Formation, Phase Stability, and Characterization of Unstabilized Aluminum Titanate (Al_2TiO_5) Ceramics

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Abstract

In the present study, Al_2TiO_5 was prepared via the sol–gel technique then sintered at 1000°C to 1300°C for 1 h. The thermal stability of the formed ceramic bodies was explored. The densification parameters, microstructure, and phase composition of the sintered Al_2TiO_5 ceramic were examined, and the mechanical properties and thermal coefficient were characterized. The phase composition study revealed the presence of alumina and TiO_2 residuals up to 1100°C. Phase stability was observed in Al_2TiO_5 bodies sintered up to 1300°C. The vitrification behavior of the bodies was improved by increasing the sintering temperature. The thermal expansion coefficient of the sintered samples sintered at 1300°C was enhanced by the formation of rod-like Al_2TiO_5 grains. Increases in the bending strength (from 22.40 to 28.90 MPa) and hardness ($HV_{0.1}$; from 1467 to 1873) were observed when the treatment temperature was increased from 1000°C to 1300°C.

1. Introduction

Aluminum titanate (Al_2TiO_5) is drawing extensive attention because of its unique properties. Al_2TiO_5 possesses a low thermal expansion coefficient (TEC) of about $1 \times 10^{-6}\ K^{-1}$, together with a high melting temperature (1860°C). Such properties allow Al_2TiO_5 to act as an excellent thermostable, fireproof material for many high-temperature applications, such as casting tools and crucibles for the casting and melting of metallic systems [1–4]. Preparation of Al_2TiO_5 through a solid-state reaction produced orthorhombic crystals with the following parameters: a = 3.591, b = 9.429, and c = 9.636 [5, 6].

Many methods have been adopted for the preparation of Al_2TiO_5 ceramics. These include the sol–gel [7], atmospheric plasma spray (APS) [8], spark plasma sintering (SPS) [9], melt synthesis [10], impregnation [11, 12], and precipitation and co-precipitation methods [13].

Nano Al_2TiO_5 was prepared at a low temperature via the sol–gel technique using titanium tetrabutoxide ($Ti(OC_4H_9)_4$), aluminum chloride ($AlCl_3$), and citric acid monohydrate as a chelating agent [7]. A previous study [14] adopted the sol–gel technique with phase secession to prepare monolithic Al_2TiO_5. Polyethylene oxide (PEO) and formamide (FA) were found to dominate the phase secession and gel formation. The usage of adequate quantities of PEO and FA permitted the formation of an Al_2TiO_5 xerogel that had a monolithic structure with a continual macroporosity exceeding 60%. Heat treatment of the dried gel at 1300°C produced Al_2TiO_5 as the only present phase.

The solid-state reaction technique was adopted to manufacture Al_2TiO_5-based ceramics. The starting materials were aluminum sludge (industrial waste) and rutile ore. Findings showed that the presence of MgO, SiO_2, Fe_2O_3, ZrO_2, and CaO played a large role as stabilizing oxides that led to the production of Al_2TiO_5 ceramics with excellent properties [15].

Azarniya et al. [2] fabricated Al_2TiO_5 powder and nanofibers via citrate sol–gel-assisted electrospinning. They showed that the presence of citric acid encouraged the Al^{3+} and Ti^{4+} ions to form atomic clusters and to turn them up to nanosized grains during the calcination operation. The lower the citric acid–metal cation ratio, the higher the quantity of crystallized nuclei, which in turn would lead to a smaller grain size. Moreover, firing at temperatures higher than 900°C led to the decomposition of Al_2TiO_5 into rutile and alumina, and complete degradation occurred at 1050°C.

The nonhydrolytic sol–gel (NHSG) technique was used during linear self-assembly of starting materials to prepare Al_2TiO_5 fibers. Introduction of stabilizing ions (Mg and Fe ions) could form Mg-O-Ti, Fe-O-Ti, Mg-O-Al, and Fe-O-Al bonds, which enhanced the formation of Al_2TiO_5 at a low temperature of about 750°C. Simultaneously, introduction of the Mg and Fe ions into the Al_2TiO_5 lattice enhanced the stabilization of the formed phase. The produced Al_2TiO_5 fibers possessed unique properties. They had low thermal expansion and high resistance to hot salt melt corrosion [16].

Al_2TiO_5 ceramics with high resistance to crack propagation were prepared from alumina and titania co-doped with Mg^{2+} and other ions, such as Y^{3+}, La^{3+}, and Nb^{5+}. Sintering of the samples co-doped with $MgO + La_2O_3$ at 1500°C produced bimodal Al_2TiO_5 grains. Sintering at such a high firing temperature produced a glassy phase that was responsible for the formation of elongated grains. The produced elongated grains enhanced the mechanical strength through crack propagation resistance. The authors claimed that the grain length growth caused an increase in the estimated length of the frontal process zone and the grain pull-out, bridging, crack deflection, and crack branching mechanisms. Moreover, the co-doping of $MgO + Y_2O_3$ resulted in bending strength lower than that obtained from $MgO + La_2O_3$. This regression in the bending strength of the samples was due to their granular microstructure. Finally, MgO-Nb_2O_5 co-doping resulted in ceramic samples with bad mechanical properties. The reason was that large rectangular grains formed because of the liquid-phase sintering [1].

