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博士学位論文

Development of Electrically Multifunctionalized Ti-dispersed Al_2O_3 Composites with Photochemical and Crack-healing Behaviors

(電氣的に多機能性した Ti 分散 Al_2O_3 複合材料の
創製とその光化学およびき裂修復挙動)

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2018 年 7 月

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マテリアル生産科学専攻

Preface

This studies presented in this thesis were carried out under the supervision of Professor Tohru Sekino at The Institute of Scientific and Industrial Research, Graduate School of Engineering, Osaka University during 2015-2018.

Al₂O₃ is one of the most promising structural ceramics with excellent bending strength, good wear behavior, high temperature resistance and good chemical stability. However, the relatively low fracture toughness greatly limited their applications. The present study aims to solve the brittleness of Al₂O₃ ceramics by incorporating with dispersed Ti metal particles and develop new functions, such as electrical properties, photochemical and crack-healing ability to realize multifunctional applications of ceramic-based materials. In addition to properties investigated in this study, more functions remain to be developed.

The authors hope that the concepts and findings obtained in this study will contribute to the progress in science and engineering.

SHENGFANG SHI

July, 2018

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General introduction

1.1 Ceramic/metal composites

As structural materials, ceramics have favorable mechanical properties, such as superior high hardness, excellent compressive strength, good wear resistance and high elastic modulus^[1]. Ceramics have been received significant attention when subjected to sever application conditions, including high temperature, wear and chemical attack. However, ceramics are essentially brittle which greatly limits their applications. Thus, various toughening methods have been developed with the purpose of improving fracture toughness. Toughening mechanisms are concluded in Table 1.1.

Table 1.1 Classification of toughening mechanisms in ceramics^[2].

General mechanism	Detailed mechanism
• Crack deflection	Tilt and twist out of crack plane around grains and second-phase additions
• Crack bowing	Bowing in crack plane between second-phase crack-pinning points
• Crack branching	Crack may subdivide into two or more roughly parallel cracks
• Crack tip shielding by process zone activity	Microcracking; Transformation toughening Ductile yielding in process zone
• Crack tip shielding by crack bridging	Second-phase brittle fibers with partial debonding Frictional and ligamentary grain bridges Second-phase ductile ligament bridging

Recently, ceramic based composites have been extensively fabricated and studied to solve the problems of low fracture toughness with poor reliability of ceramic matrix. Niihara firstly proposed the concept of ceramic nanocomposites by introducing second metal or ceramic nanoparticles into ceramic matrix for increasing fracture toughness. Based on particle location of second phase, ceramic nanocomposites are classified into four types as given in Figure 1.1^[3].

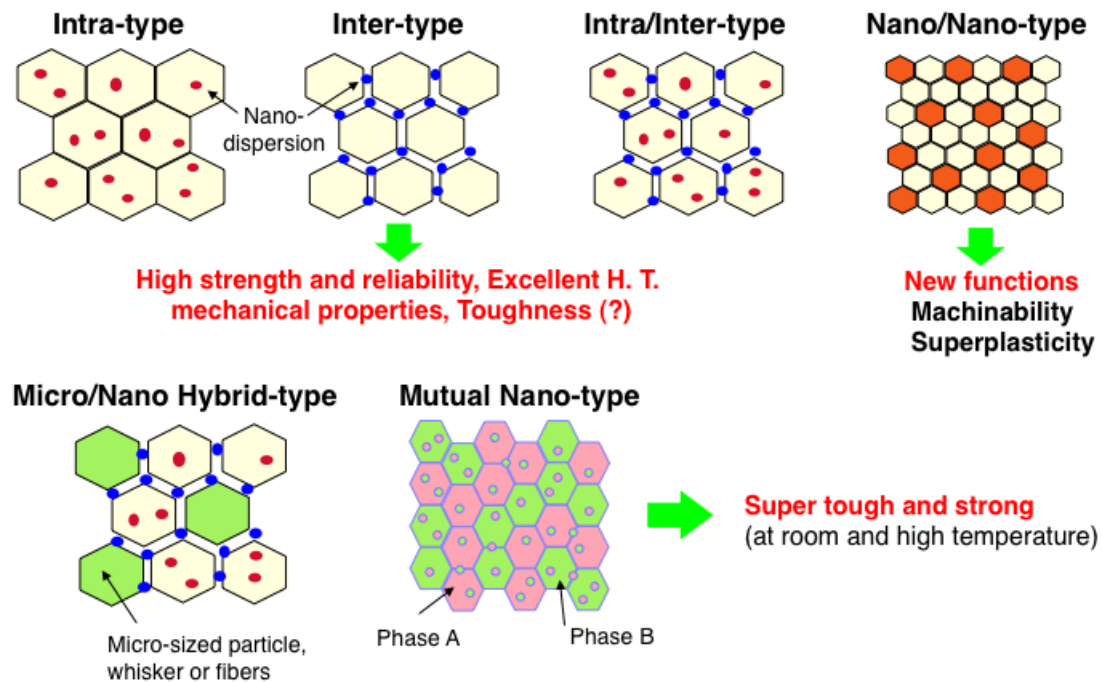


Figure 1.1 Niihara's classification of nanocomposites structures.

When second phase dispersing into ceramic matrix is metal, composites are known as ceramic-metal composites or cermet. Investigations on ceramic/metal composites have revealed that dispersing nanosized metals into a ceramic matrix can prevent crack propagation caused by plastic deformation, thereby increasing fracture toughness^[4]. Ceramic/metal composites having both ductility and toughness of metal phase and

strength and hardness of ceramic matrix makes them attractive in study and application. In addition of mechanical properties, Ceramic/metal composites could give new functions, such as magnetic, optical electrical properties. Ceramic/metal composites have been promising materials in cutting tools, lightweight armor, electrical device and anti-corrosion coating^[5].

At present, different ceramic/metal composites systems have been extensively studied and obtained better improvement effects. Sekino et al^[6] achieved nano-sized nickel dispersed $\text{Al}_2\text{O}_3/\text{Ni}$ nanocomposites and increased fracture toughness from $3.5 \text{ MPa}\cdot\text{m}^{1/2}$ of monolithic Al_2O_3 to $4.5 \text{ MPa}\cdot\text{m}^{1/2}$ of $\text{Al}_2\text{O}_3/\text{Ni}$ nanocomposites when Ni content was 20%. Composites with various volume ratios of partially stabilized zirconia (PSZ) and pure Ti were fabricated by Tohgo et al^[7]. In their report, effectiveness of sintering methods on mechanical properties were studied and it was concluded that fracture toughness of the composites fabricated by spark plasma sintering was higher than that of the composites by hot press sintering. When 5 vol% nano-sized Cr particles were imbedded into Al_2O_3 matrix, fracture toughness was found to be increased from $3.6 \text{ MPa}\cdot\text{m}^{1/2}$ to $4.0 \text{ MPa}\cdot\text{m}^{1/2}$ using a chemical method^[8]. The compositing of ZrO_2 and Ti realized the electrical properties by decreasing electrical resistivity from $10^{10} \Omega\text{cm}$ to $10^{-2} \Omega\text{cm}$ when Ti content was 30 vol% which changed ZrO_2 from insulator into conductor at room temperature^[9]. It is believed that ceramic/metal composites having both high mechanical properties and multifunctions are one of the advanced materials with wide potential application range in future.

1.2 Self-healing ceramics

Owing to essential brittleness, cracks easily occur on the surface and/or inside of ceramics causing strength degradation and resultant lowering of reliability even during general machining process and use as well. During application of ceramics, it is essentially important to prevent these surface cracks as well as various defects such as pores, micro- and nano-sized voids which were often induced during ceramic fabrication (i.e. sintering). Although toughening of ceramics is an effective way to stop the propagation of cracks, it is impossible to eliminate cracks completely. In order to avoid these surface cracks, precise polishing or lapping with high cost and low efficiency is necessary. Inducing self-healing ability into ceramics is considered to be promising method to solve these problems. At present, self-healing ability induced by heat treatment in ceramic-based composites has been already reported^[10,11,12,13,14,15,16]. At high temperature, crack healing behavior is ascribed to the filling of cracks by oxides while in monolithic ceramics, crack healing is owned to the re-sintering of cracks. For instance, by heat-treatment at 1900 °C, bending strength of Al₂O₃ recovered from 35.9 to 148 MPa^[17]. However, re-sintering needs high temperature which is usually higher than application temperature of ceramics. Therefore, dispersing second phases, e.g., Si, Ti, Si₃N₄, SiC, into ceramic matrix to form oxides by thermal heating is a general way to heal cracks. Schematic illustration of self-healing mechanism at high temperature is given in Figure 1.2^[18].

