$\text{Al}_2\text{O}_3\text{--TiO}_2/\text{ZrO}_2\text{--SiO}_2$ based porous ceramics from particle-stabilized wet foam

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Abstract: The porous ceramics based on $\text{Al}_2\text{O}_3\text{--TiO}_2/\text{ZrO}_2\text{--SiO}_2$ from particle-stabilized wet foam by direct foaming were discussed. The initial $\text{Al}_2\text{O}_3\text{--TiO}_2$ suspension was prepared by adding TiO_2 suspension to partially hydrophobized colloidal Al_2O_3 suspension with equimolar amount, to form Al_2TiO_5 on sintering. The secondary $\text{ZrO}_2\text{--SiO}_2$ suspension was prepared using the equimolar composition, and to obtain ZrSiO_4 , ZrTiO_4 , and mullite phases in the sintered samples, the secondary suspension was blended into the initial suspension at 0, 10, 20, 30, and 50 vol%. The wet foam exhibited an air content up to 87%, Laplace pressure from 1.38 to 2.23 mPa, and higher adsorption free energy at the interface of approximately 5.8×10^8 to 7.5×10^8 J resulting an outstanding foam stability of 87%. The final suspension was foamed, and the wet foam was sintered from 1400 to 1600 °C for 1 h. The porous ceramics with pore size from 150 to 400 μm on average were obtained. The phase identification was accomplished using X-ray diffraction (XRD), differential thermal analysis (DTA), and thermogravimetric analysis (TGA), and microstructural analysis was performed using field emission scanning electron microscopy (FESEM).

Keywords: Al_2TiO_5 ; direct foaming; Laplace pressure; adsorption free energy; porous ceramics

1 Introduction

Aluminium titanate (Al_2TiO_5) is well known as a material with excellent thermal shock resistance, resulting from its unique combination of low thermal expansion ($1.5 \times 10^{-6} \text{ K}^{-1}$), low Young's modulus, and high-temperature resistance (melting point 1860 ± 10 °C) [1], which qualifies it to be a suitable candidate for applications related to significant thermal shock

resistance and thermal insulation and thus high-temperature applications [2,3]. The frequently occurring grain boundary cracks present in the polycrystalline Al_2TiO_5 can be attributed to the characteristic low thermal expansion behavior of this pseudo-brookite structure [4,5]; nevertheless, the mechanical strength of Al_2TiO_5 suffers from a significant deterioration due to the presence of these microcracks at the grain boundary [6]. Although being such a wonderful thermal shock resistive material, this ceramic has a big disadvantage related to its stability as a whole in the temperature range of 750–1280 °C. During cooling, in this temperature range, Al_2TiO_5 is

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decomposed into Al_2O_3 and TiO_2 [7,8], and this decomposition results in apparently useless materials for industrial applications because they no longer exhibit the low thermal expansion coefficient and thermal shock behavior. However, the enhancement of thermal durability of Al_2TiO_5 can be possible by adding thermodynamical stabilizers such as MgO , Fe_2O_3 , and TiO_2 , which are isomorphous with pseudo-brookite minerals like Fe_2TiO_5 [9], MgTi_2O_5 [10], Ti_3O_5 (anosovite) [11], and MgAl_2O_4 (spinel) [12]. Also, Al_2TiO_5 can be mechanically stabilized through the limitation of its grain growth with additives such as SiO_2 [13], ZrO_2 [14], ZrTiO_4 [15], mullite [16], and ZrSiO_4 (zircon) [17] that constrain both the microcracks and the abnormal grain growth [18].

During the reaction–sintering process of $\text{Al}_2\text{O}_3/\text{TiO}_2$, ZrSiO_4 decomposes to form ZrTiO_4 as a transitory phase due to the addition of $\text{SiO}_2/\text{ZrO}_2$ composition. Temperatures above 1450°C are needed to dissociate the compound, yielding Al_2TiO_5 , ZrTiO_4 , mullite, and ZrO_2 [19]; these composites can be obtained at 1450°C . The temperature should not be increased to 1500°C because it produces an appreciable amount of the glass phase accompanied by the disappearance of the mullite [20]. The inorganic microballoons containing 63.2 wt% SiO_2 and 34.0 wt% Al_2O_3 can react with the sources of Al_2O_3 , ZrO_2 , and TiO_2 to form Al_2TiO_5 , ZrTiO_4 , and mullite based porous ceramics, at low sintering temperatures from 1350 to 1500°C . If the melting point of the inorganic microballoons is low, the microballoons tend to melt at temperatures from 1100 to 1300°C , allowing the pores to make contact before Al_2TiO_5 is formed [3,21].

