produce the compounds such as K$_2$Si$_n$O$_{2n+1}$ with a melting point lower than the melting point of silica (1650°C). However, as shown in Figure 2, the surface of the silica particles was melted at 1300°C. Sintering is referred to any process for forming particles to a dense mass by heating [27]. During the firing process, on the powder particles, movement of atoms or ions derives particle surface elimination, starting from the formation of necks between particles to elimination of small pores. The powder particles are in a thermodynamically non-equilibrium state, the movement of atoms or ions occurs in the direction in which the surface area of the particles decreases, and bonding occurs between the powder particles, resulting in a dense mass. In the sintering process, the entire particle does not become a complete melt, but as the movement of atoms or ions occurred, the particle surface seems to be melting. In the sintering process of silica, the SiO$_4$ tetrahedra move on the surface of the silica particles and rearranges to crystallize to cristobalite. Crystallization by melting of the particle surface by sintering has been reported by Kanlai et al. [28]. They sintered fused silica added with starch at 900 to 1300°C. The melting of the particle surface due to sintering was observed at 1150°C and the amorphous silica in the fused silica crystallized into cristobalite.

In amorphous silica in rice hull silica, the melting of particle surface due to sintering occurred at 1300°C. The SiO$_4$ tetrahedra having a random configuration in amorphous state became to move easily in the melt of the particle surface due to sintering and rearranged to crystallize to cristobalite as shown in Figure 1(a), Figure 2 and Table 2.

MgO, α-Fe$_2$O$_3$ and Al$_2$O$_3$ diffuse in the SiO$_4$ tetrahedron network at high temperatures as Mg^{2+}, Fe^{3+} and Al^{3+}. Since the voids of SiO$_2$ are large, Mg^{2+}, Fe^{3+} and Al^{3+} having ionic radii of 0.089, 0.078 and 0.054 nm diffuse easily. As these ions broke the SiO$_4$ tetrahedron network, silica remained amorphous at 1400°C. The sintering temperature of the rice hull silica added with MgO or α-Fe$_2$O$_3$ or Al$_2$O$_3$ was 200°C higher than 1300°C for that of amorphous silica without the additives. The melting of the surface of silica particles by this sintering caused the arrangement of SiO$_4$ tetrahedra, and the amorphous silica in the rice hull silica crystallized into cristobalite at 1500°C.

4. Conclusions

Rice hulls contain about 20 wt% amorphous silica. Amorphous silica generally has a large specific area and high reactivity, and is a useful raw material for syntheses involving silicon. When rice hulls are combusted, amorphous silica in rice hulls crystallizes to crystalline silica such as cristobalite depending on the combustion temperature. When small amounts of MgO, α-Fe$_2$O$_3$ and Al$_2$O$_3$ were added to rice hull silica, they diffused into rice hull silica as Mg^{2+}, Fe^{3+} and Al^{3+} ions at high temperatures. Since Mg^{2+}, Fe^{3+} and Al^{3+} had a smaller radius than the voids of silica, they easily diffused in the SiO$_4$ tetrahedron network and broke the SiO$_4$ network, so that the amorphous state of rice hull silica was maintained at 1400°C. Since sintering occurred at 1500°C in rice hull silica mixed with additives such as MgO, the melting of the silica particle surface by sintering made the SiO$_4$ tetrahedra to move easily, as a result, the SiO$_4$ tetrahedra were rearranged, and amorphous silica in the rice hull silica crystallized to cristobalite at 1500°C.

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