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Improvement on characteristics of porous alumina from platelets using a TEOS treatment

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Abstract

A porous alumina body was synthesized from anisotropic alumina particles, namely platelets. When green compacts, which had been uniaxially pressed at 1 MPa, were heated at 1200 and 1500 °C for 1 h, the average porosity of the resulting alumina bodies was 75.5 and 71.0%, respectively. The thermal conductivity of the porous alumina fabricated at 1400 °C for 1 h with 72.3% in porosity was 0.8 W m^{-1} K^{-1}. In an attempt to increase the compressive strength of the porous alumina bodies, TEOS (tetraethyl orthosilicate) solution treatment was carried out, followed by reheating to 1400 °C for 1 h. The compressive strength of the porous alumina body increased from 3.8 MPa (without TEOS solution treatment) to 10.2 MPa (with three rounds of TEOS treatment), with the porosity decreasing to 65.5% and the thermal conductivity increasing to1.2 W m^{-1} K^{-1}.

Keywords: B. Platelets; C. Thermal conductivity; Porous alumina; TEOS treatment

1. Introduction

So far, some porous alumina ceramics have been fabricated [1–5]. However, in those methods, special techniques and/or starting materials were used. Generally, simple manufacturing techniques and excellent physicochemical properties are required for porous alumina clinkers in refractories. However, desirable porous alumina clinkers have not been fabricated yet. Therefore, in order to fabricate porous alumina clinkers with high performance including fine uniform pore distribution, high pore volume, sufficient mechanical strength and low thermal conductivity, we thought of the use of anisotropic alumina particles, namely platelets. If platelets are used to fabricate porous alumina, it's porosity can be increased due to the easy formation of card house structure, although the resulting porous body has weak mechanical strength. The fabrication of alumina platelets from solutions [6,7] and fluxes [8–10] have been studied. Furthermore, alumina platelets have been already produced industrially.

In an attempt to fabricate high performance porous clinkers, commercial alumina platelets were used. First, a porous alumina body from platelets was fabricated by a simple compaction and heating technique. Generally, it is difficult to fabricate porous bodies from only alumina platelets, so fine alumina particles were added to the platelets as a sintering additive and corn starch was also added as an organic pore foaming agent. Subsequently, to strengthen the porous alumina body, a TEOS (tetraethyl orthosilicate) solution immersion, drying and then reheating was performed on the original porous alumina body. In this study, the porosity, compressive strength and thermal conductivity of the resultant porous alumina bodies were examined. Finally, the role of TEOS treatment in improving the properties of porous alumina was clarified.

2. Experimental procedures

The starting α-alumina platelets were commercial product (YFA05025; Kinseimatec, Co., Ltd., Japan), and the aspect and chemical composition are shown in Fig. 1 and

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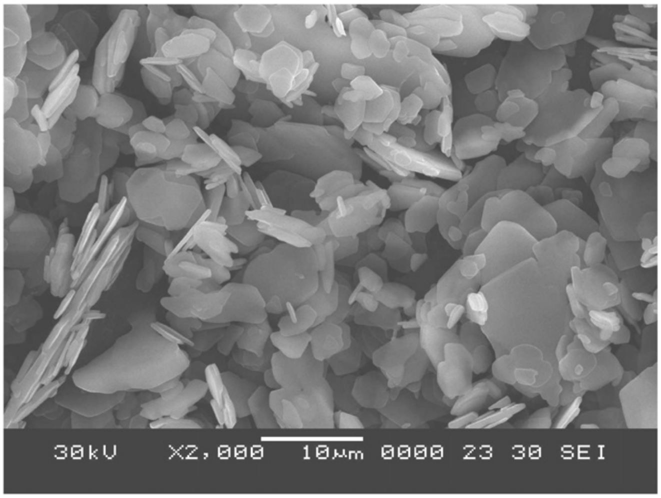

Fig. 1. SEM micrograph of the α-alumina platelets used.

Table 1
Aspect and chemical composition of the starting α-alumina platelets.

