Crystalline Phase Analysis and Thermal Expansion Coefficient Calculation of Quartz-Sand/Corundum Composites

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Abstract. Quartz-sand/corundum composites have been successfully produced by a simple solid-state reaction approach. The composites with corundum weight fractions of 10%, 20%, and 30% were prepared through grinding mixtures of purified Indonesian quartz sand and commercial high purity corundum for a half-hour with an addition of 3% polyvinyl alcohol. The composites were shaped into discs and pressed prior to the sintering at 950 °C and 1050 °C to form compact ceramic composites. The crystalline phase verification within the samples was conducted by means of X-ray diffraction (XRD). The coefficient of thermal expansion (CTE) of the composites was semi-theoretically evaluated, after being taken into consideration the XRD data analysis results, by means of Halpin-Tsai formula. The detected major crystalline phases within the sintered samples, based on the XRD profiles analysis, were quartz-\(\text{SiO}_2\) and corundum-\(\text{Al}_2\text{O}_3\). Meanwhile, the minor crystalline phases were wollastonite-\(\text{CaSiO}_3\) (below 7%) for all samples and cristobalite-\(\text{SiO}_2\) (around 1%) for the composite with 1050 °C sintering temperature. Generally, the addition of corundum into the quartz-sand/corundum composites reduced the CTE, having the value from 10.5 to 11.5 ppm/°C.

Keywords: Crystalline phase, coefficient of thermal expansion, quartz-sand, corundum.

1. Introduction
The advancement in materials science and engineering has encouraged researchers to investigate both fundamental and practical features of materials. The phase compositions and thermo-physical characteristics of materials play an essential role when designed as thermal environmentally responsive parts. In particular, \(\text{SiO}_2/\text{Al}_2\text{O}_3\)-based composites have been intensively studied and applied in various applications. \(\text{SiO}_2/\text{Al}_2\text{O}_3\) nanocomposites have been combined with polyalkylene glycol lubricant and exposed to have excellent thermal conductivity and viscosity for the refrigeration system at the temperature range of 30 °C – 80 °C [1]. \(\text{SiO}_2/\text{Al}_2\text{O}_3\) composites performed stronger acidity than that of pure \(\text{SiO}_2\) or pure \(\text{Al}_2\text{O}_3\) when they were applied as the support of Rh-Pd catalysts in working temperature of 250 °C – 450 °C [2]. \(\text{SiO}_2/\text{Al}_2\text{O}_3\) was also reported as the primary factor on the effectivity of coal ash sintering and slagging at very high temperatures, i.e., 1500 °C [3] and 1550 °C [4]. In fuel...
cell technology, SiO$_2$/Al$_2$O$_3$-based sealants have been widely developed to optimize the fuel cell performance [5].

Herein, what makes it distinctive from those reported studies; we prepared SiO$_2$/Al$_2$O$_3$-based ceramic composites from naturally occurring minerals, i.e., Indonesian quartz sand. It was carried out to (1) reduce the synthesis expense of the beneficial composites and (2) escalate the added value of Indonesian quartz sand. We focused on the crystalline phase compositional analysis of the as-prepared quartz-sand/corundum (SiO$_2$/Al$_2$O$_3$) using a well-known Rietveld method. In addition, a theoretical model using the rule of mixtures based on Halpin-Tsai formula [6], by virtue of its significant consideration of constituent geometry and anisotropy, was preferred to use for calculating the composites CTE values rather than the Turner model [7] which assumes that only hydrostatic stresses occur in the crystalline phases or Kernel model [8] which accounts for phase isostatic and shear stresses.