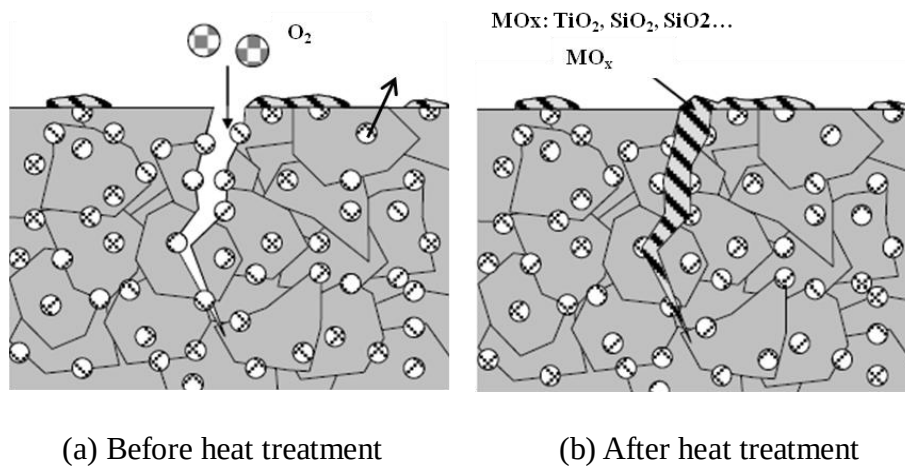


Figure 1.2 Schematic illustrates of the self-healing mechanism of ceramic-based composites.

There are several advantages to induce self-healing ability in ceramics. For example, if the surface cracks are self healed after an efficient machine operation, there is a great advantage in fabrication efficiency and fabrication cost. If surface cracks can be healed completely, a full recovery of flexural strength could be achieved or even higher than that of matrix. Nevertheless, self-healing ability reported nowadays for ceramic is induced only at high temperature with long time. It is necessary to introduce and verify new self-healing methodology which could allow the healing of cracks at relatively low, hopefully at room temperature.

1.3 Al_2O_3 /Ti composites

1.3.1 Toughening of Al_2O_3 ceramics

Al_2O_3 ceramics are widely used in the aerospace, electronics, and chemical industries along with other fields because of their high bending strength, good wear behavior, high

temperature resistance, good chemical stability, relatively low production cost and abundance of element^[19,20,21]. Due to their high wear resistance and strength, Al₂O₃ ceramics are also used as bio-compatible materials such as artificial bone, hip-joint and so on. However, the application of Al₂O₃ ceramics as structural components is limited by their brittleness, which is attributed to low fracture toughness^[22,23].

Nowadays, various methods have been developed to improve mechanical properties of Al₂O₃ ceramics. Lach et al^[22] prepared Al₂O₃/YAG (aluminum-yttrium garnet) composites and increased fracture toughness from 4.5 MPa·m^{1/2} of monolithic Al₂O₃ to 6.6 MPa·m^{1/2} of Al₂O₃/10%YAG composite. Sekino et al^[24] achieved the dispersion of nano-sized tungsten particles into Al₂O₃ matrix indicating improved fracture toughness. Lee et al^[25] reported at 1200°C, Al₂O₃/10 wt% FeNi composite showed the highest fracture toughness of 5.1 MPa·m^{1/2} while it was 2.6 MPa·m^{1/2} of monolithic Al₂O₃.

However, among all these composites, as mentioned above, when the second phase is metal, dispersing metal particles into ceramic matrix has been widely attempted to improve mechanical properties. In addition to showing improved mechanical properties, compared to the corresponding monolithic ceramics, ceramic/metal composites also exhibit new electrical, optical, and magnetic properties along with metal-like machinability and superplasticity^[4,6, 26, 27, 28]. In order to realize high mechanical properties and new functions, it is essentially important to choose appropriate second metal phases to disperse into Al₂O₃ matrix to improve brittleness and apply multifunctions. In the present study, I have focused and chosen Ti meal dispersion into Al₂O₃ ceramics to develop the multifunctional ceramic-metal system.

1.3.2 Metallic Ti

Titanium (Ti) with high strength-to-weight ratio makes it a quite ductile metal with low density. Ti and its alloys are widely used as structural components and biocompatible metal materials because of their high fracture toughness, relatively low density ($\sim 4.5 \text{ g}\cdot\text{cm}^{-3}$), and good biochemical stability^[29,30]. Owing to the good physicochemical consistency with Al_2O_3 , Ti was chosen as second metal phase to prepare $\text{Al}_2\text{O}_3/\text{Ti}$ composites in this study in order to improve mechanical properties of Al_2O_3 ceramic and to realize multifunctionality simultaneously.

1.3.3 Preparation of $\text{Al}_2\text{O}_3/\text{Ti}$ composites

$\text{Al}_2\text{O}_3/\text{Ti}$ composites can be formed by dispersing Ti particles into Al_2O_3 matrix. Considering these characteristics of Al_2O_3 and Ti along with the advantages of ceramic/metal composites mentioned above, incorporating nanosized Ti into Al_2O_3 might produce a composite with both the high strength of Al_2O_3 and high fracture toughness of Ti. Such a composite would have promising applications in advanced structural materials and biomaterials (e.g., artificial joints).

There are different preparing processes to obtain $\text{Al}_2\text{O}_3/\text{Ti}$ composites, which lie in the differences of raw materials and sintering methods. At first, there are two kinds of raw Ti materials. One is direct use of raw Ti powder by mixing with Al_2O_3 powder. The other is utilizing the decomposition of titanium hydride (TiH_2) during sintering to obtain fine Ti particle in situ. The decomposition temperature of TiH_2 into metal Ti is 400 - 600 °C. Liu et al^[1] prepared $\text{Al}_2\text{O}_3/\text{Ti}$ composites with pure Ti as original sintering material and the bending strength was higher than $5 \text{ MPa}\cdot\text{m}^{1/2}$. Meir et al^[31] reported that $\text{Al}_2\text{O}_3/\text{Ti}$ composites prepared by sintering the mixture of Al_2O_3 and TiH_2 powders

showed increased flexural strength while fracture toughness decreased with the increase of Ti content. Compared with pure metallic Ti, TiH_2 is brittle leading to fine TiH_2 powder by simple power processing such as ball milling. This method allows Ti to be homogeneously dispersed into the Al_2O_3 matrix via the in situ decomposition of the ball-milled TiH_2 fine powder during matrix consolidation. Secondly, there are different sintering methods in preparing $\text{Al}_2\text{O}_3/\text{Ti}$ composites, such as spark plasma sintering (SPS, often described also as PECS), pressureless sintering (PLS) and hot press sintering (HPS)^[31,32,33]. All of these sintering methods can obtain dense composites with improved mechanical properties by careful tuning of appropriate sintering sequences such as temperature, duration, atmosphere, pressures and powders/performs used for sintering as well.

1.3.4 Properties improvement of $\text{Al}_2\text{O}_3/\text{Ti}$ composites

In $\text{Al}_2\text{O}_3\text{-Ti}$ system, strong interfacial reactions between Ti and Al_2O_3 at high temperature lead to the formation of abundant Ti-Al intermetallic compounds, such as TiAl and TiAl_3 and oxides, such as Ti-O and TiAl_2O_5 . The thermodynamic study in $\text{Al}_2\text{O}_3/\text{Ti}$ system was conducted by G. Shi et al.^[32] and they provided the equations to calculate the value of Gibbs free energy of Ti_3Al and TiAl . At 1500°C , $\Delta G_{\text{Ti}_3\text{Al}}$ and ΔG_{TiAl} are calculated to be -138.0 kJ/mol and -77.8 kJ/mol , respectively. Due to the thermodynamic stability, intermetallic compound are easily formed at high temperature. These unfavorable interfacial reaction products will fill up grain boundary and bring about weakened bonding force to decrease the mechanical properties and restrict the application of $\text{Al}_2\text{O}_3/\text{Ti}$ composites^[33,34,35]. In particular, the existence of TiAl_2O_5 is adverse to the increase of fracture toughness due to intergranular micro-cracking, which

greatly limits its fracture toughness^[36]. Therefore, it is necessary to further control the interfacial reaction for optimized mechanical properties.

Nowadays, rare earth elements have been used as sintering additives to accelerate densification and increase mechanical properties by inhibiting the formation of these unfavorable phases in fabricating $\text{Al}_2\text{O}_3/\text{Ti}$ composites. The detail results available at present are concluded in table 1.2.

The pinning effect of additives to prevent grain boundary mobility for inhibiting the growth of grain size was reported and the change of morphology as a function of additive content is shown in Figure 1.3^[48]. Owing to the pinning effect, crack propagation could be prevented. However, the increased content in additives changed the combination mode of pinning particles from pinning to adhesion which changed the interfacial bonding mode between Al_2O_3 and Ti leading to a decrease in bending strength and fracture toughness. Therefore, it is essentially to determine the content of additive for improving mechanical properties.