Average diameter	4.6 µm
Aspect ratio	15–20
Composition	%
Al_2O_3	99.2
SiO_2	0.06
Na_2O	0.23
Fe_2O_3	0.02

Table 1, respectively. Fine alumina was used as a sintering additive, with purity and diameter of 99.9% and 0.14 µm, respectively. In addition, corn starch with 10 µm in diameter was added as a pore foaming agent to form a card house structure from platelets easily. The powder mixture consisting of 85 mass% α-alumina platelets, 5 mass% fine alumina, and 10 mass% corn starch were mixing at a rate of 30 rpm for 24 h without any media. The resultant powder mixture was uniaxially pressed at 1 MPa to form a green compact $(20 \times 20 \times 10)\ mm^3$ in size. A porous alumina body was synthesized by heating the compact at 1200–1500 °C for 1 h in air. In order to strengthen the porous alumina body, it was immersed in a TEOS ($Si(OC_2H_5OH)_4$: tetraethyl orthosilicate) solution composed of 16.69 g of TEOS, 23.15 g of C_2H_2OH, 8.64 g of distributed water and 3.33 mL of H_2NO_3 (1 mol/L) for 30 min in vacuum. Subsequently, the TEOS solution with porous alumina was heated to 70 °C to lead to a hydrolysis reaction and thus precipitate amorphous silica sol. After solution immersion and drying for 24 h at 60 °C, the resultant compact was reheated at 1400 °C for 1 h in air. If necessary, this process was repeated.

The crystal phases of the porous alumina were examined using X-ray diffraction (XRD: XD-D1; Shimazu, Co., Ltd., Japan), and its microstructure was observed using a scanning electron microscopy (SEM: JEOL 5200; JEOL, Co., Ltd., Japan). In order to estimate the content of SiO_2 formed in the porous alumina, a calibration curve based on the various ratios of SiO_2 and regent grade of alumina (several micro meters in diameter, 99%) was prepared using the integrated intensity of the strongest reflection of SiO_2 and alumina. For example if crystal phase of SiO_2 is cristobalite, regent grade of amorphous silica was heated at 1500 °C for 1 h to prepare the cristobalite phase sample. The compressive strength of the porous alumina was measured using an INSTRON 5582 (INSTRON, Co., Ltd.). Several samples were used to determine the compressive strength for each preparation condition. The specific heat and thermal diffusivity were measured by a differential scanning calorimeter (DSC8230, Rigaku, Co., Ltd., Japan) and a laser flash device (TC-7000, Optronics, Co., Ltd., Japan), respectively, using the method (JIS R 1611). For this measurement, specimens in the form of a disk shape with thickness of 1 mm and diameter 10 mm were used. From these results, thermal conductivities of the porous alumina were calculated.

3. Results and discussion

3.1. Normal heating fabrication

Fig. 2 shows the changes in the compressive strength and porosity of the fabricated porous alumina bodies after heating at 1200–1500 °C for 1 h. The porosity of the porous alumina body decreased with the increase of the heating temperature. When green compacts had been heated at 1200 and 1500 °C for 1 h, the porosities of the resulting alumina bodies were 75.5 and 71.0%, respectively. In contrast, the average compressive strength of the green compact after heating increased from 1.4 to 6.2 MPa for 1200 and 1500 °C, respectively. Of particular interest is the compressive strength and porosity of the porous alumina fabricated at 1400 °C for 1 h which were 3.8 MPa and 72.3%, respectively. The porous alumina after heating at 1400 °C is thought to be readily available

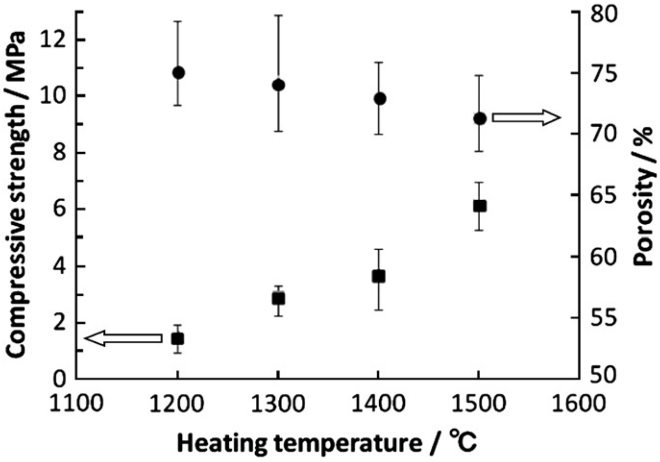

Fig. 2. Changes in porosity and compressive strength of the fabricated porous alumina bodies after heating at 1200–1500 °C for 1 h.

for use in steel-making refractories as a clinker. Therefore, the heating conditions were fixed at 1400 °C for 1 h for the subsequent experiments.