Furthermore, ZrSiO_4 has been used as a refractory material due to the excellent thermo-physical properties: low thermal expansion ($4.10 \times 10^{-6} \text{ K}^{-1}$), low thermal conductivity, and high dissociation temperature (1675°C), as well as a sound corrosion resistance. Pure ZrSiO_4 , however, tends to decompose via a solid-state reaction during the heat treatment between the stated dissociation temperatures of 1285 and 1700°C [22,23]; therefore, those thermo-physical properties are very important for the prediction of the thermal durability of ZrSiO_4 , zirconia-based refractories, and the ZrSiO_4 parts that are in contact with silica-containing melts [24].

In this work, a lightweight porous material that is based on the $\text{Al}_2\text{O}_3\text{--TiO}_2/\text{ZrO}_2\text{--SiO}_2$ composites and comprises fine and homogeneous pores with well-developed microstructural properties was

fabricated through the adjustment of the compositions of Al_2TiO_5 , ZrTiO_4 , mullite, and ZrSiO_4 by the direct foaming method. The versatility of this method for porous ceramics synthesis is due to its simplicity, ease of reproducibility, and low cost [25,26]. The direct foaming process was applied to synthesize porous Al_2TiO_5 , with the use of Al_2O_3 and TiO_2 as raw materials, $\text{ZrO}_2/\text{SiO}_2$ of 1:1 mole ratio for the ZrSiO_4 phase. In this process, high-volume stable wet foam was prepared through the incorporation of air into the colloidal suspension. The wet foam was characterized, and the average bubble size, air content, adsorption free energy, Laplace pressure, and wet foam stability were subsequently investigated. Later, the wet foam was dried and sintered to produce open- or closed-cell porous ceramics with high porosity. X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), field emission scanning electron microscopy (FESEM), differential thermal analysis (DTA), and thermogravimetric analysis (TGA) were used for phase identification and microstructural investigation.

2 Experimental

2.1 Materials

To prepare $\text{Al}_2\text{O}_3\text{--TiO}_2/\text{ZrO}_2\text{--SiO}_2$ suspension, raw materials used were as follows: $\alpha\text{-Al}_2\text{O}_3$ powder (KC, R. O. Korea) with an average particle diameter (d_{50}) of $4 \mu\text{m}$ and a density of 3.95 g/cm^3 , TiO_2 powder (Junsei Chemicals Co. Ltd., Japan) with a d_{50} of $2 \mu\text{m}$ and a density of 4.23 g/cm^3 , ZrO_2 powder (Junsei Chemicals Co. Ltd., Japan) with a d_{50} of $3.5 \mu\text{m}$ and a density of 2.65 g/cm^3 , and SiO_2 powder (Junsei Chemicals Co. Ltd., Japan) with a d_{50} of $3.5 \mu\text{m}$. The short-chain carboxylic acid used for the surface modification was propyl gallate (Fluka Analytical, Germany), 10(N) HCl (Yakuri Pure Chemicals, Osaka, Japan) and 4(M) NaOH solutions (Yakuri Pure Chemicals, Kyoto, Japan) were used for the pH adjustment, and double deionized (DI) water was used for the suspension preparation and the volume adjustment.

2.2 Preparation of suspensions

2.2.1 Preparation of the $\text{Al}_2\text{O}_3\text{--TiO}_2$ suspension

The $\alpha\text{-Al}_2\text{O}_3$ powder and TiO_2 powder were added to DI water, and an aqueous suspension was prepared separately. The colloidal suspension was kept in a

polyethylene bottle, and the zirconia ball was added with 2:1 ball/powder ratio then mixed homogeneously by ball milling for 48 h with the rotation speed of 60 rpm. For the hydrophobization of the suspension, 0.2 wt% propyl gallate was added dropwise to the Al_2O_3 suspension (after ball milling) under mechanical stirring. The suspension was mixed with the stirring speed of 500 rpm. The pH of final suspension was set to 4.75 by the adding (4)M NaOH and/or (10)N HCl dropwise. The solid content of the final suspension was set to 30 vol% by adding required amount of water. After that, the TiO_2 suspension and Al_2O_3 suspension of equimolar concentration were mixed homogeneously; the procedure is shown in schematic diagram (Fig. 1).

