1. Introduction

Metal and steel industries are the world largest consumers of refractories, especially ladle furnace that requires refractories with high resistance to corrosion by steel slag, mechanical wear and thermal shock [1,2]. Therefore, the alumina-spinel (Al$_2$O$_3$–MgAl$_2$O$_4$) monolithic refractory is the first choice due to its advantage in resistance to thermal shock [3–5] and easy installation. Particularly, calcium aluminate cement (CAC) is one of the main raw materials which has been widely used as binder in the monolithic refractories [2,6–9]. It is not only the formation of MgAl$_2$O$_4$ from alumina (Al$_2$O$_3$) and magnesia (MgO) fired at 1100–1400°C, but other calcium aluminate phases such as grossite (CaO•2Al$_2$O$_3$, CA2) and calcium hexaluminate or hibonite (CaO•6Al$_2$O$_3$, CA6) are also formed by the reaction between Al$_2$O$_3$ and calcia (CaO) from CAC. The formation process of calcium aluminate phases of CAC upon heating has been investigated by many researchers [3,6,10–13]. CaO and Al$_2$O$_3$ reappeared after decomposition of hydrate phases in CAC as AlO(OH) and 3CaO•Al$_2$O$_3$•6H$_2$O [13,14] and they reacted upon firing in following reactions:

12CaO•7Al$_2$O$_3$ [C12A7] + 5Al$_2$O$_3$ → CaO•Al$_2$O$_3$ (CA) around 800–1000°C

CaO + Al$_2$O$_3$ → CaO•Al$_2$O$_3$ (CA) around 800–1000°C

CaO•Al$_2$O$_3$ + Al$_2$O$_3$ → CaO•2Al$_2$O$_3$ (CA2) around 1000–1300°C

CaO•2Al$_2$O$_3$ + 4Al$_2$O$_3$ → CaO•6Al$_2$O$_3$ (CA6) around 1400–1600°C

CA6 is observed as hexagonal plate-like morphology with an anisotropic grain growth which supports important properties such as toughness and self-control physical stability [8]. Moreover, magnetoplumbite structure with interspinel layer of CA6 [15] helps to improve corrosion resistance from cation that would be incorporated into a vacant position of this layer without changing volume [16]. In addition, the presence of silica (SiO$_2$) in the refractory composition causes the formation of low-melting phase in CaO–Al$_2$O$_3$–SiO$_2$ system [17]. It also affects (1) the reduction of CA2 content, (2) the morphology of CA6 in acicular platelet shape, (3) the expansion behavior, and (4) the thermomechanical properties. The impact of this low-melting phase helps to accelerate Ca$^{2+}$ and Al$^{3+}$ dissolution and gain high amount of CA6 [3,4,9].

Many researchers have tried to synthesize CA6 composite materials from various important factors such as raw materials selection, preparation methods, equipment, sintering condition, etc [18–24]. More than a decade, a novel utilization of CA6 has emerged; for example; CA6 insulating aggregates replacement of ceramic fiber at cover linings of steel.
ladle, CA6 aggregates in castable for spray coating of nozzles or pre-cast insulating brick of reheating steel furnace, glass and ceramic industries’ furnace [25]. These aggregates have CA6 as the major phase around 90 mass% with hexagonal plate-like microstructure and small amount of corundum (α-Al2O3) and CA2 with two kinds of apparent porosity as 10 and 70–75 volume%, respectively [16].

However, the controlling of amount and size of hexagonal plate-like microstructure was not yet attained. In order to investigate the behavior of CA6 formation and the effect of SiO2 content on the formation, the in-situ CA6 monolithic refractories were achieved by using CAC and sintered Al2O3 as two main raw materials under stoichiometric composition for 1 mol of CaO and 6 mol of Al2O3.