Among these sintering additive, Y_2O_3 is reported as effective additives in preparing ceramics to improve mechanical properties by suppressing interfacial reactions, strengthening grain boundaries, refining grain size, increasing oxidation resistance and accelerating densification^[32,37,38,39]. During sintering, Y_2O_3 reacts with Al_2O_3 to form stable yttrium aluminum garnet ($\text{Al}_5\text{Y}_3\text{O}_{12}$, YAG) phases which shows superior high fracture toughness, high Vickers hardness and high temperature creep resistance^[40,22]. YAG particles, serving as reinforcing phase, are considered to homogenize stress field distribution^[41] and plays an important role in crack deflection which is recognized as an effective toughening mechanism^[42,43,44]. Phase diagram of Al_2O_3 - Y_2O_3 system is shown in Figure 1.4^[45]. It indicates that when Y_2O_3 content is below 30 mol% and sintered at

1500 °C, YAG phase could be formed.

Table 1.2 Properties of different sintering additives added $\text{Al}_2\text{O}_3/\text{Ti}$ composites.

Sintering additives	Sintering temperature	Appropriate addition content	Bend strength (MPa)	Vickers hardness (GPa)	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	Ref.
Nb	1420°C	2 vol%	390 (320)		9.8 (7.8)	[46]
Y_2O_3	1450°C	1 vol%	488 (280)	16.3 (10)	8.2 (5.5)	[33]
Y_2O_3	1420°C	1 vol%	302 (267)	16.8 (14.7)	6.5 (4.9)	[32]
Nd_2O_3	1420°C	3 vol%	412 (302)	15.8 (10.5)	8.8 (6.3)	[1]
CeO_2	1420°C	3 vol%	406 (335)	15.7 (13.3)	6.4 (4.4)	[47]
Pr_6O_{11}	1420°C	2 vol%	457 (335)	16.2 (11.8)	7.8 (4.5)	[48]

* Data in () is the value of corresponding properties of additive-free $\text{Al}_2\text{O}_3/\text{Ti}$ composites reported in each reference.

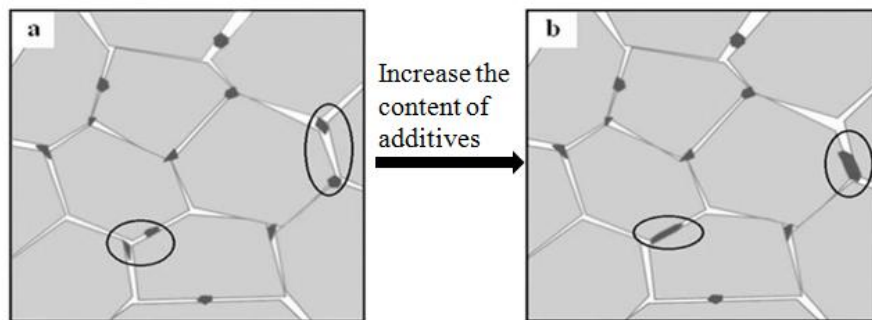


Figure 1.3 Change of morphology of pinning particles as a function of additive content.

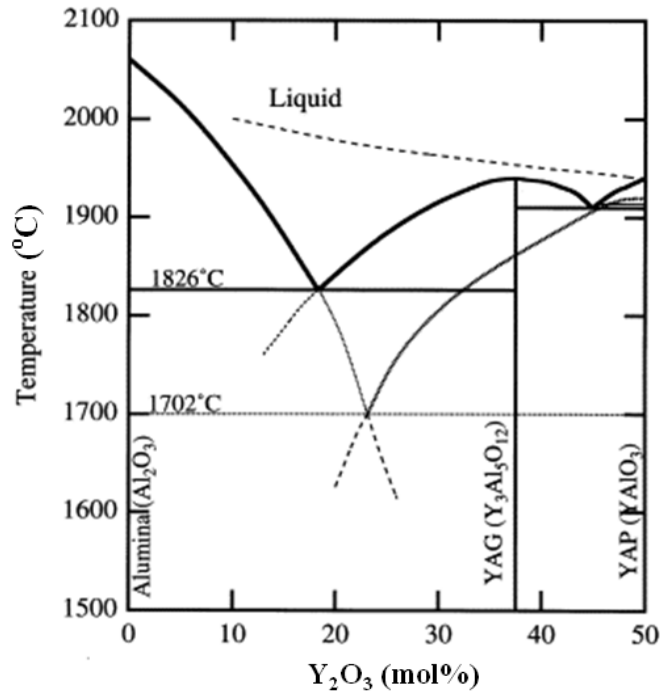


Figure 1.4 Phase diagram of Al_2O_3 - Y_2O_3 system.

1.4 Property characterization of $\text{Al}_2\text{O}_3/\text{Ti}$ composites

1.4.1 Mechanical properties

For structural ceramic, mechanical properties are essentially important. The characterization of mechanical properties of brittle ceramics usually contains Vickers hardness (H_v), Young's modulus (E), bending strength (σ) and fracture toughness (K_{IC}). It is well known that mechanical properties strongly depend on microstructures including grain size and shape, second or third dispersed (or precipitated) phases, grain boundaries and interfaces. Refined microstructure and homogeneously dispersed grains with small size are benefit for improving mechanical properties. In addition, densification has great effect on bending strength. The relationship between bending strength and porosity is given in equation 1.1^[48] indicating that with the increase in densification, bending

strength exponentially increases. Therefore, in preparation of Al₂O₃/Ti composites, it is significant to accelerate densification to obtain dense composites.

$$\sigma = \sigma_0 \exp (-np) \quad (1.1)$$

Where σ_0 is the theoretical strength, n is constant and p is the porosity.

1.4.2 Electrical properties

When the second phase is metal, one of the additional advantages of ceramic-metal composites is the electrical conductivity which leading to a wide application range. According to the Percolation theory, when second conductive metal phases are dispersed into insulated ceramic matrix, owing to the contact of metal particles with each other, a number of continuous conductive pathways could be formed. Electrical current can pass through these pathways and accordingly lead to the increased electrical conductivity. Possible current pathways in ceramic-metal composites are schematic in Figure 1.5.

Electrical properties of several ceramic-metal composites have been reported, e.g., Al₂O₃-Ti, ZrO₂-Ti, ZrO₂-Nb, ZrO₂-Ti and ZrO₂-Ni^[49]. In these systems, Brittleness of ceramics determines that cutting process is the only applicable machining method for making simple-shaped parts, such as rectangles or cubes. It is generally impossible to machine along curves for circle or more complex shapes. However, ceramic composites having high electrical conductivity can be machined by electrical discharge machining (EDM) method, which is a convenient and cost-effective way for preparing complex ceramic pieces and also avoid the damage caused by traditional machining process. In

addition, ceramic-metal composites with better electrical properties can be potentially used in a wide application range. For example, when composites show electrical resistivity behavior with positive temperature coefficient (PTC), which is usually found in metallic materials, it is possible to build devices sensible to temperature variation^[49].

As the proportion of metal phase increases to a certain level, namely the percolation threshold, metal particles start to connect with each other, forming a 3D network within a bulky-body, which exhibits a significant increase in the effective electrical conductivity. In composite materials that contain insulating and conducting phases, there is an important phenomenon that the insulating to conducting transition happens in a narrow percolation range by depending on the size and distribution of conductive 2nd phase. The value of percolation threshold is represented by volume percent of conductive phase. At the value of the percolation threshold, a conducting network spanning the whole composite occurs.

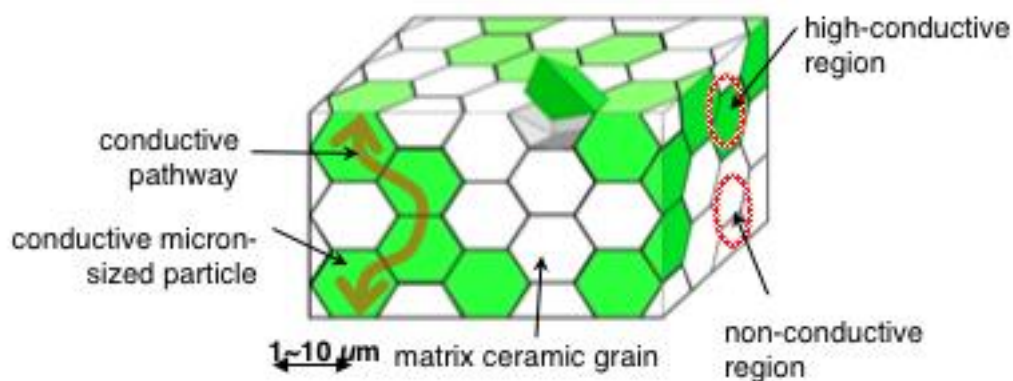


Figure 1.5 Possible current pathways in ceramic-metal composites.