2.2.2 Preparation of the ZrO_2 - SiO_2 suspension

For the ZrO_2 - SiO_2 suspension, the SiO_2 suspension and an aqueous suspension of ZrO_2 powder were mixed together homogeneously with a 1:1 ZrO_2 / SiO_2 mole ratio under the same condition as above. 10, 20, 30, and 50 vol% of this suspension were added to the initial suspension containing the equimolar concentration of Al_2O_3 / TiO_2 to form a post-sintering Al_2TiO_5 phase. In terms of the final suspension, the volume percentages of Al_2O_3 - TiO_2 for Al_2TiO_5 and the added suspension ZrO_2 - SiO_2 for ZrSiO_4 are shown in Table 1.

Table 1 Volume percentage of Al_2O_3 - TiO_2 and added suspension ZrO_2 - SiO_2 in final suspension (Unit: vol%)

Sample	AT	ATZS1	ATZS2	ATZS3	ATZS5
Al_2O_3 - TiO_2	100	90	80	70	50
ZrO_2 - SiO_2	0	10	20	30	50

2.3 Contact angle and surface tension

The analysis of surface tension and contact angle of the final colloidal suspension was carried out by pendant drop method (KSV-Instruments Ltd., Helsinki, Finland). The drop volume was set to 5–10 μL for the suspension with amphiphile.

2.4 Foaming and foam characterization

The foaming of the final suspension was conducted at room temperature using the highest power of a general hand mixer (150 W, Super Mix, France) for 15 min; here, the mechanical frothing facilitated the air incorporation throughout the whole volume of the suspension. The air content was analyzed by calculating the volume increase percentage of the suspension after foaming, as follows:

$$\text{Air content} = \frac{V_{\text{wet foam}} - V_{\text{suspension}}}{V_{\text{wet foam}}} \times 100\% \quad (1)$$

Fig. 1 Schematic diagram of the direct foaming technique for the preparation of the Al_2O_3 - TiO_2 / ZrO_2 - SiO_2 porous ceramics.

where $V_{\text{wet foam}}$ indicates the post-foaming wet foam volume and $V_{\text{suspension}}$ indicates the pre-foaming suspension volume.

The average wet-bubble size was measured through an analysis of optical microscope images using an optical microscope (Somtech Vision, R. O. Korea) and linear intercept software (TU Darmstadt, Germany); 100 bubbles were evaluated for each sample.

The most critical issue regarding the direct foaming method is the approach used to stabilize the air bubbles that are incorporated into the suspension. In this experiment, the propyl gallate (0.2 wt%) was used as a surface modifier that imparted hydrophobicity to the particle surface, thereby improving the foam stability. To measure the wet foam stability, the samples were filled into cylinder-shaped measuring cylinders of a constant volume and left for 48 h. The foam stability was evaluated according to the volume loss percentage of the foam as follows:

$$\text{Wet foam stability} = \frac{V_{\text{final}}}{V_{\text{initial}}} \times 100\% \quad (2)$$

where V_{final} indicates the wet foam volume after 48 h and V_{initial} indicates the wet foam volume before 48 h.

2.5 Drying/sintering

The wet foams were poured into cylinder-shaped molds and left to dry at 22–25 °C for at least a day or two. After the specimens were dried, they were sintered in a Kanthal Super furnace (1650 °C maximum) at 1300 °C for 1 h. The heating rate was set to 1 °C/min and cooling rate to 3 °C/min, and the microstructures of thus produced sintered samples were observed using FESEM (JEOL, Japan). The phase compositions of the sintered bodies were characterized using XRD (Rigaku D/Max 2500, Japan).

3 Results and discussion

Figure 2 illustrates the influence of the $\text{ZrO}_2\text{--SiO}_2$ suspension on the contact angle and surface tension of the colloidal suspension. The attachment of the particles at the gas–liquid interface occurs when the particles are not completely wetted, i.e., when the particles are partially hydrophobic. This attachment phenomenon enables the production of the high-volume stable foam, which after drying and sintering, produces the porous ceramics. The final suspension exhibits partially

Fig. 2 Contact angle and surface tension of the $\text{Al}_2\text{O}_3\text{--TiO}_2$ suspension versus different volume percentage of the $\text{ZrO}_2\text{--SiO}_2$ suspension.

hydrophobic characteristic, exhibiting a contact angle of $< 75^\circ$. In the graph, the suspension exhibits contact angles of $45^\circ\text{--}74^\circ$, and this enables the high wet foam stability because it indicates that a partial hydrophobization of the particles has occurred.