2. Experimental procedure

2.1 Raw materials

CA6 monolithic refractory was in-situ prepared by using sintered Al2O3 (Itochu Ceratech Corp., mean diameter 550 μm, Al2O3 99.7 mass%) and CAC (Denka Co. Ltd., mean diameter 2.8 μm, Al2O3 80.0 and CaO 17.2 mass%). Those two major raw materials were provided under appropriate stoichiometric composition of 1 mol of CaO and 6 mol of Al2O3. After stoichiometric calculation based on chemical composition of raw materials, the primary CA6 monolithic refractory constituent was composed of sintered Al2O3 51.84 mass% and CAC 48.16 mass% which denoted as AS0.

The influence of SiO2 addition (Quartz form, Kanto chemical Co. Inc., mean diameter 35 μm) was examined by mixing 2, 4, 6, 8 and 10 mass%, separately, into primary admixture which denoted as AS2, AS4, AS6, AS8, and AS10, respectively.

To ensure the composition, all raw materials were firstly characterized for phase composition by using X-ray diffractometer (XRD, Cu–Kα radiation, RINT2200 Rigaku corp., Japan) before blending. The reference ICCD data were as follows: Quartz #75–1555, Corundum (α-Al2O3) #10–0173, Mayenite (12CaO·7Al2O3, C12A7) #78–0910, and calcium aluminate (CA) #70–0134.

2.2 Sample preparation

Raw materials were mixed with deionized water and cast in the 10 mm x 10 mm x 60 mm mold. Due to the hydration of CAC [7,8], the specimens were kept at ambient temperature (25°C) for 24 h before demolding. The consolidated specimens were subsequently dried at 110°C for 24 h and fired on different sintering condition at 1400–1500°C and holding time for 1–5 h to control CA6 formation and microstructure as the first controlling factor. Furthermore, the mixtures with a variation of SiO2 content were fired at 1500°C for 5 h as the second controlling factor.

2.3 Characterization

After firing, the specimens were investigated for phase composition, physical properties and microstructure as followed. Phase identification and transformation were analyzed by XRD. Phases’ quantities were computed by reference intensity ratio technique (RIR, PDXL software Rigaku corp., Japan). Apparent porosity was evaluated by Archimedes’ principle. Microstructures and chemical identification were observed by scanning electron microscope (SEM, JSM-7600F JOEL Ltd., Japan) and energy dispersive spectroscopy on SEM (EDS, X-MAX Oxford instruments plc., United Kingdom). The reference ICCD data were as follows: Corundum (α-Al2O3) #10–0173, Hibonite (CA6) #76–0665, Grossite (CA2) #72–0767 and Gehlenite (2CaO·Al2O3·SiO2, and C2AS) #79–1725.

3. Results and discussion

3.1 Phase composition of raw materials

The phase composition of raw materials as shown in Figure 1 explained that the sintered Al2O3 composed of corundum (α-Al2O3) and SiO2 composed of quartz. Moreover, CAC mainly consists of corundum (α-Al2O3), calcium monoaluminate (CA) and Mayenite (12CaO·7Al2O3, C12A7). By these findings, as described before in introduction, CAC was responsible for CaO or Ca2+ source before further reaction with Al2O3 to form important phases as CA2 and CA6 [3,6,10,12,13]. From quantitative analysis by XRD-RIR, it could confirm that an average oxide content in CAC was estimated as CaO around...

Figure 1. X-ray diffraction patterns of each raw material.
18.2 ± 2.5 mass% and Al₂O₃ around 81.8 ± 2.5 mass %.
These figures are close to chemical composition of CA6 as stated in Section 2.1.

3.2 CA6 formation control under variation of sintering condition

The CA6 monolithic refractory in the present study was performed through the in-situ preparation by using CAC and sintered Al₂O₃. The firing temperature and holding time together with the addition of SiO₂ were determined. Due to the chemical composition of CAC, it was responsible for CA2 formation by the reaction between CA and Al₂O₃ during firing. Furthermore, Al₂O₃ turned to play an important role in the formation of CA6 phase by the diffusion of Al³⁺ from α-Al₂O₃ [26] to CA2 layer.