2. Materials and Methods

The detail purification of Indonesian quartz sand (in which contains 97.97.8 (18)% quartz and 2.2(2)% calcite) was reported elsewhere [9]. The quartz-sand/corundum composites were prepared via sintering of quartz sand and corundum mixtures. 3% of polyvinyl alcohol was introduced to the mixtures to effectively bind the powder during pressing (with a force of 600 N to form a cylindrical sample with a diameter of 1.3(1) cm). The prepared quartz-sand/corundum pellets were then sintered at 950 °C and 1050 °C for 4 h to form ceramic composites. XRD test, using Cu-K$_\alpha$ radiation, was conducted to investigate the crystalline phase in the composites. After accurate phase identification, crystalline phase quantification was run by means of Rietica software [10] using the Rietveld method [11]. Furthermore, the CTE values of the sintered quartz-sand/corundum composites were calculated by means of Halpin-Tsai formula [6].

3. Results and Discussion

The XRD profiles of quartz-sand/corundum powders prior to sintering are depicted in Fig. 1. The major phases of the samples, after search-match analysis, are hexagonal quartz-SiO$_2$ (PDF reference code: 01-082-0511) and rhombohedral corundum-Al$_2$O$_3$ (PDF reference code: 01-081-2267). A very few and small peaks refer to rhombohedral calcite-CaCO$_3$ (PDF reference code: 00-001-0837) are also detected. The calcite phase is the remaining impurity in the purification of quartz from natural silica sand. Clearly, the Bragg peak intensities of corundum, particularly (102), (104), (110), and (113) are higher as the addition of corundum into the mixtures.

The phase weight fractions produced from the acceptable Rietica-assisted Rietveld refinements ($\chi^2 < 4$) are listed in Table 1. The table quantifies the exact values of the weight phase percentages. Calcite does not influence the corundum weight fractions since it already exists in the purified quartz-based silica sand. Phase quantification in the quartz-sand/corundum composites is crucial to predict the coefficient of thermal expansion values of the composites and to investigate the chemical reactions between quartz and corundum. The phase quantification was conducted by Rietved analysis using Rietica software.

The successful XRD data refinements have been achieved for all XRD data, and the sample plots of the refinement outputs for QS20A950 (the composite with 20% corundum and sintering temperature of 950 °C) and QS20A1050 (the composite with 20% corundum and sintering temperature of 1050 °C) are respectively given in Fig. 2 and in Fig. 3. The measured and calculated XRD profiles are respectively visualized by the plus (+) sign and solid line. The difference of the refinement is represented by the green line.
Figure 1. XRD profiles of pre-sintered quartz-sand/corundum mixtures. QS10C, QS20C, and QS30C represent quartz-sand/corundum mixtures with corundum weight fractions of 10%, 20%, and 30%.

Table 2 represents the crystalline phase quantification acquired from Rietveld analysis. From Table 2, the sintered composites contain quartz-SiO$_2$, corundum-Al$_2$O$_3$, and wollastonite-CaSiO$_3$. Cristobalite-SiO$_2$ grows at the sintering temperature of 1050 °C. The growth of cristobalite-SiO$_2$ in the 1050 °C sintered composites is due to the phase transformation of silica (from quartz to cristobalite) above 1000 °C [12]. Since the attachment of corundum reduces SiO$_2$ content, then the descent of cristobalite-SiO$_2$ becomes a chemical consequence. However, the drop of cristobalite content in this study is not drastic.

| Sample | Quartz (SiO$_2$) | Corundum (Al$_2$O$_3$) | Calcite (CaCO$_3$) |
|--------|-----------------|------------------------|-------------------|
| QS10C  | 86.9(29)        | 10.6(12)               | 2.5(7)            |
| QS20C  | 79.2(15)        | 19.5(5)                | 1.3(3)            |
| QS30C  | 68.3(17)        | 30.5(17)               | 1.2(3)            |
Another “new” phase that is possibly formed in the quartz-sand/corundum composites is mullite. It is a rare silicate mineral produced from a solid solution of SiO$_2$ and Al$_2$O$_3$ which can be in the form of 2Al$_2$O$_3$·3SiO$_2$ or 2Al$_2$O$_3$·SiO$_2$. From the SiO$_2$-Al$_2$O$_3$ phase diagram [13], the solidus line of mullite changes as the addition of Al$_2$O$_3$ above the silica-mullite eutectic temperature. The nucleation and growth of mullite occur above 1587 °C. On the other hand, quartz-SiO$_2$ is totally transformed to cristobalite-SiO$_2$ at 1570 °C [12]. Prior to mullite precipitation, the SiO$_2$-Al$_2$O$_3$ system may produce liquid phase formation after heating in the contact area of SiO$_2$ and Al$_2$O$_3$. Thus, it makes sense if the XRD data do not reveal the presence of mullite in our composites.