A previous study reported that doping with MgO, Fe_2O_3, or SiO_2 as a sole additive improved the mechanical properties and decreased the TEC of Al_2TiO_5 ceramics prepared from α-alumina and TiO_2 via a solid-state reaction. Co-doping of MgO with Fe_2O_3 or SiO_2 enhanced the densification parameters and mechanical properties of samples fired for 3 h. In the case of co-doping with $MgO + SiO_2$, $MgAl_2O_4$ and Mg_2SiO_4 might form. These newly formed phases would enhance the stability of the Al_2TiO_5 by increasing the Al_2TiO_5 lattice constant (c). Furthermore, co-doping with $MgO + Fe_2O_3$ improved the thermal shock resistance of the produced bodies, but its effect on the mechanical properties was limited [4]. Some authors claimed that modulation of Al_2TiO_5 ceramics prepared via a solid-state reaction with MgO, SiO_2, Fe_2O_3, or their combinations can only prevent the decomposition of Al_2TiO_5, hence stabilizing the Al_2TiO_5 structure [17, 18]. In a recent study, the authors proved that the addition of MgO, Fe_2O_3, and their combination enhanced the formulation of elongated grains and grain boundary microcracks. Such elongated grains tend to interconnect, thus hindering crack diffusion and improving mechanical properties [19].

2. Materials And Methods

In this work, the starting materials for the synthesis of Al_2TiO_5 were aluminum tri-isopropoxide $(C_3H_7O)_3$-Al with a purity > 99% trace metals basis (Sigma-Aldrich, Germany), titanium tetrabutoxide ($C_{16}H_{36}O_4Ti$) [titanium (Ⅳ)-n-butoxide] (Strem Chemicals, Newburyport, MA, USA), distilled water, ethanol, and nitric acid.

2.1. Preparation of Al_2TiO_5

The stoichiometric weights of aluminum tri-isopropoxide and titanium tetrabutoxide were calculated for the synthesis of 100 g powder of Al_2TiO_5. The required amount of aluminum isopropoxide was hydrolyzed in distilled water at a ratio of 1:10 (Al:H_2O) under vigorous stirring at 80°C for 3 h. Peptization of the produced sol was attained by the addition of 2 ml nitric acid to form a stable, homogeneous sol (sol A). Concurrently, an equivalent amount of titanium butoxide was dissolved in absolute ethanol and H_2O then added dropwise to the Ti-ethanol mixture until a complete Ti:H_2O ratio of 1:20 was achieved under vigorous stirring at room temperature. Nitric acid was added to ensure complete hydrolysis of the mixture into a stable, homogeneous, transparent sol (sol B).

Sol B was added dropwise to sol A under gentle stirring at 80°C until gelation. This honey-like gel was dried at 120°C in a drier for 24 h and then ground into powder. The powder was calcined to remove all organic and nitrate species in an electric oven for 2 h at 900°C. After being cooled, the powder was collected at ambient temperature. The heating and cooling rates were kept constant at 5°C/min. The grain size of the powder was then reduced, and deagglomeration was conducted in a planetary ball mill by using a zirconia jar, lid, and 3 mm balls at 300 rpm for 2 h.

2.2. Characterization

For physical and microstructural characterization, 220 MPa uniaxial pressing was performed to create disks with a 13 mm diameter and ~ 4 mm height. For mechanical and thermal evaluation, rectangular bars measuring 6 × 6 × 60 mm were formed.

The formed samples were subjected to pressureless heat treatment up to 1300°C in a static air atmosphere at a heating rate of 5°C/min with 1 h soaking at the peak temperature. The phase compositions of the prepared powders and sintered samples were examined with a Philips PW 1730 X-ray diffractometer.

The particle size, morphology, and agglomeration tendency of the Al_2TiO_5 powder calcined at 900°C for 2 h were studied via transmission electron microscopy (TEM; JEM-2100-HR electron probe microanalyzer, JEOL, Japan) at 200 kV. The TEM sample was prepared by dispersing a small amount of powder in acetone using ultrasonic energy (20 kHz, 500 W) for 30 min. A drop of the well-dispersed suspension was deposited onto a carbon-coated grid (400 mesh), which was then dried for the evaporation of the solvent.

Scanning electron microscopy (SEM; JSM-T20, JEOL, Japan) was used to examine the microstructure of the sintered specimens. The densification characterizations of the specimens in terms of apparent porosity and bulk density were evaluated via Archimedes' method (ASTM C-20).

The bending strength of the sintered samples sintered at different sintering temperatures was evaluated using the three-point bending test according to ASTM C1161-13 using a universal testing machine with a 5 kN capacity (LRX5K, Lloyd). The bending strength of at least ten specimens at each temperature was measured according to the following equation:

$\sigma = (3P_fL)/(2wt^2)$,

where σ is the bending strength; P_f is the load at the fracture point; and L, w, and t are the specimen length, width, and thickness, respectively.