Figure 2 demonstrates the effect of holding time at 1400–1500°C of firing temperature in the formation of CA6 and other phases compositions of the monolithic refractories’ samples with and without SiO₂ (AS0 and AS2, respectively) based on quantitative analysis by RIR technique. The SEM observation of hexagonal plate like microstructure was achieved as a function of firing temperature (Figure 3) and holding time (Figure 4). The identification of plate-like morphology was distinguished by SEM and EDS images in Figure 5. Moreover, the evaluation of apparent porosity was made as seen in Figure 6.

3.2.1 Sample without SiO₂ addition

The phase formation of primary composition (AS0) upon raising firing temperature and prolonging holding time confirmed an increase of CA6 content and the change of microstructure into more plate-like

Figure 2. Phase composition from XRD–RIR analysis of powdered primary monolithic (AS0) and 2 mass% of SiO₂ addition (AS2) samples fired at 1400 (a,d), 1450 (b,e), and 1500 (c,f) °C for 1–5 h.

Figure 3. Microstructures of fractured primary monolithic (AS0) and 2 mass% of SiO₂ addition (AS2) samples fired at 1400–1500°C for 3 h.
shape with constant apparent porosity. The explanations for phase transformation at each firing temperature and holding time were gradually demonstrated as followed.

For the sample of AS0 in Figure 2(a), phase transformation showed that trace amount of CA6 phase formed after firing at 1400°C for 3 h together with the decrease of α-Al₂O₃ phase, which continued to around 43 mass% at 5 h. However, the CA2 phase remained almost constant around 45 mass% at 1400°C. Thus, α-Al₂O₃ phase or Al³⁺ ion played a dominant role to form CA6 at 1400°C. Due to the small amount of CA6, the presence of plate-like microstructure was not noticed in the microstructure of sample AS0 in Figure 3. The microstructure of AS0 at 1400°C also corresponded to the finding of Wang Y. et al [14].

After firing at 1450°C (Figure 2(b)), however, CA6 phase was mostly formed in larger quantity,
especially, where a decrease of $\alpha$-$\text{Al}_2\text{O}_3$ from about 43 mass\% (at 1400°C 5 h) to nearly 30 mass\% (at 1450°C 5 h) was confirmed opposite to a small decrease of CA2. By this mean, $\alpha$-$\text{Al}_2\text{O}_3$ phase still had a strong influence in CA6 formation and took a burden at this level of firing temperature. At 1450°C, Figure 3 shows the irregular grain growth which was bigger than microstructure after firing at 1400°C. Moreover, from the SEM and EDS micrographs in Figure 5 fired for 5 h, it could be confirmed that this irregular plate-like structure was mostly CA6 phase from the stoichiometric calculation of phase followed the atomic ratio of CA6.

After all, as seen in Figure 2(c) fired at 1500°C, CA6 content could reach around 44 mass\% only, with the gradual decline of CA2 which was used to form CA6. Therefore, at 1500°C, holding time would be the important factor on further formation of CA6 for sample without SiO$_2$. Particularly, the plate-like microstructure became bigger with higher facet, but irregular shape, as seen in Figure 3 when increased heat treatment to 1500°C. The prolonged holding time for 5 h in Figure 4 caused an anisotropic grain growth in both elongation and expansion of plate-like microstructure. It could be assumed that more CA6 was generated until $\alpha$-$\text{Al}_2\text{O}_3$ and CA2 were used up, at higher firing temperature with longer holding time than those in this study.

However, the apparent porosity of the sample without SiO$_2$ (AS0) in Figure 6 reported that the formation of CA6 in sample AS0 did not affect the apparent porosity, especially the formation of plate-like microstructure as seen in Figures 3 and 4.

### 3.2.2 Sample with SiO$_2$ addition

The specimens with SiO$_2$ (AS2), it was assured that an increase of firing temperature enhanced the formation of CA6 and hexagonal plate-like microstructure by the assistance of melting phase on accelerating the ion mobility [26] of Al$^{3+}$ to react with CA2. The prolonged holding time resulted in the anisotropic growth of hexagonal grain and the increase of apparent porosity as clarified by following results.

