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# Microstructural Characterization of Porous Alumina Prepared by Direct Ink Writing Using Rice Husk as Pore Forming Agent

**Debabrata Majumder and P Karuna Purnapu Rupa***

*Department of Material Science and Engineering, Tripura University, Suryamaninagar, Tripura, India*

***Correspondence to:**
P Karuna Purnapu Rupa
Department of Material Science and Engineering, Tripura University, Suryamaninagar, Tripura, India.
**E-mail:** pkprupa@tripurauniv.ac.in

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## Abstract

Porous alumina ceramics have been prepared by direct ink writing using Pluronic F-127 hydrogel as binder and rice husk a pore former. The ink for direct ink writing (DIW) consisted of hydrogel, alumina, and rice husk. The composition of the ink consisted of 65 wt.% solid loading and the rest 35 wt.% is hydrogel. Within the 65 wt.% solid loading, the ration of alumina and rice husk was varied. Overall, the wt.% of the rice husk was, 1 wt.%, 3 wt.%, 5 wt.%, 7.5 wt.%, and 10 wt.%. The particle size of rice husk was less than 45 μm. After DIW, hydrogel debinding was carried out. Subsequently, sintering was carried out at 1600 °C for 90 minutes. The microstructure of the samples before and after sintering showed the formation of porous structure after sintering, due to the addition of rice husk. The lowest density of the sample measured is 3.05 g/cc for sample with 10 wt.% rice husk and the highest density of 3.37 g/cc was obtained by sample with 1 wt.% rice husk.

## Keywords

Alumina, Rice husk, Pluronic F-127, Direct ink writing

## Introduction

Low density highly porous alumina possesses excellent properties such as chemical stability, high refractoriness, thermal shock resistance, and low thermal conductivity. For this reason, porous alumina ceramics are extensively used as an insulating lining [1], filter materials [2], catalytic substrate [3], bio-medical scaffold [4], and gas separation application [5]. Traditional methods such as direct foaming [6] and foam-gel casting [7] are used for porous structure preparation. Fabrication of porous structure by using a natural pore-forming agent is studied vastly. Nutshells, rice husk, and saw dust are some of the natural pore-formers [8].

Recently, DIW, also known as robocasting, is widely used to build ceramic objects in different shapes and sizes [9]. From the available literature it is found that the alumina porous structure that are developed using traditional method with 63% porosity and compressive strength of 9.7 MPa [10]. DIW of *in situ* mullite porous structure with porosity of about 75% and compressive strength of about 8 MPa successfully developed [11]. This result is compared to traditionally prepared porous alumina. 78% porous alumina with good shape retention is also successfully prepared in a bio-inspired hierarchical structure [12]. DIW with sintering can also produce a porous structure, the optimum sintering temperature for the fabricated part should be 1300 -1400 °C [13].

Rice husk is an organic waste material obtained after the harvesting of rice. But rice husk to be used as a pore-forming agent also requires treatment for pore former as it affects the rheology of the prepared ink. If the developed ink is shear thinning in nature, the prepared ink is easily flowing through the nozzle,

but increasing the rice husk weight percentage makes the ink shear thickening in nature and clogs the nozzle. The available literature on the fabrication of porous alumina by direct ink writing using rice husk as natural pore former is scanty. In this paper synthesis of porous alumina ceramic using grinded rice husk as a pore-forming agent by DIW using hydrogel as binder and the effect of rice husk on the microstructure and density are discussed.

# Materials and Methods

## Materials

The primary starting material for the ink preparation includes alumina powder (ALCOA, 99.9%, particle size less than 10 μm), raw rice husk as a pore former, Pluronic F-127 as a binder and distilled water as a solvent, ammonium poly acrylate as dispersant.

## Methods

The 35 wt.% stock solution of Pluronic F-127 hydrogel was prepared by adding distilled water. At first, 9 wt.% of Pluronic F-127 powder was mixed with 26 wt.% of distilled water. As the polymer is temperature responsive, the stock solution was left in a fridge (below 17 °C) for one day to remove trapped air bubbles and properly mix the polymer with distilled water.

The rice husk obtained from local markets was washed, dried, and ground. The ground rice husk was sieved through a 45 μm sieve. Therefore, the rice husk used in the experiments consisted of particle size of less than 45 μm. The alumina and rice husk were mixed in a pot milling for 24 hours. Five variations of alumina and rice husk have been used in the experiments, as shown in table 1.

The ink has been prepared by using alumina and rice husk mixture in the previously prepared Pluronic F-127 hydrogel. At first 65 wt.% of alumina and rice husk (S1, S2, S3, S4, and S5) mixed with 35 wt.% of Pluronic F-127 hydrogel using mechanical mixing method. To this mixture, 0.32 grams of ammonium poly acrylate was also added as dispersant. The mixture was then vigorously stirred for one-hour using a mechanical stirrer. The prepared ink was then deposited by direct ink writing using a syringe of 2 mm diameter nozzle on an alumina substrate at room temperature.