The Vickers microhardness of the mirror-polished samples sintered at 1000°C, 1200°C, and 1300°C was determined using a microhardness tester (OmniMet automatic MHK system and MicroMet 5114 microindentation hardness tester, Buehler, USA). The Al_2TiO_5 specimens were polished down to 5 µm surfaces, finished using 1 µm diamond paste, and thermally etched at 1000°C for 30 min in air. Indentations were made on the polished surfaces with a 0.1 N load and 15 s dwell time. The average hardness of at least 30 indents was calculated according to the following equation:

$H_v = 1.8544(P/d^2)$,

where p and d are the applied load and length, respectively, of the impression diagonal [20].

Thermal expansion measurements were conducted on specimens sized 25 × 5 × 5 mm at room temperature up to 1000°C using alumina thrust at a heating and cooling rate of 5°C/min using a dilatometer (DIL 402 PC, Netzsch). The TEC (α) was calculated according to the following equation:

$\alpha = (dL/L) / dT$,

where L is the length of a sample at room temperature (T).

3. Results And Discussion

3.1. Phase composition and grain size

The X-ray diffraction (XRD) patterns of the prepared Al_2TiO_5 gel calcined at different calcination temperatures are presented in Fig. 1. The figure indicates the presence of alumina and TiO_2 residuals up to 1100°C, which means that calcination up to 1100°C was insufficient for reaction completion. According to Azarniya et al. [21], the preparation technique greatly affects the purity of the produced Al_2TiO_5 phase. They reported that the hydration of Al^{+3} during the sol–gel process, ion oxidation, and

slow Al_2TiO_5 phase formation are the main reasons for the presence of Al_2O_3 and TiO_2 phases at low calcination temperatures up to 1100°C. They also found that the thermal instability of Al_2TiO_5-based ceramics reached its maximum level at around 1100°C. This thermal instability is responsible for the decomposition of Al_2TiO_5 into Al_2O_3 and TiO_2 [22].

In the present work, increasing the calcination temperature to 1200°C enabled the full formation of the Al_2TiO_5 phase. During calcination at 1300°C, the intensity of the Al_2TiO_5 phase peak was increased, indicating the full formation of the phase. Notably, the increase in the calcination temperature to 1300°C did not result in dissociation of the formed phase.

The grain size of the calcined Al_2TiO_5 powder, as examined via TEM, is shown in Fig. 2. The figure indicates that the size of the formed Al_2TiO_5 was at the nanoscale. The grain size ranged between 55.62 and 88.06 nm.

3.2. Densification

The densification parameters of the Al_2TiO_5 bodies are given in Figs. 3a and 3b. The figures show that the densification parameters of the samples, namely, the bulk density and apparent porosity, were considerably influenced by the sintering temperature. The bulk density gradually increased while the apparent porosity reduced with the rise in the sintering temperature. The samples exhibited the maximum bulk density and minimum apparent porosity during sintering at 1300°C. Traditional Al_2TiO_5 preparation techniques, such as reaction sintering of mechanically alloyed starting materials and solid-state reaction preparation routes, produce Al_2TiO_5 at high temperatures ranging between 1400°C and 1500°C [23, 24]. In the present study, the use of the sol–gel technique to prepare Al_2TiO_5 powder enabled the production of nanosized powder, which in turn enhanced the densification of the produced bodies at a low sintering temperature of 1300°C.

In addition, the calcination of the starting batches aided in the vitrification of the studied samples. Hareesh et al. [25] found that the vitrification efficiency of Al_2TiO_5 bodies is affected by the calcination temperature, as the formation of metastable phases, such as anatase and transition alumina (which form during the calcination process), is highly reactive and thus enhances the sintering and densification of Al_2TiO_5 samples. They found that the sintered density of the studied bodies (sintered at 1300°C) increased from 79–97% upon increasing the calcination temperature from 600°C to 1000°C. The observed enhancement in bulk density and reduction in porosity with the increase in sintering temperature was attributed to the grain boundary improvement and the high ion propagation rate [26].

3.3. Microstructure

The SEM study indicated that the microstructure of the sintered samples was generally composed of homogeneously distributed Al_2TiO_5 grains. The high reactivity and chemical homogeneity produced from the sol–gel technique might have been responsible for this result. The micrograph in Fig. 4 shows that

the sintered samples consisted of Al_2TiO_5 grains with different shapes and sizes. Some of the Al_2TiO_5 grains were rod-like in shape and had a fine grain size. Remarkably, the microstructure of the samples did not suffer from the presence of microcracks.

3.4. Thermal Expansion Coefficient (TEC)

The TECs of the sintered samples at 1300°C were measured at different temperatures from 100°C to 1000°C, and the results are presented in Fig. 5. The TECs of the sintered samples at all tested temperatures (100°C to 1000°C) were small (0.25 to 0.73 × 10^{-6}/°C). These findings suggest hysteresis, which is exemplary for Al_2TiO_5 bodies [27]. Furthermore, the TEC is generally inversely proportional to the grain growth of Al_2TiO_5. However, in the present study, the fabricated Al_2TiO_5 samples had a fine grain size and a low TEC of 0.73 × 10^{-6}/°C at 1000°C. The increase in the TEC by the rise in the sintering temperature might have been due to the reinforcement of the rod-like grains via the glassy phase sintering, which gave the Al_2TiO_5 samples excellent thermal properties [28].