For all of the evaluated samples, the surface tension of the suspension decreases upon the increasing of the volume percentage of the added suspension $\text{ZrO}_2\text{--SiO}_2$ for the ZrSiO_4 phase; this can be clarified with an increase of the surface hydrophobicity of the particles with the increasing of the particle concentration. The porosity of directly foamed ceramics is related to the amount of air that is incorporated into the suspension, or the liquid medium, during the foaming process; alternatively, the pore size is dependent on the stability of the wet foam.

Figure 3 establishes the air content and average bubble size of the $\text{Al}_2\text{O}_3\text{--TiO}_2$ equimolar suspension versus different volume percentage of the added suspension $\text{ZrO}_2\text{--SiO}_2$. High-volume wet foam with air content up to 95% is foamed, which strongly indicates the air bubble stabilization, due to the particle attachment at the air–water interface [27,28]. The average bubble size was measured, and upon the addition of 10 vol% $\text{ZrO}_2\text{--SiO}_2$ suspension, the bubble size suddenly decreases; this may be because of increment in viscosity of the suspension due to a higher particle concentration. The additions of 20, 30, and 50 vol% suspension, however, enhance the average bubble size, which might be explained by the achievement of the optimal surface hydrophobicity due to the increased particle concentration.

Figure 4 establishes the relationship between the adsorption free energy and the wet foam stability, with

Fig. 3 Air content and average bubble size of the $\text{Al}_2\text{O}_3\text{--TiO}_2$ suspension versus different volume percentage of the $\text{ZrO}_2\text{--SiO}_2$ suspension.

Fig. 4 Adsorption free energy and wet foam stability of the $\text{Al}_2\text{O}_3\text{--TiO}_2$ suspension versus different volume percentage of the $\text{ZrO}_2\text{--SiO}_2$ suspension.

respect to different volume percentage of the added suspension $\text{ZrO}_2\text{--SiO}_2$ for the ZrSiO_4 phase. The energy of adsorption plays an important role in the stabilization of foams. The particles that become attached to the gas–liquid interface of the foams lower the systemic free energy by replacing a part of the gas–liquid interfacial area. The attachment energy or the free energy gained (G) of the particle with radius (r) at the interface can be calculated with the following equation:

$$\Delta G = \pi r^2 \gamma (1 - \cos \theta)^2, \text{ where } \theta < 90^\circ \quad (3)$$

where γ represents the surface tension of the suspension and θ represents contact angle. The low adsorption free energy resulted from spontaneous bubble growth leads to foam instability [16]. The investigated samples exhibit a much higher adsorption free energy of approximately 5.8×10^8 to 7.5×10^8 J at the interface, resulting in an irreversible adsorption of the particles at the air–water interface that leads to an outstanding stability of up to 87%.

Figure 5 exhibits the graph of Laplace pressure (ΔP) and the wet foam stability of all the evaluated suspensions versus different volume percentage of the $\text{ZrO}_2\text{--SiO}_2$ suspension. The Laplace pressure results imply the difference between the inner and the outer pressures of a gas bubble, which plays vital role in the wet foam stabilization as follows:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R} \text{ (spherical bubble)} \quad (4)$$

where γ represents the surface tension of the suspension, and R_1 and R_2 represent the radii of two interfacing bubbles. In this experiment, the bubbles are almost spherical, and the above equation is used because of the narrow size distribution. Smaller bubbles exhibit higher pressure in comparison to the larger ones, which results in a gas diffusion from the smaller to the larger bubbles that leads to the destabilization of the foam [29,30]. The bubbles with lower Laplace pressure are found to be unstable. The wet foam stability from 80% to 85% occurs when the Laplace pressure is approximately 1.4 to 1.6 mPa. The degree of the particle hydrophobization determines the average bubble size of the resultant foams.