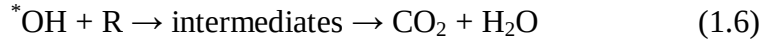
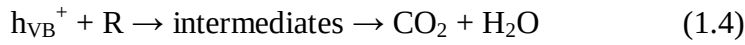
In ceramic-metal binary system, percolation threshold can be calculated by the general effective media (GEM) equation^[50] which is based on the percolation criterion. Basic GEM equation is shown in equation 1.2.

$$f_1 \frac{\sigma_1^{1/t} - \sigma_m^{1/t}}{\sigma_1^{1/t} + \frac{f_c}{1-f_c} \sigma_m^{1/t}} + (1 - f_1) \frac{\sigma_2^{1/t} - \sigma_m^{1/t}}{\sigma_2^{1/t} + \frac{f_c}{1-f_c} \sigma_m^{1/t}} = 0 \quad (1.2)$$

Where f_1 is the volume fraction of the low-conductivity (σ_1) ceramic phase, f_2 is the volume fraction of the high-conductivity (σ_2) metal phase, f_c is the percolation threshold volume, t is the fitting parameter independent from structure of system and is predicted as $t = 2$ in 3-dimensional continuum, and σ_m is the effective conductivity of composite. With different metal content, electrical conductivity of ceramic-metal composites could be measured. According to the GEM equation, the f_c of composite could be determined by the least squares method using calculated and observed conductivity value (σ_m).

1.4.3 Photocatalytic properties

There has been significant attention on the developments of semiconductor photocatalysts owing to their potential applications in renewable energy from water splitting and environmental cleaning by the decomposition of organic pollutants^[51,52,53]. Recently, TiO_2 photocatalyst has been extensively applied to water purification, environment cleaning and organic pollutants decomposition because of its good chemical stability, high oxidizability and non-toxicity^[54,55,56,57]. The process of organic degradation by TiO_2 photocatalyst is list from equation 1.3 to equation 1.6^[58,59]. The mechanism of the electron hole-pair formation when the TiO_2 is irradiated is given in Figure 1.6.



where R represents the organic compound.

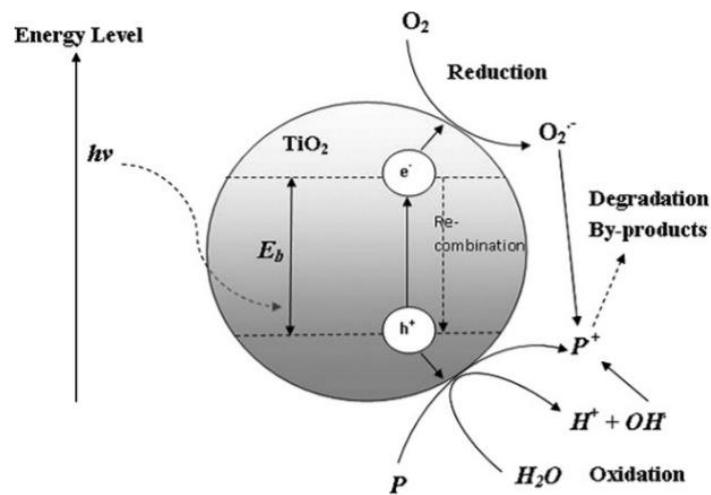


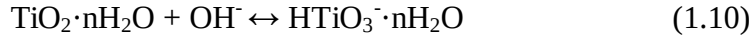
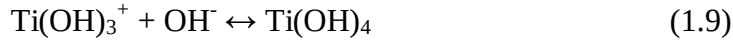
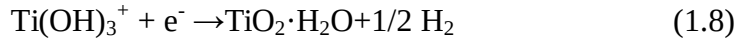
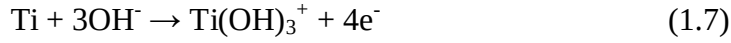
Figure 1.6 Mechanism of the electron hole-pair formation when the TiO_2 is irradiated.

However, TiO_2 photocatalysts which have been reported are almost in the form of suspended powder. When used in dealing with organic pollutants, suspended TiO_2 powder is easy to diffuse into water to cause secondary pollutant. It is a difficult and costly process to separate photocatalysts from aqueous solution. Therefore, more study has been focused on immobilized TiO_2 photocatalysts^[60,61,62]. Compared with powdered photocatalysts, immobilized photocatalysts could be continuously operated and have no need for an additional catalyst separation operation. Table 1.3 summarized the advantages and disadvantages of suspended and immobilized photocatalysis^[63].

Table 1.3 The advantages and disadvantages of suspended and immobilized photocatalysis.

	Advantages	Disadvantages
Suspended powder	·Fairly uniform catalyst distribution ·High surface photocatalytic area ·Limited mass transfer ·Well mixed particle suspension	·Require post-process filtration ·Important light scattering and adsorption in the particle suspended medium
Immobilized material	·Continuous operation ·Improved removal of organic material from water phase while using a support with adsorption properties ·No need for an additional separation operation	·Low light utilization efficiencies ·Restricted processing capacities ·Possible catalyst deactivation and catalyst wash out

There are various methods to prepare immobilized TiO₂ photocatalysis on various substrates, such as sol-gel method^[64,65,66,67]. Chemical and heat treatments of metallic Ti or its alloys are considered one of the advantageous way for the purpose, and thus they have been developed to be a simple method to generate nano-porous layer on the surface of metals to induce photocatalytic ability^[68,69]. Among these methods, chemical treatment such as alkaline- (NaOH, KOH, etc.) or acidic-solution (HNO₃, H₂SO₄, etc.) oxidation of Ti might be one of the advantageous way to fabricate TiO₂ photocatalyst immobilization on Ti or various substances due to its simple and facile processability without using high-temperature. The forming mechanism by NaOH treatment is given in following equations^[70].



Based on the performance of metal Ti, It is believed that the treatment of Al₂O₃/Ti composites by NaOH has the same effects to generate nano-porous surface layer on Ti for inducing photocatalytic activity. Moreover, it is necessary to survey appropriate treatment conditions including the concentration of NaOH, treatment temperature and time to generate nanoporous layer also covering Al₂O₃ surface to maximize the photocatalytic ability. As ceramic-based photocatalysis, Al₂O₃/Ti composites have unique advantages, such as high bending strength, good wear behavior, high temperature resistance, good chemical stability which could be served under sever application conditions. Therefore, if TiO₂ layer is completely formed on Al₂O₃/Ti composites, I am sure that these ceramic-based composites are expected to be applicable as an environmental purification material having both excellent mechanical properties and photocatalytic activity and as various TiO₂-based electrode such as for sensitized solar cells, photochemical and/or biochemical sensors, which might open the new-window for the ceramic-based composites in the future.

1.4.4 Self-healing ability

Although self-healing ability induced by heat treatment in ceramic-based composites has been the effective method to heal cracks for recovering mechanical strength at high temperature, however, when ceramics component are applied at low temperature,

high-temperature thermal healing is not an optimal solution. Decreasing healing temperature is a challenging for healing ceramics. At present, self-healing polymer composites at room temperature have been reported^[71,72,73]. However, no reports about healing cracks inside ceramics at low temperature, especially at room temperature are available until now. In this study, I try to develop another way to induce self-healing ability in ceramic-based composites at room temperature.

On the base of crack-healing mechanism caused by crack filling by oxides, electrochemical anodization, which is an effective method for forming metal oxides at room temperature, has been taken into consideration. In order to apply anodization on ceramic, one should solve two problems in advance. First is appropriate intermediate metal phases embedded into ceramic matrix, which could be changed into oxides after anodization to heal cracks. Second requirement is that these embedded metal particles must change insulated ceramics into conductor. In this study, I have hypothesized that, if these two aspects would be met, self-healing ability in ceramic induced by anodization at room temperature could be achieved. As mentioned above, the dispersion of Ti particles into Al_2O_3 matrix could change insulated Al_2O_3 ceramic to conductor. It is expected that cracked $\text{Al}_2\text{O}_3/\text{Ti}$ composites could be healed by anodization associated healing procedure with recovered bending strength. The schematic diagram of crack-healing behavior of $\text{Al}_2\text{O}_3/\text{Ti}$ composites by anodization hypothesized in this study is given in Figure 1.7.

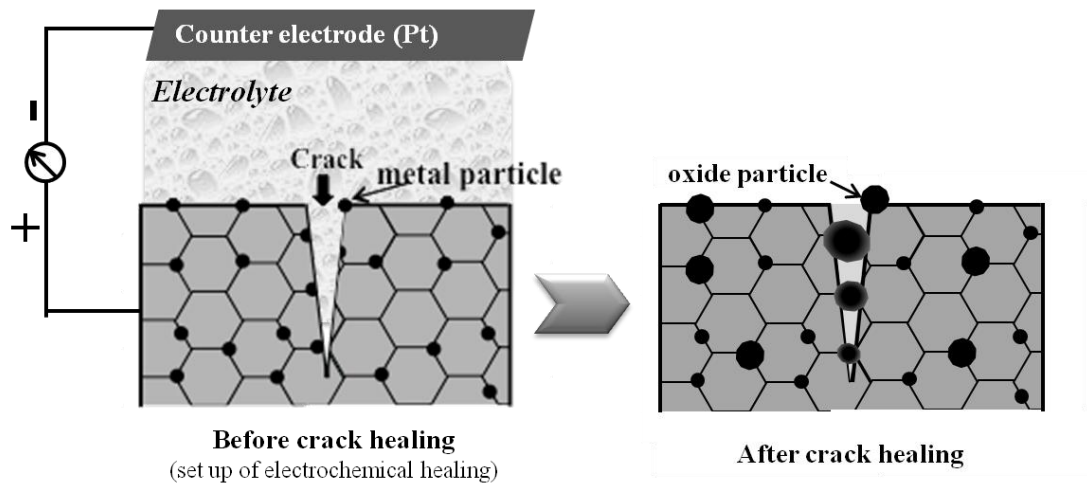


Figure 1.7 Schematic illustrates of crack-healing behavior in composite via anodization.