3.2. TEOS treatment

In an attempt to strengthen the porous alumina body while maintaining a high porosity, solution immersion and then reheating treatment was performed. So far, aluminum isopropoxide solution and magnesium nitrate solution treatments for porous alumina have been studied, and mechanical properties of the resultant porous alumina have been improved [11]. Newly, if TEOS solution treatment is performed, precipitated silica and/or mullite have the possibility of exhibiting high performance at high temperatures. First, the porous alumina body after heating at 1400 °C for 1 h was immersed in TEOS solution. After drying, the porous alumina was reheated at 1400 °C for 1 h. Here, TEOS solution immersion and then reheating treatment is defined as "TEOS treatment". Subsequently, the effects of the number of rounds of TEOS treatment on the porosity, compressive strength, precipitated SiO_2 content and thermal conductivity of the resultant porous alumina on rounds of TEOS treatment were investigated.

Fig. 3 shows the change in porosity of the porous alumina body with and without rounds of TEOS treatment. With increase of the number of rounds of TEOS treatment, the porosity of porous alumina body slightly decreased from 72.3% to 65.5%. Fig. 4 shows the change in compressive strength of the porous alumina body with and without rounds of TEOS treatment. According to Fig. 4, compressive strength increased with the number of rounds of TEOS treatment. The compressive strength of the porous alumina with three rounds of TEOS treatment increased to 10.2 MPa, that is 2.7 times strength compared to that of porous alumina without TEOS treatment: 3.1 MPa. Hence, compressive strength after TEOS treatment remarkably increased, maintaining the high porosity of the alumina.

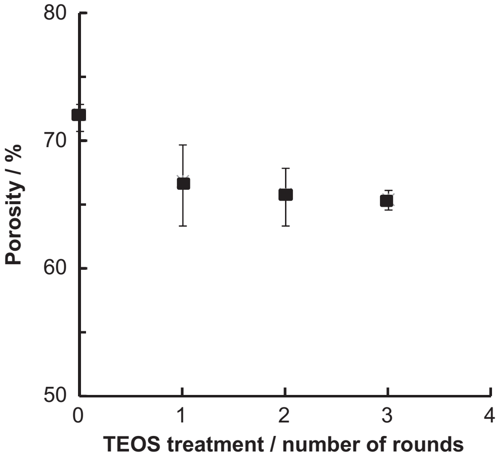

Fig. 3. Change in porosity of the porous alumina body with rounds of TEOS treatment.

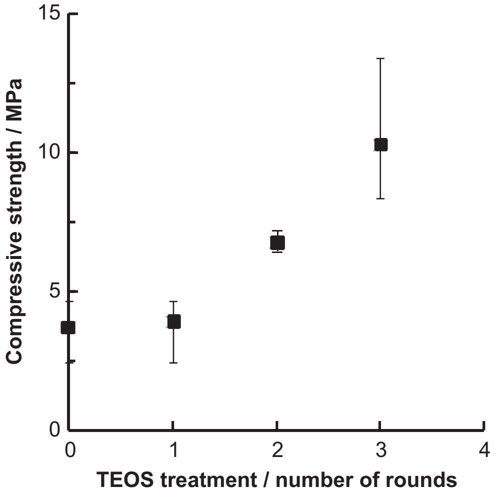

Fig. 4. Change in compressive strength of the porous alumina body with rounds of TEOS treatment.