## Characterization

The sintering of the sample was done for 90 minutes in a muffle furnace under atmospheric conditions, at 1600 °C. The microstructural and elemental analysis of the sample was observed using FESEM (Field Emission Scanning Electron Microscope; Carl Zeiss, Germany). The density of the sample was measured by the Archimedes principle using a density measurement unit (Wenser, India). The sample designation used in this study is given in table 1.

# Results and Discussion

## Microstructure of green sample and binder removed sample

The FESEM image of the alumina and sieved rice husk are shown in figure 1a and 1b. The effect of adding rice husk is observed in the microstructure and now discussed. From figure 1c the fracture surface image of printed sample S3 shows ceramic particles are attached to each other by a binder. From the literature it is found that the rice husk, after burning at 600 °C turns into white ash [14]. The microstructure of the debinding body at 600 °C of sample S3. Figure 1d shows the sample has many pores (black arrow) and burned rice husk (black circle). The visual observation of rice husk in the green sample of experiment S5 is shown in figure 1e by a black circle, and the pore shown by the black arrow are higher than from sample S3. It is also clearly seen from the debinding body that the burned rice husk at 600 °C is clustered and shown by the black circle. The porosity of the sample S5 is also increasing, which is observed from figure 1f. The Energy Dispersive Spectroscopy analysis of the green and debinding sample confirms the presence of silicon in the matrix. It is observed that the wt.% of silicon is higher in the debinding sample compared to green sample. This phenomenon is also observed for the sample S5 (10 wt.% rice husk), in the case of a green sample; the wt.% of silica is also lower compared to the debinding sample.

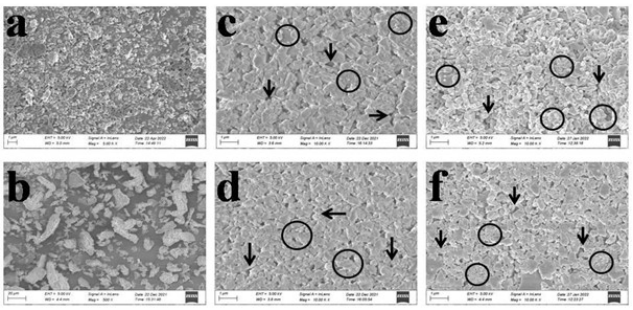


**Figure 1:** FESEM image of **(a)** Alumina raw powder, **(b)** Grinded rice husk, **(c)** Fracture surface of sample S3 printed (green) body, **(d)** Fracture surface of sample S3 debinding body, **(e)** Fracture surface of sample S5 printed (green) body, and **(f)** Fracture surface of sample S5 debinding body.

**Table 1:** Ratio of alumina and rice husk used for the experiment and density of sample S1 to S5 measured by Archimedes principle.

| Sample ID | Alumina (wt.%) | Raw rice husk powder (wt.%) | Hydrogel (wt.%) | Density (g/cc) |
|---|---|---|---|---|
| S1 | 64 | 1 | 35 | 3.37 |
| S2 | 62 | 3 | 35 | 3.18 |
| S3 | 60 | 5 | 35 | 3.17 |
| S4 | 57.5 | 7.5 | 35 | 3.09 |
| S5 | 55 | 10 | 35 | 3.05 |

### Microstructure of sintered alumina

After the removal of the binder carried out at 600 °C, the samples were then sintered at 1600 °C for 90 minutes. The FESEM images of the fracture surface of sintered samples S1-S5, are shown in figure 2. For the sample S1, figure 2a at lower magnification porosity is observed. But, from the higher magnification image figure 2a1, it is observed that the pores are interconnected and irregular in shape. It is also observed that the particles are densely packed at some parts, leaving the large adjacent pores, which implies the particle are diffused and make large particles shown in figure 2a1. From figure 2b for the sample S2, it is observed that there is an increase in the porosity as compared to the sample S1. At higher magnification image figure 2b1, it is clear that the different diameter pores are present, and the pores are interconnected in nature. The alumina particle and silica are well diffused into one another to form large particles seen in figure 2b1. For the Sample S3, from figure 2c, at a lower magnification FESEM image, there is an increase in the number of pores compared to S1 and S2 as there is an increase in the wt.% rice husk from 1%, 2% to 5%. For S1, S2 and S3, respectively. From figure 2c1 the maximum pore size at higher magnification was approximately 22 µm. Figure 2d shows the fracture surface of sample S4. It can be observed that the porosity increases compared to samples S1 - S3. The higher magnification image figure 2d1, it is seen that the alumina particles along with the silica from the rice husk are sintered well to form a continuous network and porosities due to the burning of the rice husk. Also, the porosity is continuous and irregular in shape. Smaller porosities and bigger porosities are observed due to the size distribution of the rice husk. The FESEM image of fracture surface sample S5 figure 2e shows the increased presence of porosities compared to samples S1 to S4. This is due to the fact that the sample has 10 wt.% rice husk. Even at lower magnification, uniform distribution of the porosities can be clearly observed. The pores are in the micron range and regular. No cluster of pores is observed, and the pores are uniformly distributed all over the fracture surface. At higher magnification, the pores are also observed to be higher in size to a lower range. And the particles have highly diffused one another due to complete sintering of the sample at 1600 °C for 90 minutes. It is further noted that there is no presence of voids due to interparticle sintering is observed. One of the reasons for the absence of voids due to sintering is the presence of silica form in the rice husk, which is acting as a sintering aid [15]. From the microstructural image of experiments S1 to S5, there is a variation in pore size and distribution. A smaller magnification image of all the samples reveals a gradual increase in the porosity. Similar result is observed from the literature where with the increasing percentage of rice husk increases the porosity of the sintered alumina [16]. The higher magnification images of the fracture surface show complete sintering of alumina and silica without the presence of voids. The density of the samples S1 - S5 is shown in table 1. The density measurements clearly show the density is decreasing with the increase in wt.% of rice husk. The density for S1 was found to be 3.37 g/cc and decreased to 3.05 g/cc for Sample S5.