Figure 6 shows the DTA and TGA curves of (a) AT, (b) ATZS1, (c) ATZS3, and (d) ATZS5 porous ceramic samples that were dried at room temperature. A broad endothermic peak is observed initially, around 170 °C for the AT, ATZS1, ATZS3, and ATZS5 samples with weight loss of 0.23–0.29 wt%; this peak is attributed to the vaporization of the physically adsorbed water molecules within the samples. A sharp exotherm is seen to appear between 360 and 411 °C in all of the samples, which shows the weight loss of 1.4–1.9 wt% because of

Fig. 5 Laplace pressure and wet foam stability of the $\text{Al}_2\text{O}_3\text{--TiO}_2$ suspension versus different volume percentage of the $\text{ZrO}_2\text{--SiO}_2$ suspension.

Fig. 6 DTA and TGA curves of the porous ceramics: (a) AT, (b) ATZS1, (c) ATZS3, and (d) ATZS5.

the decomposition of the amphiphile. The decomposition reaction continues to occur with the increase in temperature, until it gets stabilized in the temperature region of 1150–1300 °C. For the AT sample, the formation of Al_2TiO_5 is illustrated by an endothermic-enthalpy effect around 1283 °C, which is in agreement with that of the pure AT (rate constant $k = 4.025 \times 10^{-21} \text{ m}^2/\text{s}$ at 1250 °C) [31,32].

For the ATZS1, ATZS3, and ATZS5 samples, the endothermic peaks around 1260–1300 °C should be correlated to the formation of the inorganic ceramic phase, as well as the crystallization. Upon careful observation of the TGA curves, it can be seen that, for the AT, ATZS1, ATZS3, and ATZS5 samples, the weight loss is only up to 1.97, 1.82, 1.14, and 1.62 wt%, respectively, when a green composite body is heated from room temperature to 1400 °C. It is interesting to report the slight increase in weight (approximately 0.25 and 0.16 wt%) in the TGA curves from 401 to 1400 °C for the AT and ATZS1 samples, respectively. The weight loss of the ATZS3 and ATZS5 samples is seen to be more or less constant till 1400 °C.

Figure 7 shows the XRD patterns of the porous Al_2TiO_5 and Al_2TiO_5 , ZrTiO_4 , mullite, and ZrSiO_4

Fig. 7 XRD patterns of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ and $\text{ZrO}_2\text{-SiO}_2$ porous ceramics sintered at 1500 °C for 1 h. Inset: XRD patterns of the ATZS2 sintered at 1400, 1500, and 1600 °C for 1 h.

composites that were formed at 1400–1600 °C for 1 h from the individual oxide sources and the adjustments of the Al_2O_3 , TiO_2 , SiO_2 , and ZrO_2 ratios. The symbolic representations of the solid-state compatibility relationships in the $\text{Al}_2\text{O}_3\text{-TiO}_2/\text{ZrO}_2\text{-SiO}_2$ system show the part of the system where Al_2TiO_5 is one of the phases, as follows: AT(023), Al_2TiO_5 at $2\theta = 33.6^\circ$; ZT(111), ZrTiO_4 at $2\theta = 30.5^\circ$; A3S2(110), $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite) at $2\theta = 26^\circ$; ZS(200), ZrSiO_4 at $2\theta = 27.8^\circ$; C(113), Al_2O_3 at $2\theta = 20.8^\circ$; Z(111), ZrO_2 at $2\theta = 28.4^\circ$; S(101), SiO_2 at $2\theta = 22.2^\circ$, respectively. The preferable procedure for the making of the composition involves the formation of a mixture containing the equivalent of 50–90 vol% $\text{Al}_2\text{O}_3\text{-TiO}_2$, or a solid solution containing a substantial amount of Al_2TiO_5 , and 10–50 vol% $\text{ZrO}_2\text{-SiO}_2$ for the Al_2TiO_5 phase, followed by the heating of the mixture to 1400, 1500, and 1600 °C. The presence of 10–30 vol% $\text{ZrO}_2\text{-SiO}_2$ helps in the densification of these materials

and increases the temperature for the Al_2TiO_5 formation [5,32].