For sample AS2 fired at 1400°C in Figure 2(d), no CA6 was detected. Only CA2 and $\alpha$-$\text{Al}_2\text{O}_3$ were presented at this temperature. The explanation for this situation was mainly due to the presence of low-melting point phase CaO-$\text{Al}_2\text{O}_3$-SiO$_2$ as gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3$-$\text{SiO}_2$, C2AS) in the sample. Nishikawa [10] reported that C2AS was formed around 900°C and it was crystallized from an amorphous phase in CAC. At 900°C, apart from C2AS, the decomposition of hydrate phases in CAC as AlO(OH) and 3CaO-$\text{Al}_2\text{O}_3$-$6\text{H}_2\text{O}$ occurred and it caused the reappeared oxide phases such as CaO and $\text{Al}_2\text{O}_3$ [13,14]. Various calcium aluminate phases such as CA, CA2 and CA6 were taken place from the recombination of these 2 oxides after increasing of heat treatment [13,27].

From XRD–RIR of sample AS2 at 1400°C in Figure 2(d), it was hardly detected C2AS phase due to the small amount of SiO$_2$ addition. However, 2 mass\% of SiO$_2$ was enough to form low-melting phase of C2AS according to Kubota’s findings [17] and help the ion diffusion [26]. This C2AS phase had eutectic point at 1380–1405°C due to phase equilibrium diagram of Osborn and Muan [28], leading to the formation of low-melting phase after firing AS2 samples at 1400°C. At 1400°C, therefore CA2 formation together with some of Al$^{3+}$ diffused to low-melting phase of C2AS. The formation of C2AS caused the deviation of CA2 and $\alpha$-$\text{Al}_2\text{O}_3$ amount from the stoichiometric calculation. However, after increase in holding time, $\alpha$-$\text{Al}_2\text{O}_3$ content had tendency to slightly increase to around 60 mass\% in correspondence with the decrease of CA2 to around 40 mass\% due to the disappearance of C2AS.

It could be confirmed that SiO$_2$ addition caused low-melting phase at 1400°C and retarded the formation of CA6 at this firing temperature. From SEM pictures in Figure 3 at 1400°C for 3 h, AS2 sample presented an agglomeration into a bulk which caused higher densification. The apparent porosity of AS2 was lower than AS0 in Figure 6(a) in supporting the formation of low-melting phase and densification of microstructure that occurred in sample AS2. After increase in the holding time, the apparent porosity had tendency to gradually decrease from around 25 volume\% at 1 h to around 18 volume\% at 5 h.

After increasing firing temperature up to 1450°C (Figure 2(e)), there was a small decrease of $\alpha$-$\text{Al}_2\text{O}_3$ content from 1–3 h of holding time corresponded to the formation of CA6. Besides, difference tendency occurred after 5 h that CA2 content decreased instead and led to the increasing of CA6. In this case, at shorter holding time (1–3 h), $\alpha$-$\text{Al}_2\text{O}_3$ played a dominant role in the formation of CA6. After a longer holding time (5 h), CA6 formation depended mainly on CA2. It was noticed that the reaction between CA2 and $\text{Al}_2\text{O}_3$ was gradually occurred and alternatively selected the dominant phase.

In addition, the micrograph in Figure 3 of AS2 at 1450°C exhibited the modification of the shape of aggregates into more facet without separation from the bulk. Therefore, the nucleation of CA6 hexagonal microstructure followed the formation of CA6 phase in XRD–RIR results. It could be confirmed that the hexagonal plate-like microstructure was CA6 as seen in the SEM and EDS micrographs (Figure 5) after firing for 5 h. The stoichiometric calculation from atomic amount verified main phase of CA6 from Al and Ca element ratio. In addition, the presence of Si element in the EDS micrograph which confirmed the
existence of low-melting phase on hexagonal plate CA6. Moreover, the low apparent porosity around 12–17 volume% of AS2 samples (Figure 6(b)) also verified the influence of low-melting phase after firing at 1450°C for 1–5 h.