3.5. Mechanical behavior

The mechanical properties (bending strength and Vickers hardness) of the Al_2TiO_5 sample sintered at 1000°C, 1200°C, and 1300°C are shown in Figs. 6a and 6b. The increase in the sintering temperature from 1000°C to 1300°C improved both the bending strength (from 22.40 to 28.90 MPa) and the hardness (from 1467 to 1873) of the sintered bodies. Such effect was attributed to the improvement in the densification parameters of the samples with the sintering temperature increase. Likewise, the absence of cracks at the grain boundaries and the fine grain size of the microstructure enhanced the mechanical properties of the samples [28]. Moreover, the start of the formation of the rod-like grains with the increase in the sintering temperature effectively helped improve the mechanical properties of the samples [29, 30].

4. Conclusions

1. Al_2TiO_5 was synthesized via the sol–gel technique, and full formation of Al_2TiO_5 was detected at 1200°C. Calcination at 1300°C increased the intensity of the Al_2TiO_5 phase peak without decomposing the formed phase.

2. Preparation of Al_2TiO_5 powder through the sol–gel technique led to the production of nanosized Al_2TiO_5 powder, which in turn benefited the studied batches' densification.

3. The bending strength and Vickers hardness increased by 30% and 28%, respectively, as the sintering temperature rose from 1000°C to 1300°C.

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Figures

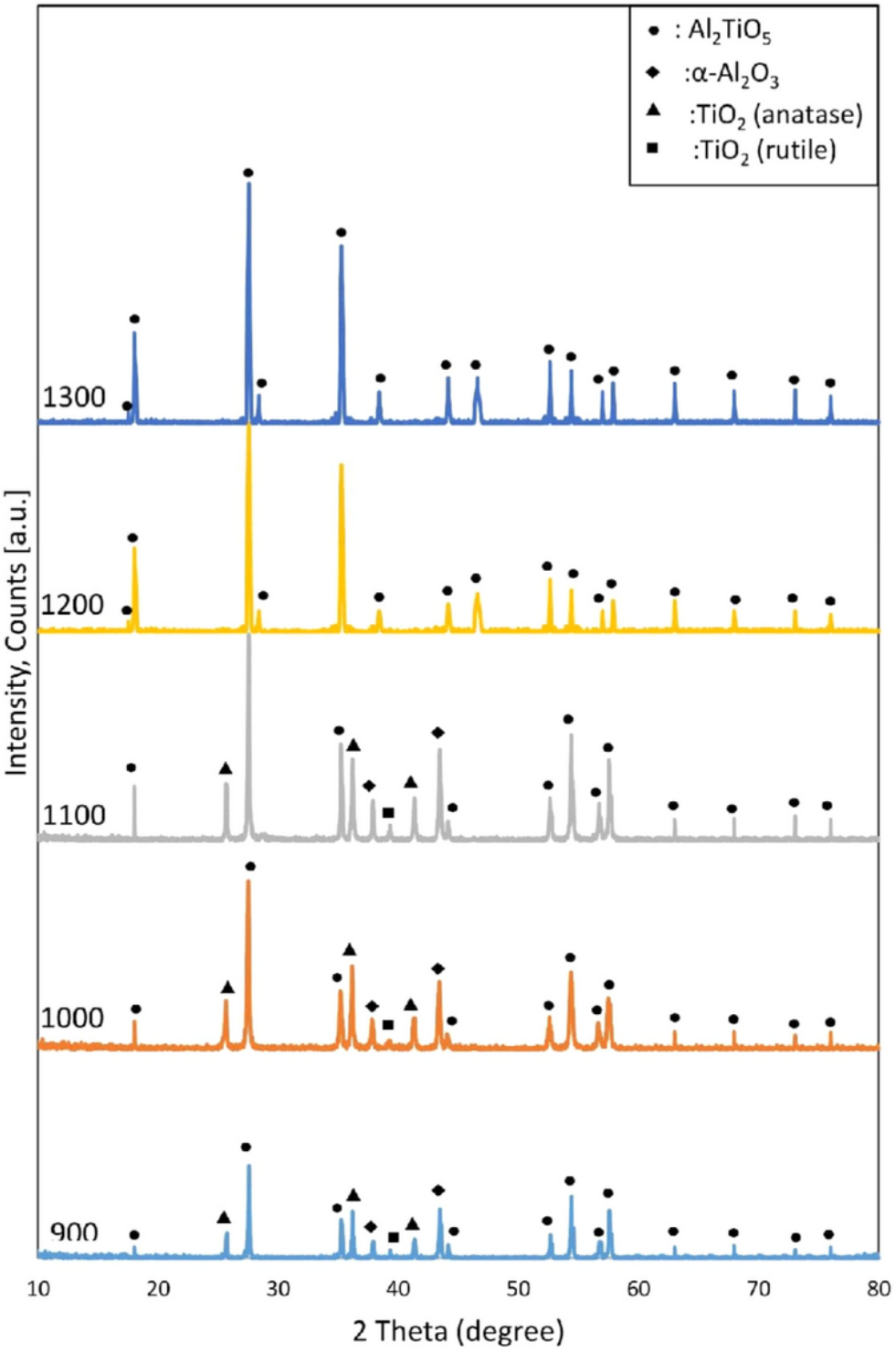


Figure 1

XRD patterns of Al2TiO5 gel calcined at different temperatures.