The ZrSiO_4 decomposes into ZrO_2 and SiO_2 over 1450°C during reaction-sintering process; to form mullite [28,29], ZrTiO_4 , and Al_2TiO_5 based porous ceramics with an Al_2O_3 source at low temperature, the mechanism is explained as follows [33,34]:

The main phase of the AT is Al_2TiO_5 , while traces of rutile (3.5%) and corundum (5.86%) are also identified, as shown in Fig. 8. This might be explained by the pure Al_2TiO_5 trend; whereby a partial decomposition into Al_2O_3 and TiO_2 is enabled in the temperature region from 800 to 1300°C [5]. With the addition of the 10 vol% ZrO_2 – SiO_2 suspension, the characteristic main peak of Al_2TiO_5 , 61.98%, is found along with a secondary mullite peak of 11.1% (with remnants of ZrTiO_4 , ZrSiO_4 , and corundum). Interestingly, with the increasing addition of the stoichiometric ZrO_2 – SiO_2 suspension that is for the ZrSiO_4 phase to the Al_2O_3 – TiO_2 suspension, the ZrTiO_4 , mullite, and ZrSiO_4 peaks are observed at lower temperatures in the ATZS2 and ATZS3 samples when they were sintered at 1400 – 1500°C ; meanwhile, at the same temperatures, minor Al_2TiO_5 and ZrSiO_4 phases appear in the ATZS5 sample. As it is well known that pure ZrSiO_4 usually dissociates at a temperature higher than 1500°C [23], the temperature should not be increased to 1500°C because this produces an appreciable amount of the glass phase accompanied by the disappearance of the mullite [35]. The XRD pattern of ATZS2 exhibits the

formation of Al_2TiO_5 and ZrTiO_4 showing smaller peaks at 1400°C , and on elevating the temperature till 1500°C , Al_2TiO_5 and ZrTiO_4 dominate the system with maximum yielding where mullite, rutile, ZrSiO_4 , and ZrTiO_4 tend to get decreased on further increasing the temperature to 1600°C ; Al_2TiO_5 phase shows the maximum yield with higher peaks. So, to get the tailored microstructure of Al_2TiO_5 – ZrTiO_4 porous ceramics, 1500°C is taken as the optimal temperature, as shown in Fig. 7.

The XRD analysis results of the final crystalline phase content are reported in Fig. 8, which shows the crystalline phase percentages of the sintered AT and ATZS porous ceramics with respect to different volume percentage of the ZrO_2 – SiO_2 suspension. The data reported in the graph of clearly show the presence of 61.98, 39.97, 23.57, and 8.3 wt% Al_2TiO_5 in the ATZS1, ATZS2, ATZS3, and ATZS5 samples, respectively. The phase content of the Al_2TiO_5 is decreased gradually from 90.66 wt% in the AT sample to 8.3 wt% in the ATZS5 sample. A substantial ZrSiO_4 phase content of 14.87 wt% is found in the ATZS5 sample, as measured by the XRD pattern, which indicates the enhanced thermal stability that is provided by the ZrTiO_4 and mullite phases [32,34,35]. Moreover, with the additions of the 10 and 20 vol% ZrO_2 – SiO_2 suspensions, the characteristic main peak of Al_2TiO_5 , 8.2 wt%, is found along with a secondary ZrTiO_4 peak of 29.53 wt%. For the composites of ATZS1, ATZS2, ATZS3, and ATZS5, 11.1, 12.51, 14.21, and 18.98 wt%, respectively, are expressed by the crystalline phase content of the mullite. The complete dissociation of the ZrTiO_4 is achieved at 1500°C , as shown in Fig. 7. This unique pseudo-binary oxide system is apparently due to a microcracking combination that is caused by the huge thermal expansion anisotropy of the crystal axes of the ZrSiO_4 phase and the grain growth limitation of Al_2TiO_5 phase by the ZrSiO_4 phase [5,36].

The microstructures of the porous ceramics that were sintered at 1500°C for 1 h are shown in Fig. 9. The microstructures thus obtained generally consist of open and interconnected pores with a fine size distribution of the Al_2TiO_5 and ZrTiO_4 grains in the AT, ATZS1, and ATZS3 samples. A microcracked open porous Al_2TiO_5 matrix phase with the presence of an abnormal grain growth can be seen in the samples where there has been no addition of the ZrO_2 – SiO_2 suspension (Fig. 9(a)). With the increasing of the ZrO_2 – SiO_2 suspension content, the abnormal grain growth of the Al_2TiO_5

Fig. 8 Crystalline phase content of Al_2TiO_5 , ZrTiO_4 , mullite, ZrSiO_4 , TiO_2 , Al_2O_3 , and ZrO_2 in the AT and ATZS ceramics sintered at 1600°C for 1 h with respect to different volume percentage of the ZrO_2 – SiO_2 suspension.

