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Use of Natural Silica Sand as A Component for Prospective Fuel Cell Sealing Materials

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Abstract. A study to enhance the value of natural silica sand from Tanah Laut, South Kalimantan, Indonesia has been initiated. A number of local sands were selected as the candidates for the study. The selected sand contained more than 90% quartz was further processed to obtain a high purity initial powder using magnetic separation and immersion with HCl. The sealing materials were prepared by mixing the natural-sand-based silica (SiO_2) powder with magnesia (MgO) and boria (B_2O_3) with composition of 70:10:20 by weight followed by uniaxial pressing and finally sintering at 1150°C for 1h and 4 h to produce ceramic composites. XRD measurement revealed that the ceramic contained quartz, protoenstatite, and clinoenstatite. The 1h and 4h ceramics exhibited 1.89% and 0.43% apparent porosity, 7.00×10^6 and 6.63×10^6 Ωcm electrical resistivity, 3.60 and 2.29 GPa Vickers microhardness, and 11.20×10^{-6} and 11.55×10^{-6} ppm/°C thermal expansion coefficient respectively. The 4h sample is more appropriate for sealing function in fuel cell than the 1h sample.

Introduction

Development of sealing materials for fuel cell is acquiring more attention recently, particularly based on oxide systems. A seal material plays important role in fuel cell systems because it seals the cells and prevent gas leakage [1]. A good sealing material for such systems has to meet several requirements, e.g. value of thermal expanssion coeffiecient (TEC) is $9.5\text{-}12.0 \times 10^{-6}$ ppm/°C, electrical resistivity $\geq 10^4$ Ωcm, withstand pressure up to 14-35 kPa, and leakage < 1% [2].

A glass-ceramic seal is the most preferred material today because it has superior sealing performances compared to other types [1-3]. Hidayat [4] has developed one of seal materials based on SiO_2-MgO system with predicted TEC values range of 9.5-12 ppm/°C, but relatively high porosity, i.e. 30-40 %, very much larger than that of the required criteria. Meanwhile, addition of B_2O_3 in some oxide ceramic systems can promote pore elimination due to its viscosity when liquid phase sintering process occurred [5].

This work is focused on the synthesis and characterization of sealing SiO_2-MgO system based on silica natural sand with B_2O_3 as the additive as well as sintering agent. The use of the natural sand aims to enhance the value of such sand from Tanah Laut as a material to achieve the required properties for sealing.

Experimental

The raw materials were natural sands taken from several locations in Tanah Laut District, i.e. Sungai Asem-asem (SA), Sungai Riam (SR), Tambang Ulang (TU), and Tanah Laut (TL). Distribution of elemental concentration for the samples were analyzed using energy dispersive x-ray (EDX) spectrometer. XRD was applied to observe phase compositions, using a Philips X'Pert Powder diffractometer with CuKα radiation.

The sand with highest Si or SiO_2 content according to EDS and XRD was further processed to obtain silica with highest purity. Magnetic compounds in the sand were removed by a magnetic separation procedure using a permanent magnet. After that, the sand was immersed using HCl 2M for 12 hours to increase its purity and then washed using aquadest until its pH was netral. Again, EDX and XRD were applied for its elemental content and phase compositions after purification.

The sealing material was prepared by mixing the 'purified' natural-sand-based silica (SiO_2) powder with magnesia (MgO) and boria (B_2O_3) with composition of 70:10:20 by weight followed by uniaxial pressing in a stainless steel die and finally sintering at 1150°C with 1 hour and 4 hours to produce ceramic composites. XRD data for the surface of the samples were collected, followed by phase analyses. The apparent porosity and bulk density of sintered composites were measured using the Archimedes method. Their electrical resistivity was tested by four point probe method. Vickers microhardness tests were performed on the composites to examine the mechanical strength, while the associated CTE were calculated based on Rule of Mixture (*RoM*) [4].