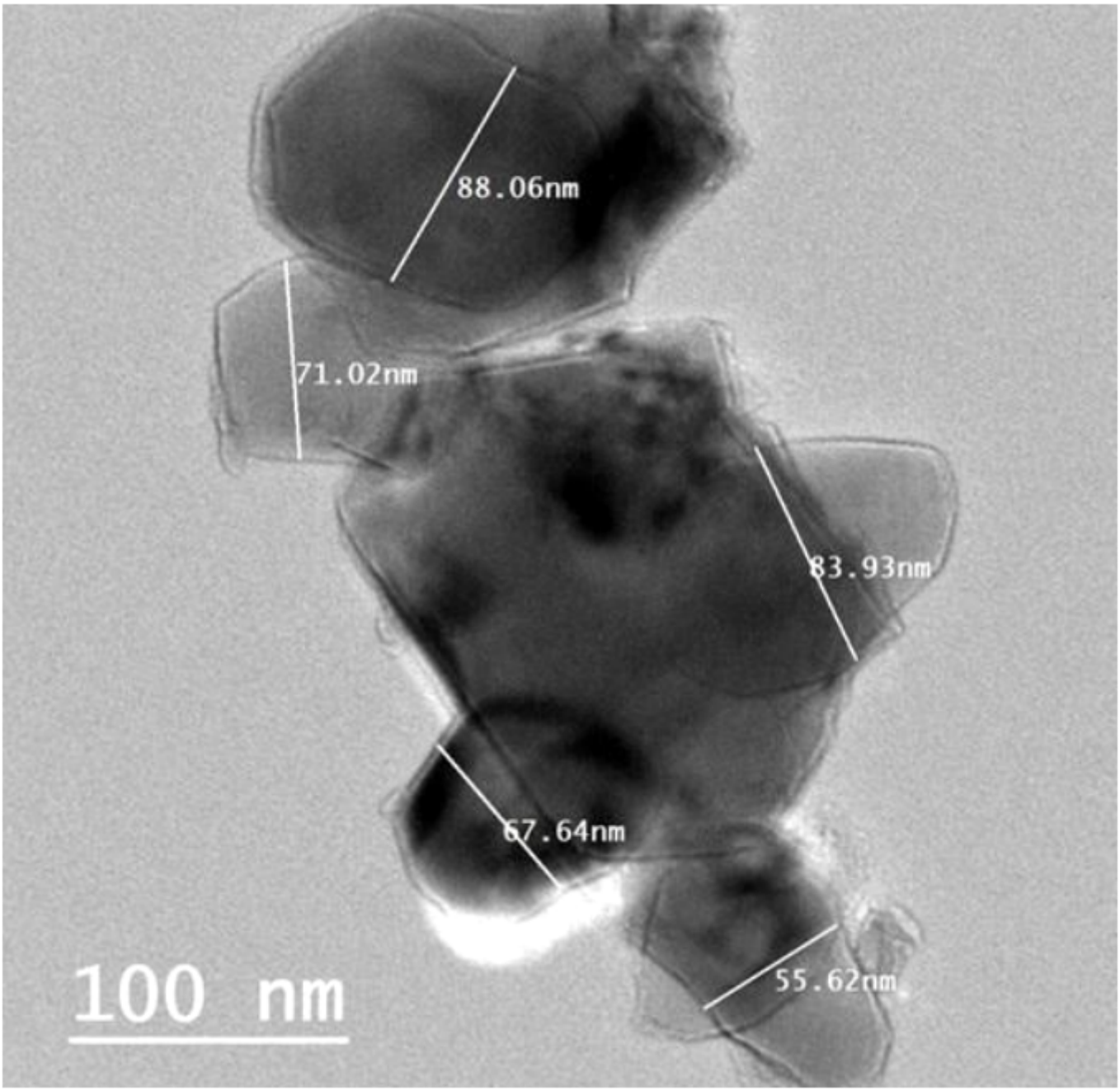
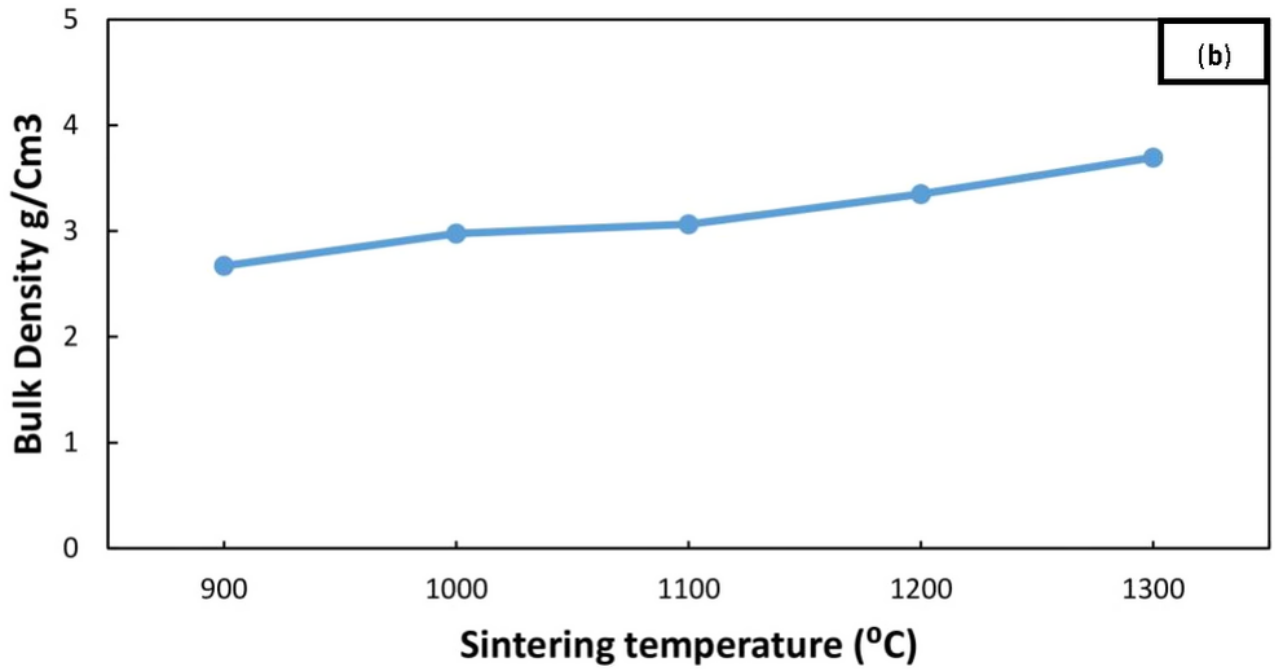