Fig. 5 shows the SEM photograph of the porous alumina before (a) and after one round (b) and three rounds of TEOS treatment (c). After one round of TEOS treatment, alumina neck growth was observed. Furthermore, after three rounds of treatment, a new precipitated phase was also observed at the surface (c). When this TEOS solution was heated at 70 °C, an amorphous silica sol formed, based on the following general hydrolysis equation [12]

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad (1)$$

After immersion treatment, upon reheating, the formed amorphous silica gel remaining at the surface of platelet and the connected part between the platelets transformed to a SiO_2 crystal phase of cristobalite. However, diffraction peaks corresponding to mullite were not detected after reheating at 1400 °C for 1 h. When coexisting with SiO_2, the mass transport of alumina is thought to be accelerated, particularly at the connected part of platelets, so that a strong chemical linkage of alumina is formed between the platelets. At the same time, there is a possibility that the cristobalite layer which covered the connection fractured due to the mismatch of thermal expansion values of cristabalite and alumina during the reheating process. Then the remarkable volume change with ~5 vol% due to $\alpha \rightleftarrows \beta$ phase transformation of cristobalite [13] at approximately 250 °C accelerated the formation of crack inside the cristobalite and the part of cristobalite scaled off on the surface of alumina. However, TEOS treatment was performed repeatedly, so the connection between the platelets would be also covered with new SiO_2 each round and alumina mass transport occurred continuously to strengthen the chemical linkage. That is, precipitated SiO_2 was considered as acting as a sintering additive in this system. Fig. 6 shows the schematic diagram of the above strengthening mechanism by this TEOS treatment.

Fig. 7 shows the changes of XRD patterns and contents of SiO_2 (cristobalite) in the porous alumina sample with the

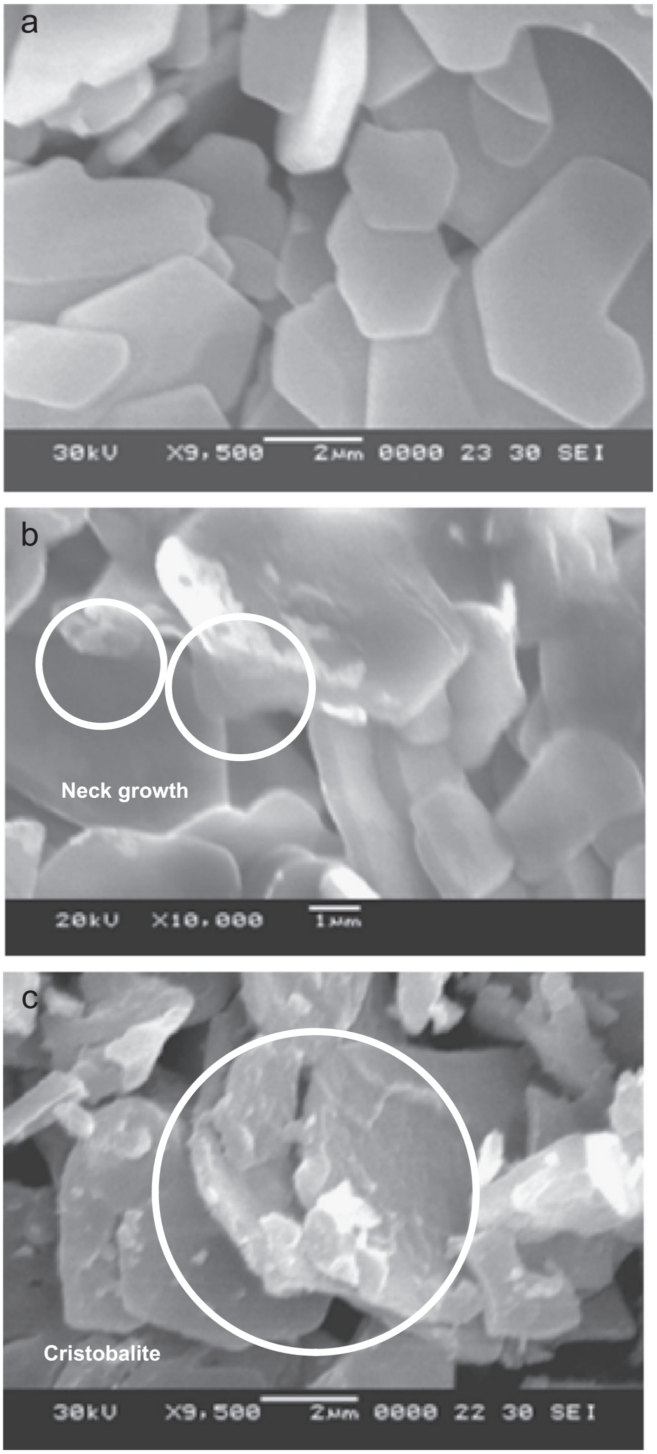

Fig. 5. SEM photographs of the porous alumina before (a) and after one round (b) and three rounds of TEOS treatment (c).