1.4.5 Other plausible multifunctional properties

In addition to properties mentioned above, it is believed that more new functions of $\text{Al}_2\text{O}_3/\text{Ti}$ composites may be developed, such as fracture sensing and biomaterials which were clarified in detail as follows.

Fracture sensing:

With better electrical properties, $\text{Al}_2\text{O}_3/\text{Ti}$ composites are considered to be used as fracture sensing during in-operation. When fracture including micro-crack formation occurs inside composite body, due to the interrupt of current pathways, electrical conductivity might be decreased. According to the change of electrical conductivity, the damage in materials is expected to be detected in-situ even during the use of the composites.

Similar to the fracture sensing, deformation (i.e. strain) sensing may also be possible for the ceramic/metal composites. In general, the electrical resistivity of a conductor such as metals depends upon strain induced in a body, which is well-known as an application of strain-gauge. In such a way, ceramic-based composites with electrical

conductivity due to dispersed metal phase, a small variation of conductivity due to the elastic deformation of the body may be used to detect the strain inside of the composite.

Biomaterials:

Since NaOH and heat treatment employed on metal Ti and its alloys can obtain bioactive surface layers to increase surface roughness and the specific surface area, bioactivity could be improved and induce apatite forming ability in a simulated body fluid (SBF)^[68,69,74,75]. This is because Ti and its alloys with smooth surface cannot directly bond to living bonds due to the absence of bioactivity and the formation of fibrous tissues isolating them from living bones^[70,75]. The formation of apatite layer on the surface makes Ti and its alloys bond to living bone through this layer^[69,76,77,78]. It is expected that Al₂O₃/Ti composites could be also applicable as biomaterials owing to the biocompatibility of Ti. If nanoporous layer could cover the whole surface of Al₂O₃/Ti composite by NaOH treatment, after immersed into SBF, apatite is also expected to be generated to make Al₂O₃/Ti composite suitable for biomaterials. When Al₂O₃/Ti composites are used as biomaterials, as Al₂O₃-based composites, Al₂O₃/Ti composites have crucial advantages than metal Ti, such as high bending strength, better wear behavior, high-temperature oxidization, corrosion resistance, good chemical stability and low elastic modulus^[20,21,79].

1.5 Objective of this study

The main objective of this study is to fabricate and investigate Al₂O₃/Ti composites for improving fracture toughness of brittle Al₂O₃ ceramics and applying electrical properties on insulated Al₂O₃ ceramics simultaneously and develop and confirm other novel functions for multifunctional applications. This work also provides the basic study

for other ceramic/metal composite systems in addition of Al_2O_3 and Ti.

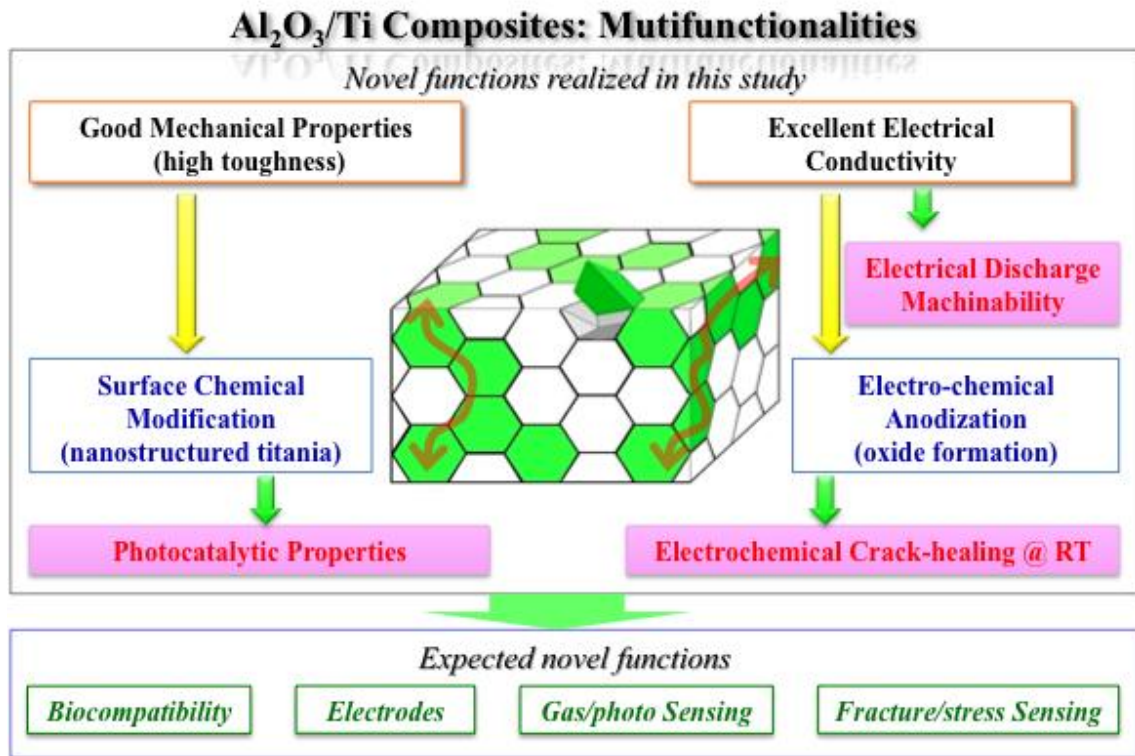


Figure 1.8 Schematic drawing for novel features of $\text{Al}_2\text{O}_3/\text{Ti}$ composites with various multifunctionalities based on the controlled structures.

In the present work, $\text{Al}_2\text{O}_3/\text{Ti}$ composites were firstly fabricated. In order to further prevent interfacial reaction and improve mechanical properties, Y_2O_3 is added as sintering additive during preparing $\text{Al}_2\text{O}_3/\text{Ti}$ composites. On the base of biological performance of metal Ti, the potential photocatalytic ability of $\text{Al}_2\text{O}_3/\text{Ti}$ composites was measured. On the base of conductive properties, anodization was firstly utilized to induce self-healing ability in $\text{Al}_2\text{O}_3/\text{Ti}$ composites at room temperature. This thesis consists of following seven chapters. Chapter 1 and chapter 2 focus on the fabrication of $\text{Al}_2\text{O}_3/\text{Ti}$ composites while other chapters focus on developing potential multifunctions.

In chapter 1, the backgrounds of this study including properties of $\text{Al}_2\text{O}_3/\text{Ti}$ composites and their multiple functions were reviewed, and the objectives, strategies and contents of this study were described.

In chapter 2, $\text{Al}_2\text{O}_3/\text{Ti}$ composites were prepared by hot press sintering method, and their mechanical and electrical properties were evaluated.

In chapter 3, Y_2O_3 was added into $\text{Al}_2\text{O}_3/\text{Ti}$ composites to further prevent interfacial reactions and improve mechanical and electrical properties.

In chapter 4, $\text{Al}_2\text{O}_3/\text{Ti}$ composites were treated by NaOH to generate porous surface layer in nanometer scale for photocatalytic application. Appropriate NaOH treatment conditions were searched for generating a complete surface layer on the composites. The degradation efficiency of RhB was used to evaluate the photocatalytic activity of composites subjected to NaOH, HCl and heat treatment at various temperatures.

In chapter 5, I investigated crack-healing behavior in $\text{Al}_2\text{O}_3/\text{Ti}$ composites induced by anodization under the controlling of electrolytic current and anodization time. Crack-healing ability was characterized by the change of surface crack and the recovery of flexural strength before and after anodization procedure at room temperature.

In chapter 6, a new method of simple heat treatment to generate nano-rod structure on the surface of $\text{Al}_2\text{O}_3/\text{Ti}$ composites for photocatalytic application was attempted. The preliminary study of treatment conditions was conducted and the photocatalytic efficiency was evaluated. A reasonable interpretation of formation mechanism of nano-rod structure was provided. The relationship between surface morphologies and heat treatment time was explained.

In chapter 7, the results of present work are summarized.