Figure 2

TEM micrograph of calcined Al2TiO5 gel.



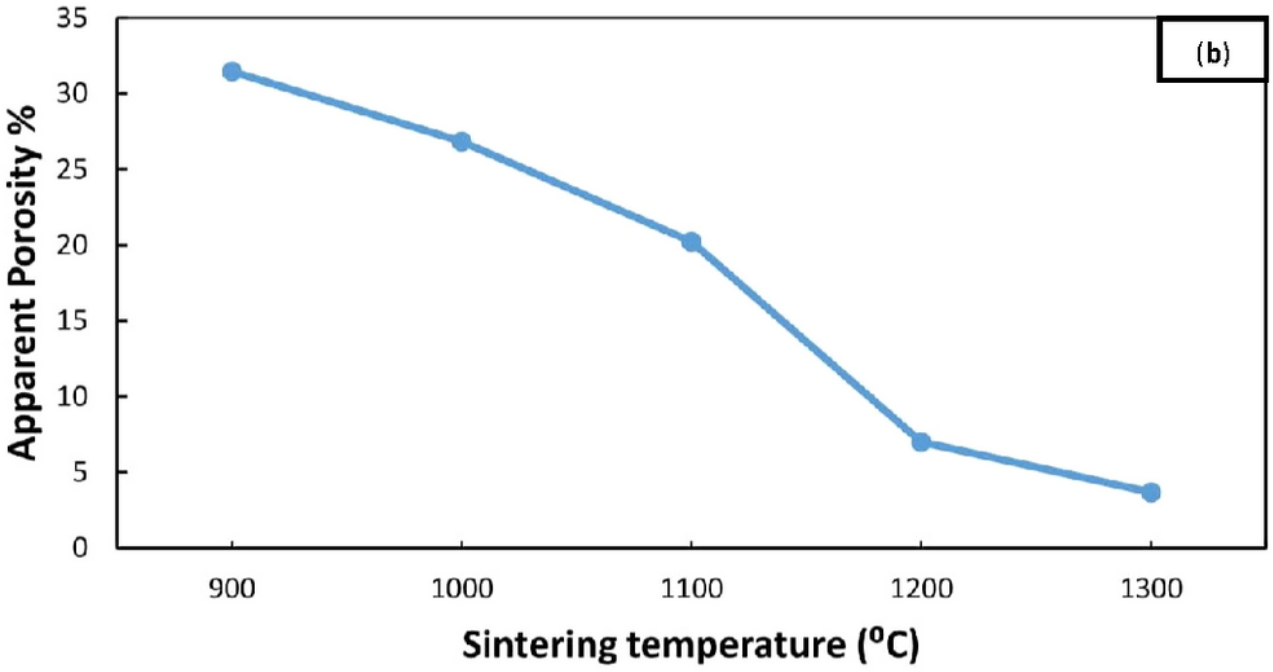


Figure 3

Vitrification parameters of Al2TiO5 samples sintered at various sintering temperatures: (a) bulk density (g/cm3); (b) apparent porosity (%).

