Phase study of SiO₂-ZrO₂ composites prepared from polymorphic combination of starting powders via a ball-milling followed by calcination

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Abstract. The effects of SiO₂-ZrO₂ polymorphic combinations as starting powders and calcination temperature on phase composition of the SiO₂-ZrO₂ composites were studied. Stoichiometric (1:1 mol%) mixtures of the SiO₂-ZrO₂ composites were mechanically activated using a ball-milling for 5 h followed by calcinations at 1000, 1100 and 1200 °C for 3 h. The composites used in the present study were a-SiO₂+ a-ZrO₂, a-SiO₂+ t-ZrO₂, c-SiO₂+ a-ZrO₂ and c-SiO₂+ t-ZrO₂ which were symbolized by AA, AT, CA and CT, respectively. Prefixes a, t and c denote amorphous, tetragonal and cristobalite, respectively. The phase composition was determined by Rietveld analysis of X-ray diffraction (XRD) data using *Rietica* software. The identified phases for all calcined samples were a combination among t-ZrO₂, c-SiO₂, m-ZrO₂ and zircon (ZrSiO₄). Amorphous zirconia formed a transient tetragonal zirconia phase during heating, which reacted with silica to form zircon. The zircon phase was not found to form even at 1200 °C in the AT and CT mixtures and at 1100 °C in the CA mixture. The AA mixture in particular crystallized to form zircon at a lower temperature with more composition fraction than the others, *ca* 82.9 (14) mol%.

1. Introduction

Zircon (ZrSiO₄) is a readily available raw material in nature and zircon ceramic has interesting physical and chemical properties for technological uses [1-3] including excellent thermo-mechanical properties such as a very low coefficient of heat conductivity (5.1 W/m°C at room temperature and 3.5 W/m°C at 1000 °C), a low coefficient of thermal expansion (about 4.1×10^{-6}°C⁻¹ between 25 and 1400 °C), and good high-temperature mechanical strength even at a temperature higher than 1400 °C [1, 2, 4, 9]. It is also highly inert even when in contact with molten glass or slag which is appropriate for elevated temperature applications with a low chemical attack such as in steel or glass industries [1, 3].

Zircon forms from an equimolar reaction of zirconia (ZrO_2) and (silica) SiO_2. The binary phase diagram of ZrO_2-SiO_2 system has been revealed by Curtis and Sowmann (1953) [10] in a range of 1400-1800 °C, completed by Butterman and Foster (1967) [11] in a range of 400-2800 °C, re-calculated and optimized by Kaiser et al (2008) [12] in a range of 1000-2800 °C. Curtis and Sowman [10] observed the formation of zircon from mixtures of zirconia and cristobalite, zirconia and quartz and zirconia and tridymite. They have determined the temperature range within which the formation of zircon can occur and reported that the lower temperature limit for zircon formation was about 1320 °C. The allotropic (polymorphic) modification silica (SiO_2) that they used in the synthesis had little effect on the final degree of the formation of zircon. Further, Itoh [13] carried out a detailed study of the process from an equimolar mixture of amorphous silica (a-SiO_2) and amorphous zirconia (a-ZrO_2) by means of a high-temperature X-ray diffraction technique. It was reported that zircon ($ZrSiO_4$) formed predominantly from amorphous silica (a-SiO_2) and tetragonal zirconia (t-ZrO_2) at temperatures as low as 1200°C. The formation of zircon dominates the transformation of (a-SiO_2) to cristobalite (c-SiO_2). Tetragonal-to-monoclinic transformation of unreacted zirconia in the reaction may occur during the quenching process. Based on that investigation, Itoh [13] suggested the following four reactions as candidates for zircon formation:

$$a\text{-}SiO_2 + a\text{-}ZrO_2 \rightarrow ZrSiO_4 \tag{1}$$

$$a\text{-}SiO_2 + t\text{-}ZrO_2 \rightarrow ZrSiO_4 \tag{2}$$

$$c\text{-}SiO_2 + a\text{-}ZrO_2 \rightarrow ZrSiO_4 \tag{3}$$

$$c\text{-}SiO_2 + t\text{-}ZrO_2 \rightarrow ZrSiO_4 \tag{4}$$

There has been a lot of research that investigates the methods to produce zircon (solid reaction, hydrothermal, sol-gel routes, chemical reaction like aerosols, reverse micelle process, and micro-emulsion process). Therefore, the equimolar mixtures of polymorphic of silica and zirconia powders in Eq. 1-4 can be used as a basis reaction to form zircon [13]. However, the method based on the mixture of amorphous ZrO_2-SiO_2 revealed the incomplete powders crystallization under heat treatment [14, 15]. Because of its relatively low free energy of zircon formation [16], slow diffusion kinetics, and kinetically high activation energy for the reaction combination between the component oxides (ZrO_2 and SiO_2) [17], the synthesis of pure zircon with reasonably high yields is difficult. This is, in part, due to the large change in the crystallographic environment of Zr between zirconia and zircon structure, and very low solid solubility of silica in zirconia [17].