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Fabrication of $\text{Al}_2\text{O}_3/\text{Ti}$ composites containing dispersed fine Ti particles and investigation of their mechanical and electrical properties

2.1 Introduction

Al_2O_3 ceramics are widely used in the aerospace, electronics, and chemical industries along with other fields because of their high bending strength, good wear behavior, high temperature resistance, good chemical stability, and relatively low production cost^[1,2,3]. However, the application of Al_2O_3 ceramics as structural components is limited by their brittleness, which is attributed to low fracture toughness^[4,5]. Investigations on ceramic/metal nanocomposites have revealed that dispersing nanosized metals into a ceramic matrix can prevent crack propagation caused by plastic deformation, thereby increasing fracture toughness^[6,7,8]. The toughening mechanism can be attributed to the plastic deformation of metal phases, crack deflection, and crack bridging by the dispersed metal nanoparticles^[9]. In addition to showing improved mechanical properties compared to the corresponding monolithic ceramics, ceramic/metal nanocomposites also exhibit new electrical, optical, and magnetic properties along with metal-like machinability and superplasticity^[6,7,8,10,11].

Titanium (Ti) and its alloys are widely used as structural components and

biocompatible metal materials because of their high fracture toughness, relatively low density, and good biochemical stability^[12,13]. Al_2O_3 ceramics are also used as artificial bone because of their high wear resistance and strength. Considering these characteristics of Al_2O_3 and Ti along with the advantages of ceramic/metal composites mentioned above, incorporating nanosized Ti into Al_2O_3 might produce a composite with both the high strength of Al_2O_3 and high fracture toughness of Ti. Such a composite would have promising applications in advanced structural materials and biomaterials (e.g., artificial joints). Therefore, in this study, Ti, which shows good physicochemical consistency with Al_2O_3 , was dispersed in Al_2O_3 to produce Ti/ Al_2O_3 ceramics with enhanced mechanical properties and biocompatibility. Recently, Meir et al.^[14] fabricated Al_2O_3 /Ti composites using spark plasma sintering at 1300°C. They found that composite hardness reached 19 GPa at a Ti content of 20 wt%, while fracture toughness decreased with increasing Ti content.

Dispersed metallic phases can also contribute electrical conductivity to insulator ceramics, potentially leading to new applications such as temperature-sensitive devices, varistors, and electrodes for fuel cells^[15]. Ceramics with controlled electrical conductivity can be machined by electrical discharge machining, providing a new route for advanced ceramic processing. However, few studies have examined the electrical properties of the Al_2O_3 /Ti composite system. In the current study, nanosized Ti particles were dispersed into Al_2O_3 to fabricate Al_2O_3 /Ti composites with good mechanical and electrical properties.

The interface between the Al_2O_3 and Ti phases is weaker than the interface of monolithic Al_2O_3 ^[16,17,18]. When Al_2O_3 /Ti composites are sintered at high temperature, strong interfacial reactions between Al_2O_3 and Ti lead to the formation of Ti–Al

intermetallic compounds such as TiAl and Ti₃Al^[17,19]. These phases exhibit brittleness, low toughness, and poor creep resistance and thus result in weakened bonding force along with degraded mechanical properties. Furthermore, Ti is easily oxidized to form Ti–O phases or reacts with Al₂O₃ to produce Ti–Al–O solid solution. To maintain the ductility of Ti in Al₂O₃/Ti composites, the interfacial reaction between Al₂O₃ and Ti should be inhibited. These also explain why nanosized Ti powder is usually unstable and thus difficult to handle safely. Therefore, a new fabrication process is needed to disperse nanosized Ti particles into ceramic matrices.

A method based on the in situ decomposition of titanium hydride (TiH₂) and sintering was developed to produce Al₂O₃/Ti nanocomposites^[20]. Because TiH₂ is brittle, fine TiH₂ powder can be obtained by simple ball milling. This method allows Ti to be homogeneously dispersed into the Al₂O₃ matrix via the in situ decomposition of the ball-milled TiH₂ powder during matrix consolidation. When commercial mesh-sized (~70 μm) Ti powder was used as the raw material, the finer Ti metal phase derived from ball-milled TiH₂ was dispersed in Al₂O₃, while large (several tens of micrometers) Ti grains remained in the Al₂O₃/Ti composite^[20]. In this study, I have attempted to disperse Ti within a Al₂O₃ ceramic matrix using TiH₂ as the sintering material while controlling the mechanical and electrical properties of the resultant Al₂O₃/Ti composite. About sintering method discussed in Chapter 1, spark plasma sintering (SPS) can make possible sintering by charging the intervals between powder particles with electrical energy and effectively apply a high-temperature spark plasma generated momentarily. In this method, the powder in a carbon die is pressed uniaxially and direct current pulse voltage is applied. SPS systems also offer many advantages over conventional systems using hot press sintering (HPS), hot isostatic pressing (HIP) sintering or atmospheric

furnaces, such as low sintering temperatures, fine grain size and shorter processing time for fabricating materials with improved microstructure and properties. However, although SPS has many merits, the most important factors that affect sintering, such as pressure, temperature, also can be studied via HPS sintering, especially that hot pressing sintering can reduce the requirements for sintering equipment. In this study, HPS was used first to investigate the microstructure and performance of $\text{Al}_2\text{O}_3/\text{Ti}$ composite.

With the goal of improving the toughness and conductivity of Al_2O_3 ceramic, $\text{Al}_2\text{O}_3/\text{Ti}$ composites with different Ti contents (0–30 vol%) were fabricated from Al_2O_3 and TiH_2 powders via hot-press sintering (HPS). The mechanical properties and electrical resistivity of the composites were then investigated and analyzed with respect to the composition and microstructure. Finally, the toughening mechanism was discussed. The findings are expected to guide the design of new multifunctional materials that combine the advantages of ceramics and metals.

2.2 Experimental procedures

2.2.1 Preparation process

TiH_2 (5–10 μm , > 99%; Kojundo Chemical Laboratory Co., Ltd., Sakado, Japan) in amounts corresponding to 0, 5, 10, 15, 20, and 30 vol% Ti in the final composite was mixed with $\alpha\text{-Al}_2\text{O}_3$ (0.2 μm , AKP-53; Sumitomo Chemicals Co., Ltd., Japan) by wet ball milling for 24 h in ethanol. The ball milling was carried out under Ar gas to prevent oxidation of the TiH_2 powder. The dried mixtures were again dry ball-milled for another 12 h under Ar gas. A graphite die with an inner diameter of 44 mm was filled with the mixed powder, and HPS was performed under an applied pressure of 30 MPa at 1500°C

for 1 h under Ar atmosphere. The heating rate was 20°C/min. During the heating sequence, the temperature was held at 800°C for 30 min to decompose TiH₂. The resulting sintered bodies were cut, ground, and polished with diamond paste to 0.5 µm for characterization. The polished specimens were subjected to thermal etching at 1350°C for 1 h in Ar atmosphere to reveal the microstructural characteristics and grain size of the Al₂O₃ matrix.

2.2.2 Characterization

Phase compositions were determined by X-ray diffraction (XRD; D8 Advance, Bruker Ltd., USA) using CuKα radiation at 40 kV and 40 mA. The relative densities were measured by Archimedes' method in deionized water. Scanning electron microscopy (SEM; SU9000, Hitachi, Japan) equipped with energy dispersive X-ray spectroscopy (EDX; Horiba, Japan) was used to observe the microstructures of the polished specimens and elemental compositions. Transmission electron microscopy (TEM; JEM-2100, JEOL, Japan) was used to observe the nanostructures and interfacial structures. Thin specimens were prepared from the bulk samples for TEM investigation using a focused ion beam (FIB; FB2000, Hitachi, Japan). Young's modulus was determined from the ultrasonic velocity data obtained using a digital storage oscilloscope (DSOX3052T, Keysight, Japan) and an ultrasonic pulser/receiver (Model 5072, PANAMETRICS, USA). Vickers hardness was measured using a Vickers Hardness Tester (FV-310e, Future-tech Corp., Japan) with an applied load of 98 N and holding time of 15 s. Fracture toughness was calculated under the same conditions using the indentation fracture method based on the lengths of observed cracks^[21]. More than 10 indentations were measured and averaged for each sample. Flexural strength was

measured using four-point bending test on 3 mm×4 mm×35 mm bars by a universal testing machine (Autograph AGS-X, Shimadzu, Japan) with a cross-head speed of 0.5 mm/min at room temperature. The upper (loading) and lower (support) spans were 10 mm and 30 mm, respectively. Six specimens were tested for each composite. Electrical resistivity was measured by the Van-der Pouw method using polished disks (diameter = 12 mm, thickness = 1.5 mm). This method is based on four-probe resistivity and Hall coefficient measurements, which were carried out using an electrical resistivity measurement system (Resitest 8310, Toyo Technica Corp., Japan) under air atmosphere at room temperature.