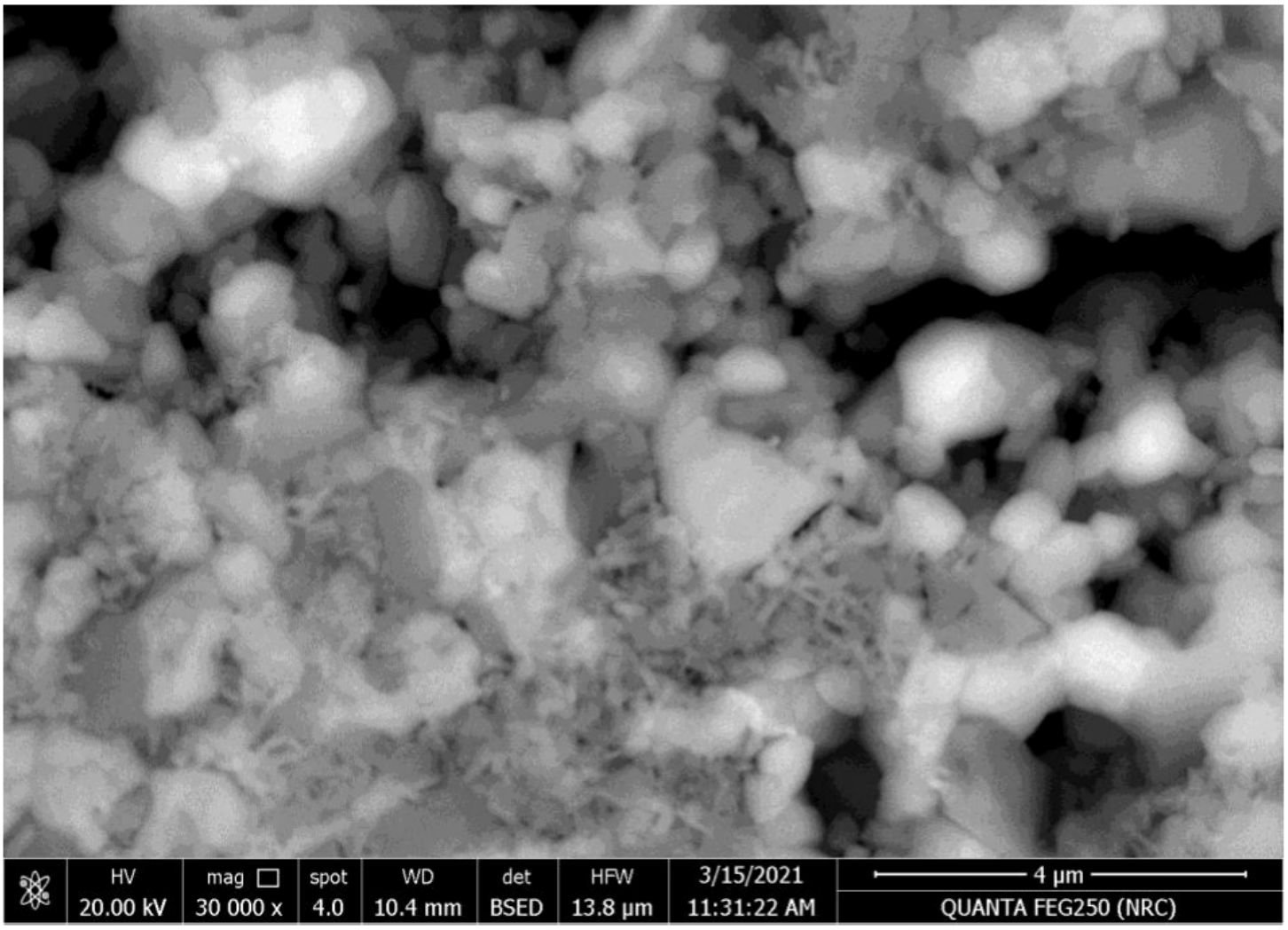


Figure 4

SEM micrograph of sintered sample sintered at 1300 °C.