In addition, Table 2 shows the absence of calcite-CaCO$_3$ and the presence of wollastonite-CaSiO$_3$. It is important to note that CaSiO$_3$ is not the chemical reaction product between SiO$_2$ and CaCO$_3$, but between SiO$_2$ and CaO. The CaO was initiated from CaCO$_3$ decomposition around 900 °C [14]. SiO$_2$ that reacts with CaO is quartz because there is a decrease of quartz as the cristobalite phase grows.
Table 2. Crystalline phase composition of sintered quartz-sand/corundum ceramics.

| No | Sample  | Relative weight fraction (%) |
|----|---------|-------------------------------|
|    |         | Quartz (SiO₂) | Corundum (Al₂O₃) | Wollastonite (CaSiO₃) | Cristoballite (SiO₂) |
| 1  | QS950   | 95.2(26)       | -                 | 4.8(4)               | -                  |
| 2  | QS10A950| 83.7(24)       | 10.0(10)          | 6.3(5)               | -                  |
| 3  | QS20A950| 76.0(26)       | 20.4(14)          | 3.6(5)               | -                  |
| 4  | QS30A950| 66.1(17)       | 31.9(17)          | 2.0(4)               | -                  |
| 5  | QS1050  | 93.2(27)       | -                 | 6.8(4)               | -                  |
| 6  | QS10A1050| 86.5(26)      | 9.2(11)           | 3.0(3)               | 1.2(1)             |
| 7  | QS20A1050| 72.0(22)      | 25.2(12)          | 1.7(2)               | 1.0(1)             |
| 8  | QS30A1050| 63.6(22)      | 34.4(19)          | 1.0(2)               | 1.0(1)             |

Figure 4. CTE values of quartz-sand/corundum composites calculated by Halpin-Tsai formula.

Furthermore, CTE calculation of the quartz sand and the composites are displayed in Fig. 4. Investigating crystalline phase composition in a composite is essential for predicting the composite characteristics, such as CTE, and for fundamental knowledge to develop new materials. Fig. 4 evidently displays that (1) the CTE values of the quartz-sand/corundum composites lie between 10.5-11.5 ppm/°C which is similar with quartz-sand/periclase/forsterite composites [15] and (2) addition of corundum, as well as sintering temperature, to the composites reduces the CTE values. When the temperature exceeds 1050 °C, the phase constituent within the quartz-sand/corundum-based composites become more complex, i.e., nearly 50 wt% of cristobalite-SiO₂ grows at 1250 °C [9]. The extra cristobalite-SiO₂ will decrease the CTE value of the composites since its CTE value is slightly smaller than that of quartz-SiO₂ or corundum-Al₂O₃ [16]. In terms of the possible application based on the CTE values, quartz-sand/corundum composites meet the criteria for fuel-cell seal materials.
4. Conclusion
A complete quantitative crystalline phase analysis on quartz-sand/corundum composites provides a feature to predict thermal coefficient expansion using the Halpin-Tsai equation. Quartz-SiO$_2$ and corundum-Al$_2$O$_3$ are found as the main phases in the composites, although minor wollastonite-CaSiO$_3$ and cristobalite-SiO$_2$ are also detected in the sintered composites, particularly at a sintering temperature of 1050 °C. The CTE values of the composites are between 10.5-11.5 ppm/°C and they decrease as the incorporation of corundum and higher sintering temperature.

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