2.3 Results and discussion

2.3.1 Phase compositions

Sintered ceramics were successfully obtained by the HPS of Al_2O_3 and TiH_2 powders under a uniaxial pressure of 30 MPa at 1500°C for 1 h. The phase compositions were determined by XRD (Figure 2.1). The major phases in the samples were clearly identified as α -type Al_2O_3 (hexagonal, corundum structure) and α -type metallic Ti (hexagonal, hpc, PDF 03-065-3362). No peaks corresponding to Ti–Al intermetallic compounds or alloys were detected. TiAl_2O_5 (PDF 00-026-0040) was present in all samples, while Ti–O phases were only detected in samples with low Ti content (<15 vol%). Here, Ti–O represents active oxygen dissolved in Ti.

In the $\text{Al}_2\text{O}_3/\text{Ti}$ system, interfacial reaction products form as a result of Al_2O_3 dissolution into Ti by diffusion during sintering^[22]. In this study, the main diffusing element was first oxygen followed by aluminum, and the diffusion of Ti into Al_2O_3 was

negligible. The interfacial reactions between Al_2O_3 and Ti can be described by the following three equations^[22,23,24,25]:



where $[\text{O}]_{\text{Ti}}$ represents active oxygen dissolved in titanium. The values of ΔG for Eqs. (2.2) and (2.3) are -1279.2 and -1753.6 kJ/mol, respectively, at 1500°C . Thus, the formation of the complex oxide (TiAl_2O_5) occurs easily because of its thermodynamic stability.

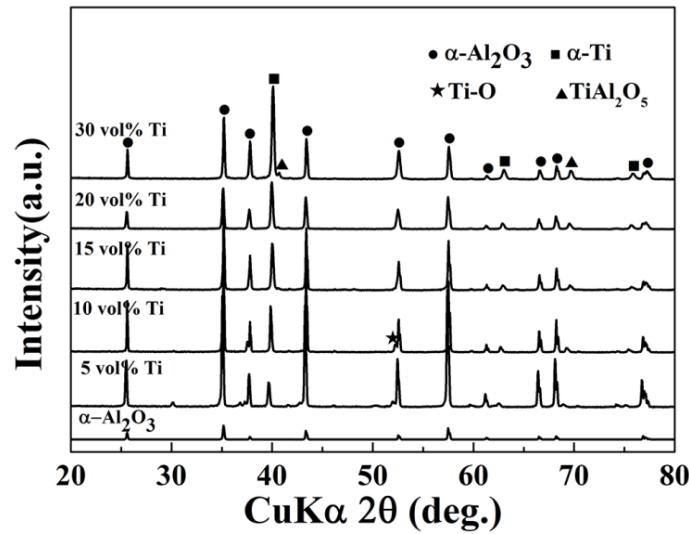


Figure 2.1 XRD patterns of $\text{Al}_2\text{O}_3/\text{Ti}$ composites prepared by HPS at 30 MPa and 1500°C for 1 h under Ar atmosphere.

In $\text{Al}_2\text{O}_3/\text{Ti}$ system, the phase equilibrium depends on chemical composition which could be explained by phase diagram of Ti–Al–O ternary system. Isothermal sections of the Ti–Al–O system at various temperatures were reported^[26]. It has been found that the

Ti–Al₂O₃ reaction is thermodynamically favorable at all temperatures. Isothermal sections indicate that with different composition of Ti, Al and O, the equilibrium phases are different which is also confirmed by the present study, e.g., Ti–O phases were only detected when the amount of Ti is below 15% while TiAl₂O₅ could appear in all composites.

In this study, the formation of TiAl₂O₅ and Ti–O phases was confirmed by EDX, and the chemical compositions of the products in the composites, which are shown as the analytical points in Figure 2.2, are summarized in Table 2.1. Aluminum and oxygen were detected at the locations of Ti (points 1 and 2 in Figure 2.2), whereas almost no Ti was detected at the location of Al₂O₃ (point 3 in Figure 2.2). This demonstrates that the interfacial reaction products were produced by the dissolution of Al₂O₃ into Ti as described in detail below.

According to the chemical compositions by the EDS analysis (Table 1), the point 2 and point 3 were regarded as TiAl₂O₅ and Ti–O, respectively, which phases were confirmed also by the XRD analysis (see Figure 2.1). As mentioned before, during sintering, oxygen in Al₂O₃ firstly diffused into Ti. The limit solubility of oxygen in α -Ti was reported as approximately 8 at% and decreased when other alloy element existed^[27]. When much more oxygen diffused into Ti, Ti–O phase was firstly formed at the outside of Ti particle, i.e. at the boundary region near to Al₂O₃ particle. Then, aluminum began to diffuse and reacted with these Ti–O phases to form TiAl₂O₅ compounds because of its thermodynamic stability. Due to longer diffusion distance of oxygen in Al₂O₃/Ti system than that of aluminum^[28], TiAl₂O₅ might be formed outside of primary Ti particle in the composites while Ti–O remained rather inside of Ti particle. As a result, reaction products near the interface, i.e. adjacent to Al₂O₃ matrix (like as point 2 in

Figure 2.2), is TiAl_2O_5 , while Ti–O layer exists rather interior of the Ti particle (point 3).

In current, the formation of Ti–Al intermetallic compounds was not confirmed. At 1500°C , the ΔG of the formation of intermetallic compounds, such as Ti_3Al and TiAl was calculated to be -138.0 kJ/mol and -77.8 kJ/mol , respectively^[29]. Owing to thermodynamic stability, these phases are possible presented in $\text{Al}_2\text{O}_3/\text{Ti}$ composites. However, here metal Ti was obtained from TiH_2 by dehydrogenation during sintering. The defect concentration is considered to be different from pure metal Ti causing relatively higher reactive activity. As a result, the higher reactivity made Ti easy react with firstly diffused oxygen completely and then formed Ti–O reacted with diffused aluminum avoiding the formation of Ti–Al intermetallic compounds. In addition, due to the relatively lower ΔG , the formation of titanium oxides (Ti–O or TiAl_2O_5) is more favorable. In current study, the short sintering time is also considered as one reason for the not formation of intermetallic compounds.

2.3.2 Microstructure and density

In our preliminary study, surface morphologies of $\text{Al}_2\text{O}_3/\text{Ti}$ composites prepared by commercial Ti powder and TiH_2 were observed and the results were shown in Figure 2.3. Comparing composites prepared by metal Ti and TiH_2 , It is found that when metal Ti was used as starting material directly, particle size was large and distribution was coarse. On the other hand, when TiH_2 was used as starting material, fine Ti particles can be obtained, and microstructure was more homogeneous.

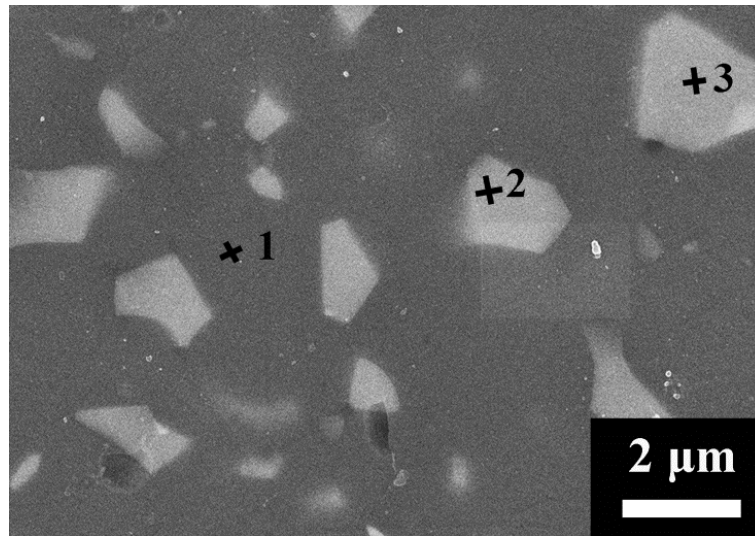


Figure 2.2 SEM image of the surface of the $\text{Al}_2\text{O}_3/30 \text{ vol\% Ti}$ composite. The cross marks with numbers represent the points of EDX quantitative analysis (Table 2.1).

Table 2.1 Chemical composition of the surface of the $\text{Al}_2\text{O}_3/10 \text{ vol\% Ti}$ composite measured by EDX.