Due to the very low solubility of SiO_2 in ZrO_2 [16], the addition of material that roles as a binder may increase the wet ability between the powders. Polyvinyl alcohol (PVA) was often used as a binder of solid state reaction between silica and magnesia [18, 19]. The mechanical activation process also has proven to be a useful technique to enhance a solid-state reaction at room temperature [20]. The ''mechanical'' effects of milling, such as the reduction of particle size and mixture homogenization, resulted in active reactants with high surface energy.

This work focuses on the effects of the SiO_2-ZrO_2 polymorphic combination as starting powders and calcination temperature on phase composition of the SiO_2-ZrO_2 composites. Stoichiometric (1:1 mol% ratio) mixtures of a-SiO_2+ a-ZrO_2, a-SiO_2+ t-ZrO_2, c-SiO_2+ a-ZrO_2, and c-SiO_2+ t-ZrO_2, symbolized by AA, AT, CA and CT respectively, were prepared by a mechanical activation process via ball-milling followed by calcination. Prefixes a, t and c denote amorphous, tetragonal and cristobalite, respectively.

2. Experimental
The raw material was zircon natural sand taken from Kalimantan Tengah, Indonesia. The sand was processed to obtain zircon powder with high purity by magnetic separation, soaking with HCl, and reaction with NaOH. This extraction processes produced sodium silicate (Na_2SiO_3) solution and pure zircon ($ZrSiO_4$) powders; both were further processed to obtain zirconia and silica powders. The amorphous zirconia (a-ZrO_2) powder was prepared from the extracted zircon powder by an alkali

fusion method with NaOH and followed by a co-precipitation with HCl and NH_4OH. Tetragonal zirconia (t-ZrO_2) was obtained from the amorphous zirconia (a-ZrO_2) powder which was calcined at 700 °C for 3 hours. Meanwhile, a sodium silicate solution was precipitated by HCl to produce the amorphous silica (a-SiO_2) powder. The cristobalite (c-SiO_2) powder was obtained from the amorphous silica (a-SiO_2) powder which was calcined at 950 °C for 8 hours. The zirconia (amorphous and tetragonal) powders and the silica (amorphous and cristobalite) powders with a composition of 1:1 molar ratio and polyvinyl alcohol (PVA) of 3 wt% were mixed and mechanically activated using a planetary ball mill apparatus for 5 hours at a speed of 150 rpm. The milled mixtures were then calcined at various temperatures of 1000, 1100, and 1200 °C for 3 hours. Phase compositions were obtained from X-ray diffraction (XRD) data which were collected using a Philips X'Pert Powder diffractometer with CuKα radiation (λ=1.54060 Å) for all samples. The XRD patterns were recorded with a step size of 0.0170°. The XRD patterns were analyzed using *Match!2* for phase identification and using *Rietica* based on Rietveld method to provide accurate phase compositions of the samples.