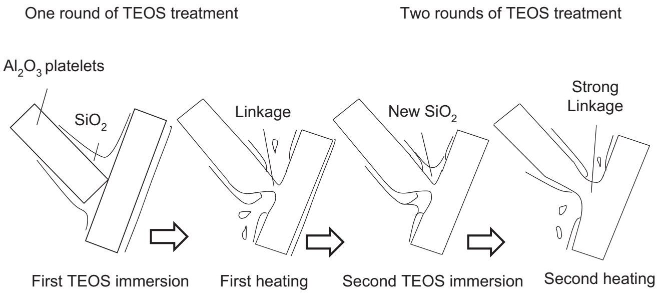

Fig. 6. Schematic diagram of the strengthen mechanism of porous alumina with rounds of TEOS treatment.

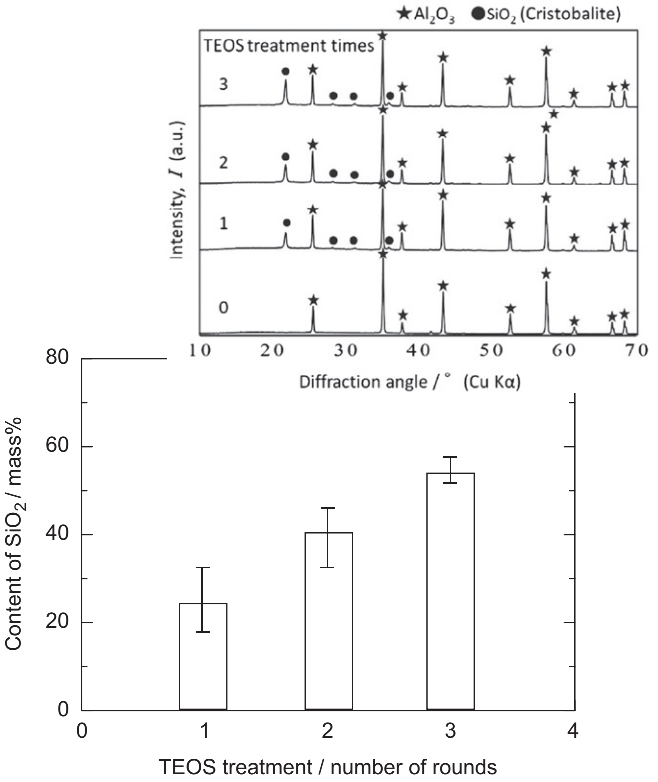

Fig. 7. Changes of XRD patterns and content of SiO_2 (cristobalite) in the porous alumina with rounds of TEOS treatment.

number of rounds of TEOS treatment using a quantitative analysis calculated from accurate XRD measurements. As a result, it is shown that the content of cristobalite increased with increasing the number of rounds of TEOS treatment. The mass ratio of cristobalite was estimated to be approximately 55.0 mass% in the porous alumina after three rounds of TEOS treatment. However, most of cristobalite acted as a surface coating of the alumina platelets, so that the actual volume fraction of cristobalite is likely to have a smaller value compared to that of the detected value using a XRD device. Furthermore, there is a possibility that the crystallinity of cristobalite derived from TEOS was lower than that of the cristobalite derived from amorphous silica. Actually, according to the intrinsic density of the porous alumina after three rounds of TEOS treatment using an Archimedes method, the amount of the formed cristobalite was estimated to be 12.2% in volume fraction.