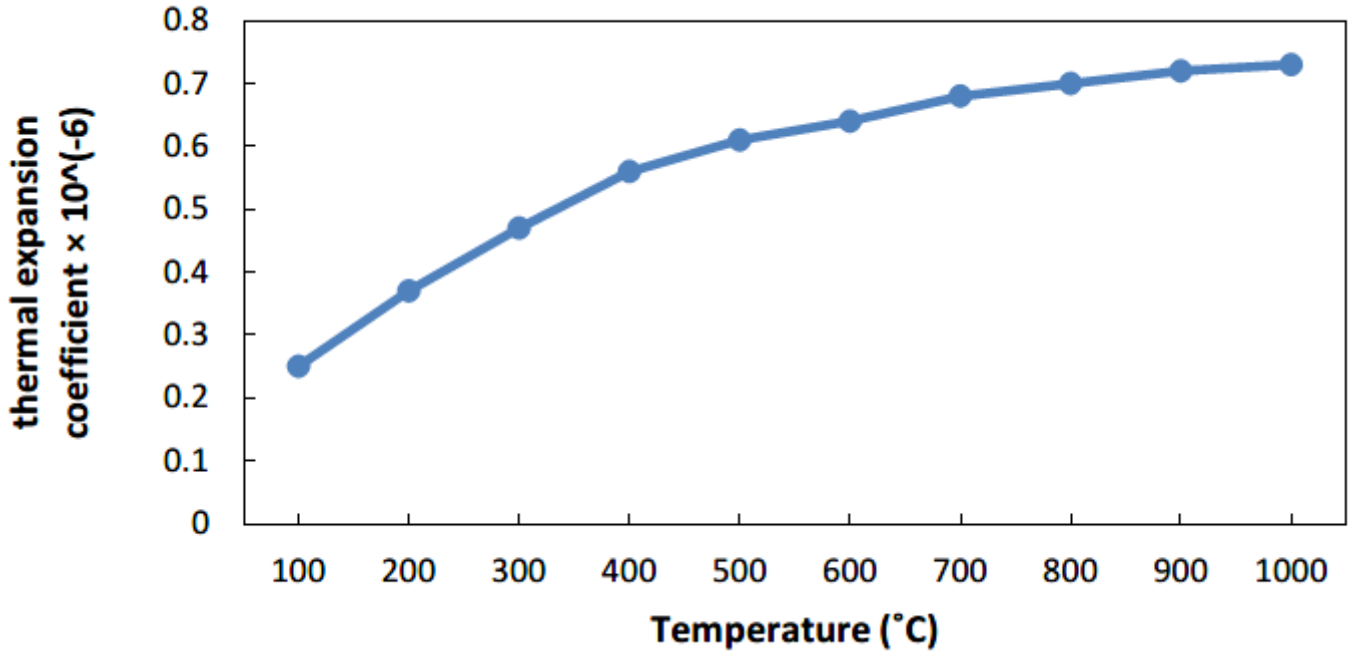


Figure 5

TEC of sintered sample measured at 100 °C to 1000 °C.

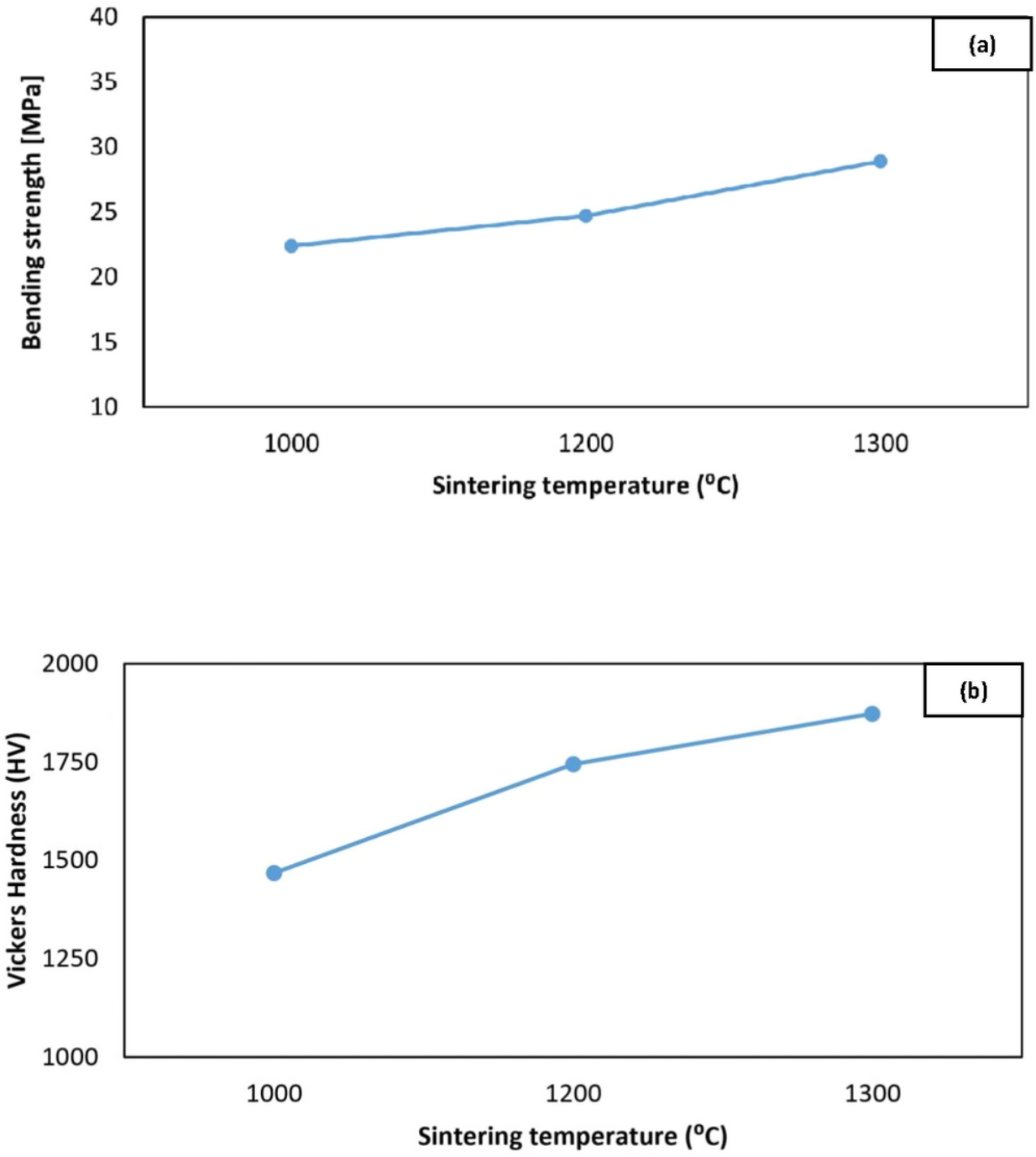


Figure 6

Mechanical behavior of Al2TiO5 samples sintered up to 1300 °C: (a) bending strength; (b) Vickers hardness.