Results and Discussion

Table 1 and Figure 1(a) show that natural sands in several locations in Tanah Laut contain various elements and phase compositions. As can be seen, TL sand has the highest content of Si and dominant phase of SiO_2 quartz – both indicates it contains higher SiO_2 content than the other sands. Subsequently TL sand was chosen for extraction to obtain silica with higher purity. The elemental content and phase of sample TL sand which been washed, magnetically separated, and submerged with HCl, was tested by EDX and the result shows that sample having 100% of Si element. Figure 1 shows the XRD patterns of the purified, TL sand sample. Further qualitive analysis indicates the existence of single phase of quartz.

Figure 2 shows the XRD patterns for the surface of the composites sintered for 1 hour and 4 hours. Qualitative analysis reveals that the ceramics contain quartz (00-046-1045), protoenstatite (00-011-0273), and clinoenstatite (00-035-0610). Furthermore, quantitative phase analyses based on the Rietveld method using *Rietica* [6] results in the relative weight fraction of these phases in SMB1h, which are 63.5%, 24.3%, and 12.2%, respectively, while in SMB4h are 34.0%, 34.2%, and 31.8%, respectively. Quartz quantity decreases with increasing holding time because it immediately react with MgO become protoenstatite and clinoenstatite.

Table 1 shows data of physical, electrical and mechanical properties of the composites. The apparent porosity decreases slightly with increasing holding time. Decreasing in porosity which occurred is caused by the role of the sintering agent B_2O_3 on the sintering process [5]. Increasing the holding time allows 20wt% of B_2O_3 to melt and cover almost all of the pores in the silica-magnesia composites. By the Archimedes method, it can be shown that the composites exhibit very low porosity, i.e. 1.89% and 0.43% for the composites sintered for 1 hour and 4 hours respectively.

CTE of the composites is closely associated with the formation of the phases. Calculation based on *RoM* [4] shows that the CTE values of the composites are 11.20 ppm/°C for the composite sintered for 1 hour and 11.55 ppm/°C for 4 hours one.

Table 1. EDX elemental content of the collected sands

Sand	Element Quantity (at.%)							
	Si	Al	Ca	Fe	Na	Mg	P	K
SA	68.92	10.13	2.44	6.75	4.42	6.52	0.81	0.00
SR	68.15	17.00	2.94	3.22	6.49	0.00	0.00	2.20
TU	26.52	1.24	1.55	4.23	0.00	64.91	1.55	0.00
TL	96.15	3.85	0.00	0.00	0.00	0.00	0.00	0.00
TL after purification	100	0.00	0.00	0.00	0.00	0.00	0.00	0.00