3.3. Thermal conductivity of the porous alumina

Generally, thermal conductivity: λ can be calculated as following Eq. (2):

$$\lambda = \rho C_p \kappa \quad (2)$$

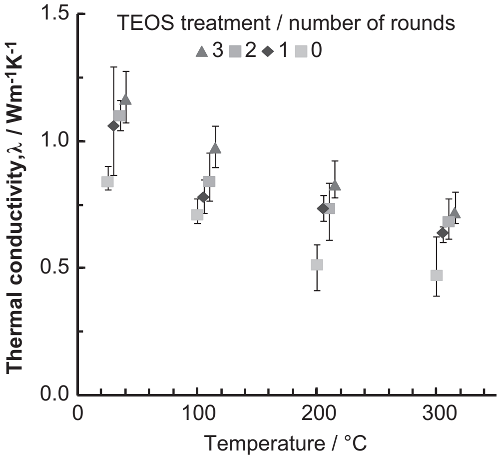

Fig. 8. Changes in thermal conductivity of the porous alumina with rounds of TEOS treatment over the temperature range: RT to 300 °C.

where ρ is true density (kg/m^{-3}), C_p is specific heat (J kg^{-1} K^{-1}) and κ is thermal diffusivity (m^{2}s^{-1}). In this study, C_p and κ were measured by DSC and laser flash devices, respectively. Fig. 8 shows the changes in thermal conductivity of the porous alumina with rounds of TEOS treatment over the temperature range: RT to 300 °C. With increasing temperature, the thermal conductivity decreased due to the increase of phonon–phonon interaction due to the lattice vibration of platelets [14]. At room temperature, the lowest thermal conductivity of the porous alumina with 72.3% in porosity before rounds of TEOS treatment was 0.8 W m^{-1} K^{-1}. This thermal conductivity of the porous alumina increased with increasing rounds of TEOS treatment. However, the difference in the thermal conductivity was only 1.1–1.3 W m^{-1} K^{-1}, so we can say that the TEOS treatment has a small influence on the thermal conductivity of the porous alumina.

Generally, we know that the thermal conductivity of a substance relates to three heat parameters; (a) heat conduction of material, (b) convective heat transfer of air and (c) radiation heat transfer from material. That is, the thermal conductivity can be determined as a combination value of these three parameters. In many cases, however, convection and radiation contributions are negligible. Particularly, since the pore size considered in this paper is several micrometers, convection can clearly be ignored. Further, according to the Stefan–Boltzman radiation law [15], radiation heat transfer is negligible compared to conduction heat transfer [4]. Therefore, heat transfer is mainly governed by conduction. In this case, "Effective Medium Percolation Theory" [16] was adopted and interconnected spherical solid particles of alumina were modeled as opposed to interconnected spherical pores as in the paper by Nait-Ali et al. [17]. Thus, the thermal conductivity: λ_o of the porous resultant alumina without TEOS treatment can be calculated using the following Eq. (3):

$$\lambda_o = \frac{1}{4}[\lambda_s(3\upsilon_s - 1) + \lambda_p(3\upsilon_p - 1) + ([\lambda_s(3\upsilon_s - 1) + \lambda_p(3\upsilon_p - 1)]^2 + 8\lambda_p\lambda_s)^{0.5}] \tag{3}$$

υ_s and υ_p are volume fraction of alumina and air filled inside the pores, respectively. The thermal conductivities of pure dense alumina: λ_s and air: λ_p at room temperature are supposed to 32 and 0.025 W m^{-1} K^{-1}, respectively. As a result, the thermal conductivity of the starting porous alumina with 72.3% porosity without TEOS treatment could be calculated as 7.49 W m^{-1} K^{-1}. This calculated value is slightly high compared to the experimental result. In this study, the resultant porous alumina has a high porosity approximately 70%, card house structure from platelets and pore size of several micrometers, so that the previous thermal conductivity equation adopted for porous materials should be adapted further in the future. From Fig.8, thermal conductivity of the sample slightly increased with increasing rounds of TEOS treatment, interconnection between alumina platelets strengthened, as shown in Fig. 6, heat conduction was proven to increase with increasing rounds of TEOS treatment.

4. Summary

Anisotropic alumina particles (platelets) 5–10 μm in diameter and 5–10 in aspect ratio were used for the fabrication of porous alumina. An alumina compact body could be fabricated by uniaxially compressing the alumina platelets at 1 MPa, and then heating at 1400 °C for 1 h. The average porosity and the compressive strength of the formed porous alumina body were 72.3% and 3.8 MPa, respectively. In contrast, the porosity and the compressive strength of the porous alumina after three rounds of TEOS treatment were 65.5% and 10.2 MPa, respectively. The thermal conductivity of the porous alumina body before and after three rounds of TEOS treatment was 0.8 and 1.2 W m^{-1} K^{-1}, respectively.

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