At 1500°C of sintering temperature in Figure 2(f), there was a remarkable increase of CA6 content together with the decrease of both α-Al2O3 and CA2. This higher temperature helped to accelerate mobility of Al3+ to react with CA2 until used up and trace amount of Al2O3 was left as seen in Figure 2(f). Figure 3 clearly presents the structure of hexagonal plate-like CA6 in AS2 which is the most stable form of CA6 as magnetoplumbite structure [15]. Meanwhile, an effect of holding time was also examined when sintered at 1500°C for 1–5 h, as seen in Figure 4. The microstructures (Figure 4) present that longer dwell time caused grain growth with larger and thicker hexagonal structure after firing for 5 h. This evidence was one of the explanations for the rise of apparent porosity in Figure 6(c) from around 20 volume% at 1 h to nearly 30 volume% at 5 h. Therefore, the utilization of SiO2, the CA6 phase formation in this mixture (AS2) could be achieved nearly 84 mass%.

3.3 CA6 formation control under the variation of SiO2 content

In this experiment, it was discovered that the addition of proper amount of SiO2 helped to achieve CA6 in hexagonal plate-like microstructure due to the formation of low-melting phase in CaO–Al2O3–SiO2 system by accelerating ion diffusion. The confirmation was proved by the variation of SiO2 content (2–10 mass%) in primary composition (AS0) fired at 1500°C for 5 h as followed results.

After firing the specimens with various SiO2 content within 0–10 mass% (AS0–AS10), the specimens were analyzed for phase constituent and quantity. The primary composition (AS0) showed various significant phases in XRD pattern (Figure 7) and the XRD–RIR results (Figure 8). It was confirmed that AS0 consisted of α-Al2O3 around 28 mass%, CA2 around 28 mass% and CA6 around 44 mass%. After adding SiO2 to primary composition (AS0), CA6 formed around 84 and 62 mass% in the samples with 2 and 4 mass% of SiO2 (AS2 and AS4), respectively. Thus, the addition of SiO2 promoted the formation of CA6 at 1500°C. Nevertheless, less formation of CA6 than AS0 occurred from 6 mass% of SiO2 addition (AS6). Particularly, no CA6 could be detected at 10 mass% of the SiO2 mixture (AS10). It was noteworthy that the CA6 tendency in Figure 8 directly corresponded to the apparent porosity results in Figure 9.

Figure 7. XRD patterns of powdered primary monolithic (AS0) and 2–10 mass% of SiO2 addition (AS2–AS10) samples fired at 1500°C for 5 h.

Figure 8. Phase composition from XRD–RIR analysis of primary monolithic (AS0) and 2–10 mass% of SiO2 addition (AS2–AS10) samples fired at 1500°C for 5 h.

Figure 9 presents the effects of SiO2 addition on apparent porosity. The addition of 2–4 mass% of SiO2 caused the increase of apparent porosity around 30 volume % due to the anisotropic grain growth of hexagonal plate-like CA6. However, the decrease of apparent porosity remarkably occurred after adding above 6 mass% of SiO2 content. The decrease tendency of CA6 associated with the amount reduction and the size expansion of noticeable hexagonal
platelet in microstructure pictures at ×500 magnification of Figure 10. Even plenty of larger pores were found in samples AS6–AS10 at ×50 magnification, but they did not relate to the apparent porosity. Microstructures at ×500 magnification exhibited the reason for the decreasing of apparent porosity even though the pore size was steady growth along with SiO$_2$ addition. In the microstructures at ×500 magnification, not only CA6 hexagonal structure was presented, but also the pores’ condition of each sample was exhibited. The samples AS0 and AS2 showed the less compaction of texture which was different to any other samples as mentioned. Only fine size of pore could be found in both samples. On the contrary, the microstructure of samples AS4–AS10 gradually became denser together with the expansion of pore size. Especially, the pores’ condition in sample AS8 exhibited nearly closed pore, but sample AS10 showed closed pore with large in size and dense in texture.