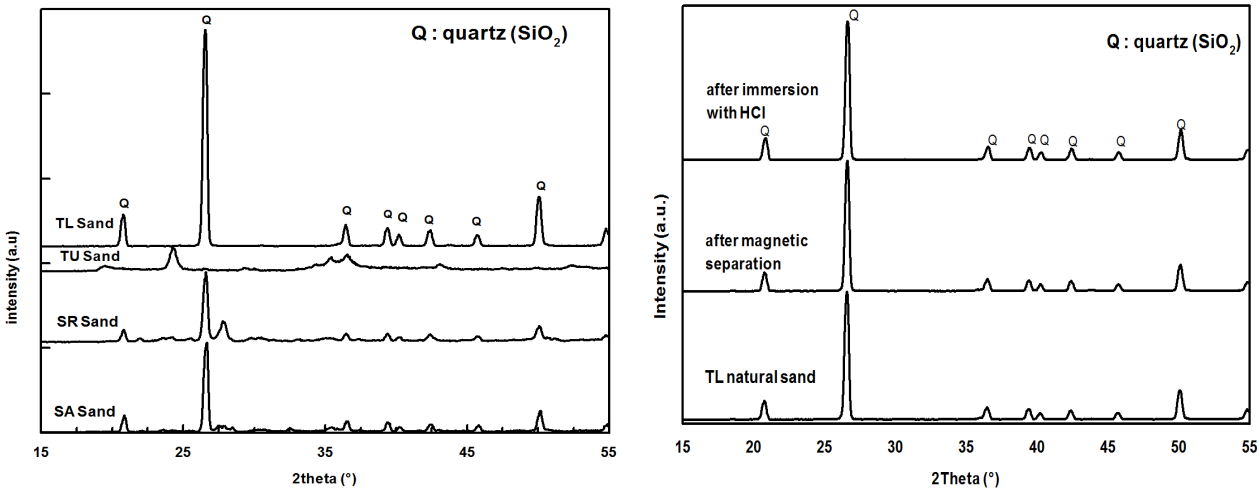

Figure 1. XRD patterns (CuKα) of (a) several natural sands and (b) TL sand before and after purification.

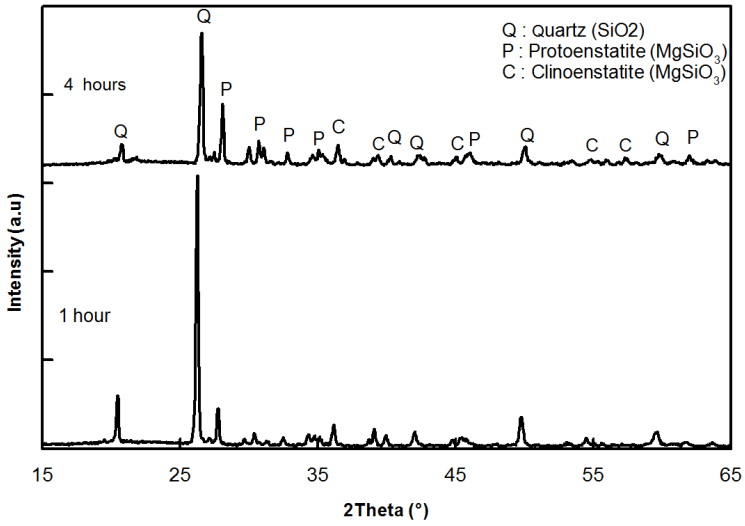

Figure 2. XRD patterns (CuKα) for the surface of the SiO_2-MgO-B_2O_3 ceramic composites with addition of 20 wt% B_2O_3.

Table 2. Characteristics of SiO_2-MgO composites with addition of 20% B_2O_3

Sample	Density (g/cm^3)	Porosity (%)	Hardness (GPa)	CTE (ppm/°C)	Resistivity (Ω cm)
1h	1.545(10)	1.891(9)	3.60	11.20	7.00×10^6
4h	1.627(10)	0.429(4)	2.29	11.55	6.63×10^6

Electrical resistivity of a seal glass depends on the composition of network formers, modifiers, and additive [1]. In our SiO_2-MgO ceramic composite system, this is due to the ionic radius of Mg^{2+} alkaline earth modifier ions. Decreasing electrical resistivity in composites is caused by increasing intermediate phases (protoenstatite and clinoenstatite) which contain higher alkaline earth ion [3].

German [7] explained that sintering at a certain temperature and holding time will decrease the porosity and increase the hardness and electrical resistivity values as it will form a strong bond between the particles in the sample. The silica content in the composite affects the microstructure, so that the composite ceramics become very hard. The ceramic sintered for 4 hours exhibit apparent porosity, electrical resistivity, hardness, and thermal expansion coefficient of which meet properties for seal in fuel cell as required [2]. The excellent properties reveal that the ceramic can be a good material for sealing in a fuel cell system.

Summary

The density, porosity, thermal expansion, hardness and electrical resistivity of silica-magnesia-boria composites sintered at temperatures of 1150 °C for the 4h composite adequately qualifies the criteria as a fuel cell seal material with porosity values was < 1 %, CTE values range 9.5-12.0 ppm/°C, hardness value above the range 14-35 kPa and electrical resistivity ≥ 10^4 Ω cm as compared to the 1h one.

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