3. Results and Discussion

3.1 Qualitative Analysis
Figure 1 shows the XRD patterns of the four mixtures of silica and zirconia which were prepared by a mechanical activation process via ball-milling before calcination. The mixed phases are confirmed by a qualitative analysis of XRD data, i.e. tetragonal-zirconia (COD No. 1-525-706) and cristobalite (SiO_2) (COD No. 1-010-938), while the "amorphous phases" (amorphous zirconia and amorphous silica) are known from the existence of peak hump. Furthermore, the XRD patterns of the calcined mixtures are shown in figure 2. The identified phases for all calcined samples were a combination among tetragonal-zirconia, cristobalite, monoclinic-zirconia (PDF No. 89-426), and zircon (PDF No. 9-582).
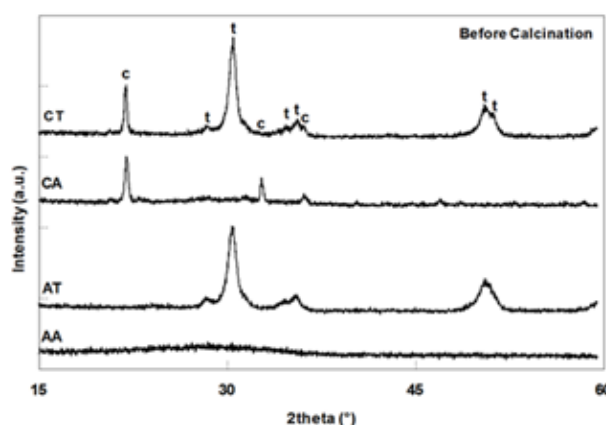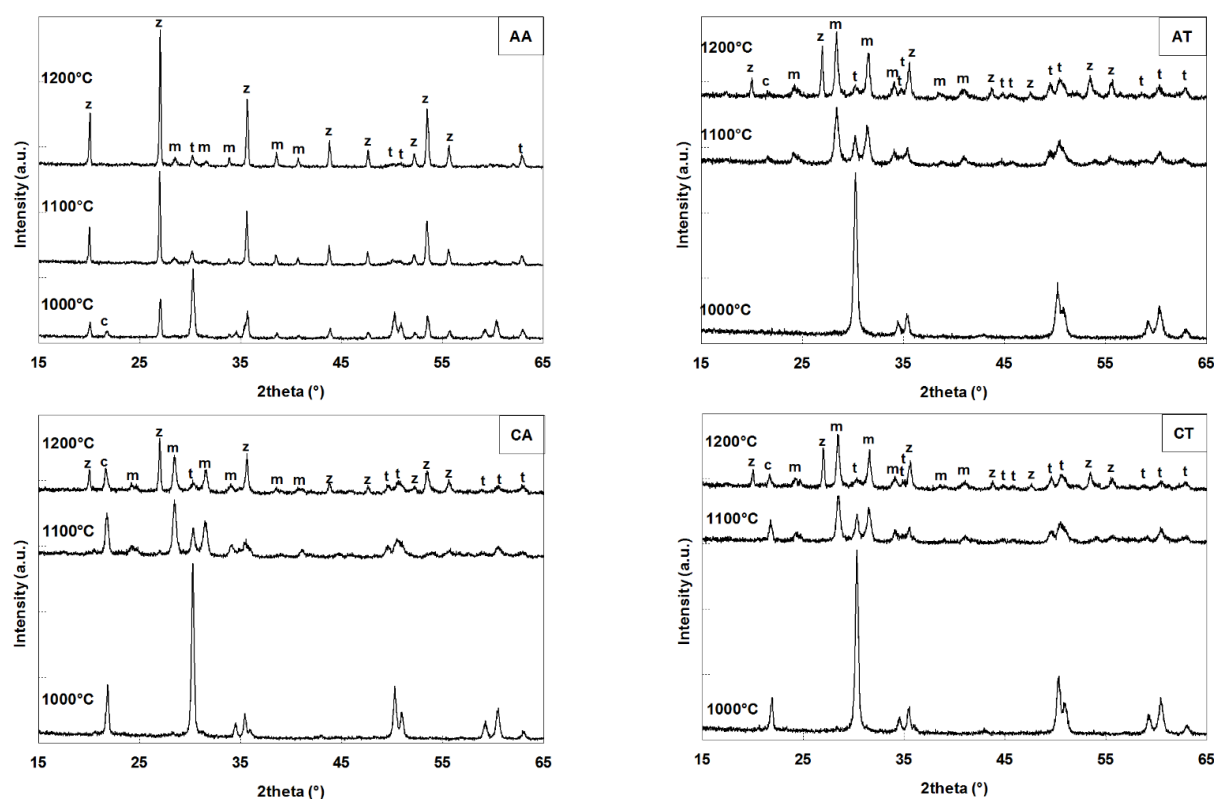

Figure 1. X-ray diffraction patterns (CuKα) of AA, AT, CA, and CT powders before calcinations.

Zircon is not identified in the 1100 °C of the AT and CT composites and in the 1000 °C of the CA composites as seen in figure 2. In contrast, zircon is identified at lower calcination temperature of 1000 °C for sample AA. Formation of zircon by the solid-state reaction usually requires a thermal treatment at 1450-1500 °C in air [21]. In this study, zircon was already formed at a temperature as low as 1000 °C. Zircon is formed at a relatively lower temperature because for the AA sample, the amorphous zirconia and amorphous silica powders have smaller particle size than the other samples. Smaller particles tend to react in an easier way than larger particles [22]. It was reported in a previous study on the mechanism of zircon formation from amorphous powders [13] that zircon formed after a reaction between amorphous-silica and tetragonal-zirconia. It was also found that the formation of zircon

dominates over the transformation of amorphous silica to cristobalite. Tetragonal $\rightarrow$ monoclinic transformation of unreacted zirconia in the reaction mixture occurs during the quenching process.

The zircon formation is not a nucleation process, but, in fact, it is a diffusion of silicon species through a zircon layer, from an external continuous or granular silica phase to the surface of zirconia grains. A model of ZrO_2-SiO_2 reaction mechanism has been proposed by Veytizou et al. [23]. They observed the kinetics of the reaction of a-SiO_2 + t-$ZrO_2 \rightarrow ZrSiO_4$ by isothermal HTXRD experiments. In a great number of solid–solid reactions, because there were no mobile species like in gas or liquids, it was considered that the growth of product was limited by diffusion. Two models of contracting spheres were proposed: in the first model, the system was described as a series of spherical t-ZrO_2 grains surrounded by a shell of zircon, which is covered by a-SiO_2. In the second model, a fast, superficial diffusion of Si^{4+} and electrons originating from silica grains on the external surface of the zircon layer produced a homogenization of the silicon concentration.