The decrease tendency of apparent porosity and the increase in densification of microstructure correlated with significant phase as C2AS which was found from XRD and XRD–RIR results in Figures 7 and 8. C2AS was detected in XRD patterns in samples AS4 and AS6 around 5 mass% together with the decrease of CA6 content. In addition, the amount of C2AS phase of samples AS8 and AS10 became double of AS4 and AS6 values which corresponded to pore’s condition in ×500 magnification microstructure. Nishikawa [10] discovered that C2AS could be formed at around 900°C by crystallization from low-melting temperature phase in CAC. In addition, Osborn and Muan [28] also drew the phase equilibrium diagram of CaO–Al$_2$O$_3$–SiO$_2$ system and found that the eutectic point among CA6, α-Al$_2$O$_3$, C2AS, and CaO+Al$_2$O$_3$·2SiO$_2$ (anorthite, CAS2) would be 1380–1405°C. From this phase diagram, the more amount of SiO$_2$ was added, the lower temperature of eutectic phase would be applied. So, at the same firing temperature, higher quantity of SiO$_2$ could help to attain C2AS. In addition, the increase in low-melting phase was directly related to lowering the porosity and enhancing the densification as seen in Figures 9 and 10, respectively. It was also the limitation of Archimedes’ method due to the difficulty for water to penetrate into high densification sample. Especially, samples AS8 and AS10 with high C2AS phase, they showed more closed pores than opened pores resulting in low apparent porosity as reported.

However, the C2AS signal and quantity could not be indicated in Figure 7–8 for samples AS0 and AS2. C2AS was obviously not found in the sample AS0 due to the fact that none of SiO$_2$ added. Besides, even C2AS did not appear in the sample AS2 through XRD results, the Si element could be detected by EDS analysis from Figure 5 as explained in Section 3.2.2. Therefore, the large amount of SiO$_2$ did not help to enhance CA6 content, but it caused excessive amount of low-melting phase CaO–Al$_2$O$_3$–SiO$_2$ system as C2AS. This phase helped the diffusion of Al$^{3+}$, Ca$^{2+}$, Si$^{4+}$ and O$^{2-}$ ions and accelerated the densification of the specimens. The remaining CaO-containing phase was insufficient to react with Al$_2$O$_3$ and form CA6, so, only two phases of α-Al$_2$O$_3$ and C2AS appeared at high SiO$_2$ content as AS10.

4. Conclusions

After investigation of CA6 formation mechanisms under various conditions as sintering temperature, holding time, and SiO$_2$ content of the in-situ CA6 monolithic refractories from CAC and sintered Al$_2$O$_3$, the results helped to clarify and to indicate the dominant factors for controlling CA6 content and hexagonal plate-like microstructure.

The sintering condition had strong influence to control both quantity and microstructure of CA6. By this mean, (1) a higher temperature (1500°C) affected the better formation of CA6 or (2) a longer holding time (5 h) helped to enhance more amount of CA6. Especially, longer holding time was the dominant factor for the growth of plate-like microstructure. In this study, CA6 was formed in slow rate due to solid state sintering from the gradual diffusion of Al$^{3+}$, Ca$^{2+}$ and O$^{2-}$ in the primary admixture (AS0). However, the morphology of CA6 in AS0 was tended to be irregular plate-like with high facet and anisotropic grain growth.

The addition of SiO$_2$ and variation of content enhanced the formation of CA6 in hexagonal plate-like microstructure due to the assistance of low-melting phase of CaO–Al$_2$O$_3$–SiO$_2$ system. The detection of C2AS phase and the identification of Si element confirmed the presence of low-melting phase that
helped to accelerate ion diffusion to generate more CA6 phase. However, specimens with massive amount of SiO₂ showed less amount of CA6 and less apparent porosity due to the formation of excessive low-melting phase. They were caused by inadequate of CaO and enhanced samples’ densification. Therefore, to control CA6 formation and microstructure, the addition of SiO₂ up to 2 mass% was recommended.

Disclosure statement
No potential conflict of interest was reported by the authors.

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