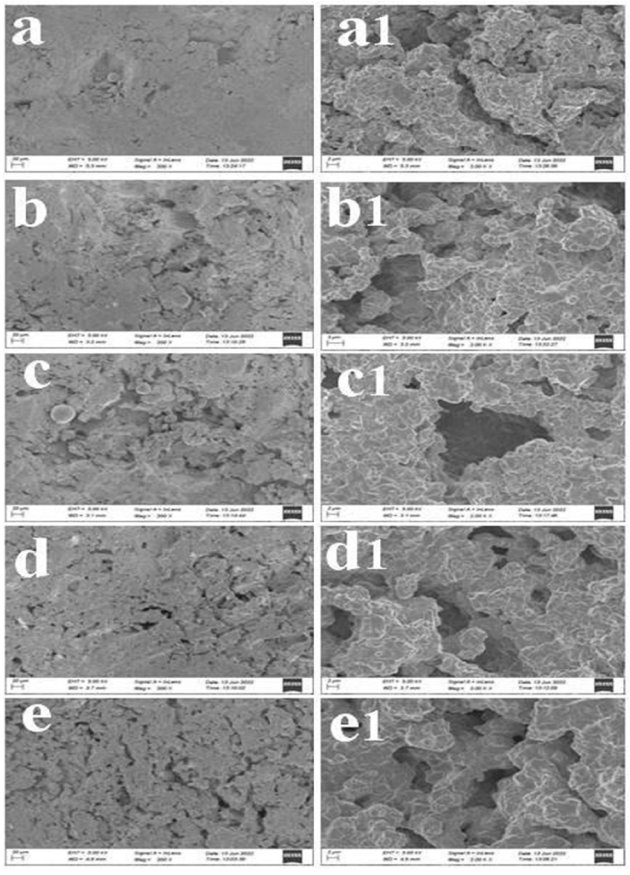


**Figure 2:** FESEM image of sintered sample S1 **(a-a1)**, S2 **(b-b1)**, S3 **(c-c1)**, S4 **(d-d1)**, and S5 **(e-e1).**

Figure 3a and 3b show the elemental mapping of the green and sintered sample S5. The silicon is due to the presence of silica from the rice husk. The mapping of silicon shows the uniform distribution of rice husk in the green sample. By comparison of the elemental mapping of sample S5, of green figure 3a and sintered figure 3b state, it is observed the distribution of silicon is uniform. The clusters of Silica observed on the green sample are no longer observed in the sintered samples.

## Conclusion

Porous alumina structure is prepared using rice husk as a pore-forming agent. DIW was achieved by making ink of suitable viscosity. The samples were sintered at 1600 °C for 90 minutes. The experiments and the microstructural analysis confirm that the porous alumina structures can be easily fabricated by DIW using rice husk as a pore former. It is observed that the porosity of the samples increases with the increase of the wt.% of rice husk in the ink. The density of the samples was observed to decrease with the increase in wt.% of

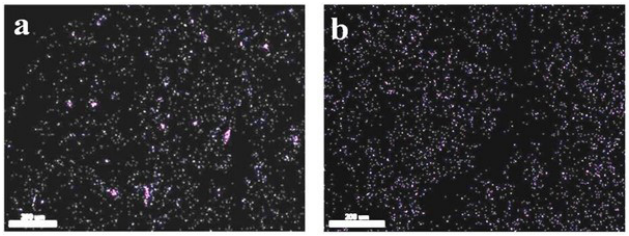


**Figure 3: (a)** Elemental mapping of printed sample (green) S5 and **(b)** Elemental mapping of sample S5 after sintering.

rice husk. The sample with 1 wt.% showed the density of 3.37 g/cc for the S1 and 3.05 g/cc for the sample S5 with10 wt.% rice husk.

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## Conflict of Interest

The authors declare no conflict of interests that are relevant to the content of this article.

## Credit Author Statement

Debabrata Majumder and P Karuna Purnapu Rupa: Equal contribution. All the authors read and approved the manuscript.

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