Figure 2. X-ray diffraction patterns (CuKα) of AA (a-SiO_2+a-ZrO_2), AT (a-SiO_2+t-ZrO_2), CA (c-SiO_2+a-ZrO_2), and CT (c-SiO_2+t-ZrO_2) powders after calcined at 1000, 1100, and 1200 °C for 3 hours.

3.2 Quantitative Analysis

Quantitative phase analyses were based on the Rietveld method using *Rietica* software to the XRD data result in the relative mole fraction of the phases in all samples as described in table 1. Its concentration increased with the calcination temperature, i.e. up to 82.9 mole% at 1200 °C for the AA sample. The mechanical activation process via ball-milling played an important role in the lower temperature of zircon formation. The mechanical activation process has proven to be an effective technique to enhance a solid-state reaction at room temperature. The ''mechanical'' effects of milling, such as the reduction of particle size and mixture homogenization, result in active reactants with high surface energy [20].

In a previous study, Pradhan [24] worked on the synthesis of zircon from stoichiometric (1:1 mole%) monoclinic zirconia and amorphous silica powder mixture also via a ball-mill process followed by a calcination. A relatively high-purity zircon was found when a sample was ball-milled for 30 h and calcined at 1200 °C for 1 h, i.e. up to 93 mole% as compared to powder with the same treatment except with milling for 5 min which has only 22 mole%. In our work, milling of AA powder for 5 h followed by calcination at 1200 °C for 3h resulted in 82.9 mole% zircon.

Table 1. Results of quantitative analysis of X-Ray diffraction pattern of samples using *Rietica* by Rietveld method.

Sample	Mole fraction (%)			
	Zircon	t-Zirconia	m-Zirconia	cristobalite
AA 1000 °C	76.4 (54)	2.4 (2)	-	21.2 (64)
AA 1100 °C	77.8 (20)	0.2 (0)	22.0 (16)	-
AA 1200 °C	82.9 (14)	0.1 (0)	17.0 (11)	-
AT 1000 °C	-	100	-	-
AT 1100 °C	-	0.4 (0)	90.7 (25)	8.9 (12)
AT 1200 °C	20.2 (6)	0.2 (0)	75.3 (11)	4.3 (7)
CA 1000 °C	-	1.7 (0)	-	98.3 (2)
CA 1100 °C	4.2 (5)	0.3 (0)	73.6 (22)	21.9 (28)
CA 1200 °C	27.1 (4)	0.3 (0)	37.0 (6)	35.6 (10)
CT 1000 °C	-	5.2 (0)	-	94.8 (1)
CT 1100 °C	-	0.4 (0)	60.6 (1)	39.0 (1)
CT 1200 °C	18.6 (0)	0.1 (0)	49.3 (0)	32.0 (1)

The role of calcinations temperature in the reaction of the powders can also be seen based on the phase composition by quantitative analysis in Table 1. Zircon was already formed at a temperature as low as 1000 °C for AA samples and 1100 °C for CA samples, but for AT and CA samples, zircon was formed at 1200 °C. The composition of zircon increased with increasing calcinations temperature.

4. Summary
The effects of the SiO_2-ZrO_2 polymorphic combination as starting powders and calcination temperature on phase composition of the SiO_2-ZrO_2 composites were studied. Stoichiometric (1:1 mol%) mixtures of a-SiO_2 + a-ZrO_2, a-SiO_2 + t-ZrO_2, c-SiO_2 + a-ZrO_2, and c-SiO_2 + t-ZrO_2 were prepared by a mechanical activation via ball-milling for 5 h followed by calcination at 1000, 1100, and 1200 °C for 3 hours. The phase composition was investigated by Rietveld analysis of X-Ray Diffraction (XRD) data using *Rietica* software. The identified phases for all calcined samples were a combination of t-ZrO_2, c-SiO_2, m-ZrO_2, and zircon ($ZrSiO_4$). Amorphous zirconia formed a transient tetragonal zirconia phase during heating, which reacted with silica to form $ZrSiO_4$. The $ZrSiO_4$ phase was not found to form even at 1200 °C in the AT and CT composites and at 1100 °C in the CA composites. The AA composites in particular crystallized to form $ZrSiO_4$ at a lower temperature with a greater composition fraction than the others, *ca* 82.9 (14) mol%.

5. Acknowledgements

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