Fig. 9 Microstructures of the porous ceramics sintered at 1500 °C for 1 h: (a) AT, (b) ATZS1, (c) ATZS3, and (d) ATZS5.

phase is suppressed, which is presumably attributed to the less microcracks than the pure Al_2TiO_5 [12]. A number of unequal connective pores that are sized from 150 to 400 μm are observed in Figs. 10(a), 10(b), and 10(c). It is clear that the introduction of the ZrTiO_4 and mullite phases results in an increase of the pore size and a reduction of the Al_2TiO_5 phase.

The microstructure and EDX analyses of the AT, ATZS, and ZS porous ceramics that were sintered at 1500 °C for 1 h are shown in Fig. 10. Figure 10(a) consists of irregular-shaped, elongated Al_2TiO_5 formations with average grain size in the region of 3–5 μm . Alternatively, the ZrTiO_4 grains are generally irregular to round in shape. The abundance of the dispersed grain-boundary microcracks may be attributed to the anisotropic thermal expansion behavior of both the Al_2TiO_5 grains and the ZrO_2 phase [16]. The synergism of the low thermal expansion anisotropy of both the titanates ($\alpha_{25-1350}^\circ\text{C}$ of $\text{ZrTiO}_4 \approx 8.29 \times 10^{-6} \text{ K}^{-1}$) [5,34] generates the microcracking system throughout the dominated Al_2TiO_5 – ZrTiO_4 phase in the samples of the ATZS1, ATZS2, and ATZS3 composites. Moreover,

the lower thermal expansion anisotropy of ZrTiO_4 reduces the thermal stresses, which in turn checks the formation of the microcracks. In addition, the EDX data of the AT sample shown in Fig. 10(a) clearly exhibit that only Al and Ti ions are contained in the AT sample. Figures 10(b) and 10(c) show the EDX data of the small and large grains in the composition, confirming that the former area contains Al ions, while the latter one is rich in Zr and Ti ions. Discontinuous mullite grains are dispersed throughout a predominant ZrTiO_4 porous ceramic matrix in the ATZS3 sample. Figure 10(d) exhibits the decomposition of the ZrSiO_4 to the starting materials giving ZrO_2 and SiO_2 where the ZrSiO_4 totally disappears [26–30].

4 Conclusions

Al_2TiO_5 -based porous ceramics were prepared from particle-stabilized wet foam according to the direct foaming method with the use of Al_2O_3 , TiO_2 , ZrO_2 , and SiO_2 as raw materials. The average bubble size

Fig. 10 FESEM and EDX images of the porous ceramics sintered at 1500 °C for 1 h: (a) AT, (b) ATZS1, (c) ATZS3, and (d) ZS.

increased after the introduction of the 10 and 20 vol% $\text{ZrO}_2\text{--SiO}_2$ suspensions, and it then decreased gradually with the increasing of the air content and the particle hydrophobicity; this is due to the decreasing of the surface tension and the increasing of the foam viscosity, both of which resulted from higher particle concentration. The influence of the variation of the $\text{ZrO}_2\text{--SiO}_2$ content on the wet foam stability from 80% to 85% exhibited high air content between 75% and 95%, which resulted in a Laplace pressure of 1.5–1.7 mPa. A much higher adsorption free energy of approximately 5.8×10^8 to 7.5×10^8 J was also exhibited at the interface, which resulted in an irreversible adsorption of the particles at the air–water interface,

thereby leading to outstanding foam stability. The DTA/TGA study revealed the formation of the Al_2TiO_5 phase, as well as crystallization, at around 1260 °C through the presence of endothermic peaks. The sintering of the pure Al_2TiO_5 foam at 1500 °C produced a large-grain and cracked microstructure, whereas the addition of the $\text{ZrO}_2\text{--SiO}_2$ suspension produced a fine-grain microstructure. The porous ceramics with pore size from 150 to 400 µm on average were obtained. Due to the presence of the ZrTiO_4 , mullite, and ZrSiO_4 phases in the porous ceramics, the grain boundary microcracks of the Al_2TiO_5 ceramics decreased, which presumably improved the mechanical properties. All of the exhibited ATZS composites basically consisted of open and interconnected pores with a fine size distribution of the Al_2TiO_5 , ZrTiO_4 , and other grains in the AT, ATZS1, ATZS3, and ATZS5 samples.

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