Point	Elements (mol%)			Possible phases
	Ti	Al	O	
1	0.5	40.06	59.46	Al_2O_3
2	14.82	29.29	55.89	TiAl_2O_5
3	53.74	7.17	39.09	$\text{Ti}(\text{O})$ or Ti-O

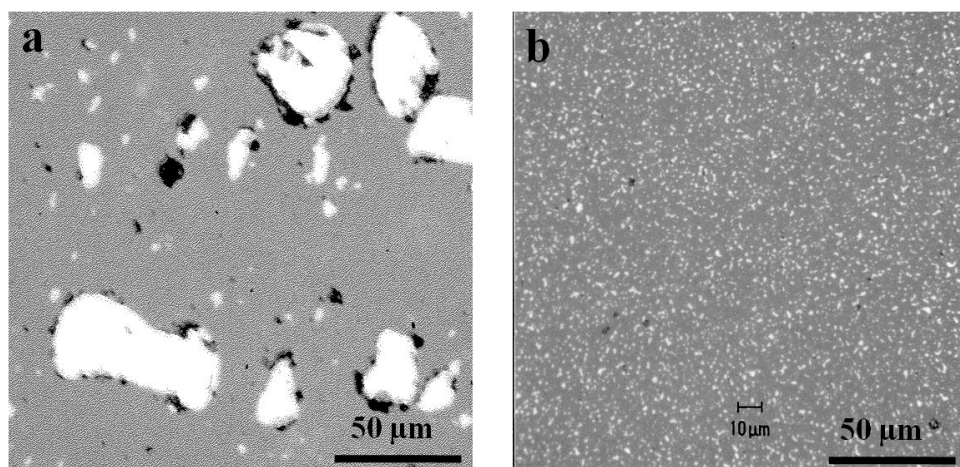


Figure 2.3 Optical microscope images of $\text{Al}_2\text{O}_3/10\text{vol}\%\text{Ti}$ composites prepared by (a) commercial Ti (350mesh) powder and (b) TiH_2 (initial size: 350 mesh) powder.

The composite microstructures in current study were observed by SEM and EDX. The bright and dark phases in Figure 2.4 correspond to Ti and Al_2O_3 , respectively. No spontaneous micro-cracks formed on the surfaces of any samples, the titanium phases were homogeneously distributed. However, the sizes and shapes of the Ti particles varied depending on the Ti content. For a small Ti content of 5 vol%, most Ti particles were in submicron-sized and isolated from each other. The particle size increased with increasing Ti content, and the particles became more interconnected, especially at Ti contents greater than 15 vol% [Figure 2.4(c)]. The Ti particles were polygonal rather than spherical (round), and this phenomenon became more apparent as the Ti content increased. That is to say the shape of Ti depends on the content of added Ti. The interface reaction might become more dominant with the increase in the amount of Ti, which would result in the increase in reaction products such as Ti-O and TiAl_2O_5 . These products existing mainly at the exterior of Ti particles might affect the shape of Ti because of the elemental diffusion, reaction and resultant formation of new phases. The

observed microstructural characteristics are also attributed to the migration of Ti particles during sintering.

The thermally etched surface of the composite containing 20 vol% Ti is shown in Figure 2.4(f). The average Al_2O_3 grain size was calculated as approximately $1.8 \pm 0.6 \mu\text{m}$ by image analysis using Image J software. Because Ti particles are larger than Al_2O_3 grains, the grain boundaries could not pass through these large dispersed Ti particles by grain growth during sintering, and the Ti particles remained at grain boundaries. In general, the second phase presented at grain boundaries can inhibit the movement of grain boundaries to retard the growth of matrix grains^[4,30]. However, in this study, the addition of Ti did not greatly decrease the grain size of the Al_2O_3 matrix (grain size of pure $\text{Al}_2\text{O}_3 = 1.2 \pm 0.4 \mu\text{m}$), and almost all Ti particles were micrometer-sized. This was attributed to the slow heating rate ($\sim 20^\circ\text{C}/\text{min}$) during sintering, the coarse mixed powders used as raw materials, and the large sizes of the Ti particles.

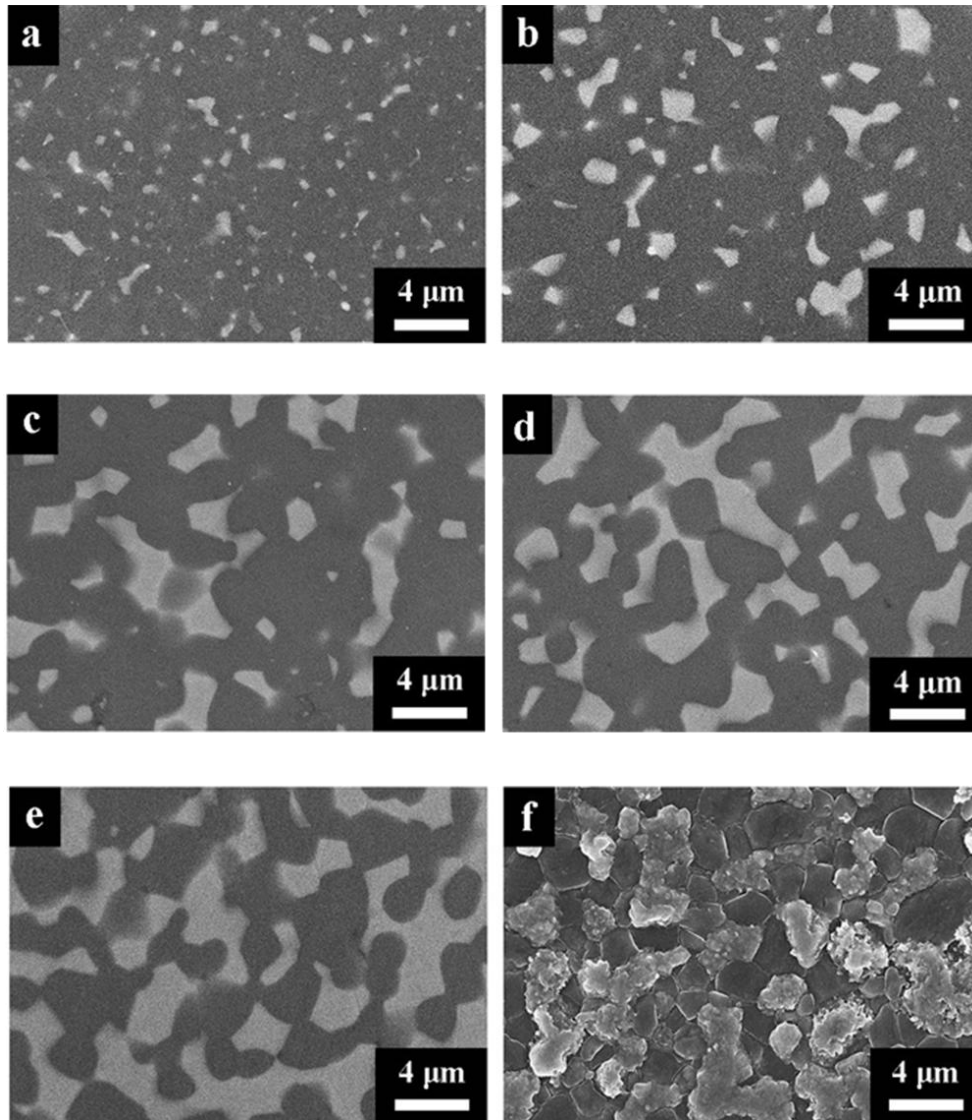


Figure 2.4 SEM micrographs of the polished surfaces of Al₂O₃/Ti composites with different Ti contents: (a) 5 vol%, (b) 10 vol%, (c) 15 vol%, (d) 20 vol%, and (e) 30 vol%. (f) SEM image of the thermally etched surface of the Al₂O₃/20 vol% Ti composite.

The TEM image of the composite containing 20 vol% Ti is shown in Figure 2.5. Large Ti particles with sizes of approximately 2 μm along with a much smaller fraction of nanometer-sized Ti particles were observed. The selected-area electron diffraction patterns of the grains are shown in Figure 2.6. The diffraction spot taken from region A in the TEM image shown in Figure 2.6 was assigned to $\alpha\text{-Ti}$ (PDF 03-065-3362). The spot of region B within the same particle was assigned to TiAl_2O_5 (PDF 00-026-0040), which was also detected by XRD (Figure 2.1). These results indicate that Al_2O_3 reacted and dissolved into Ti grain during sintering, as discussed earlier.

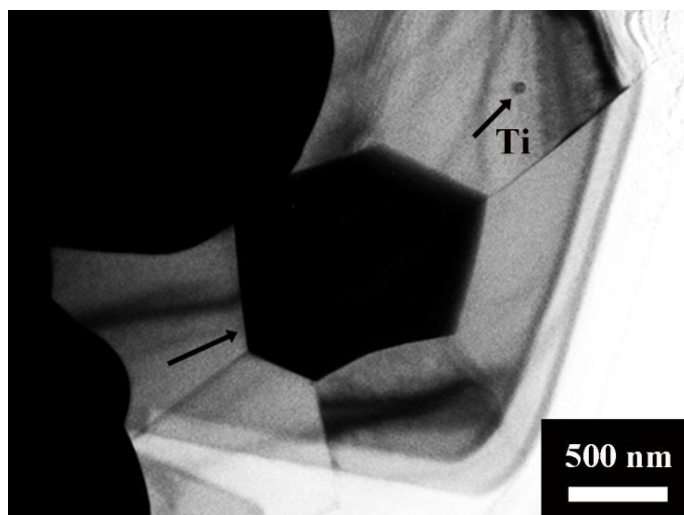


Figure 2.5 TEM micrograph of the Al_2O_3 /20 vol% Ti composite showing both large and nanosized Ti particles.

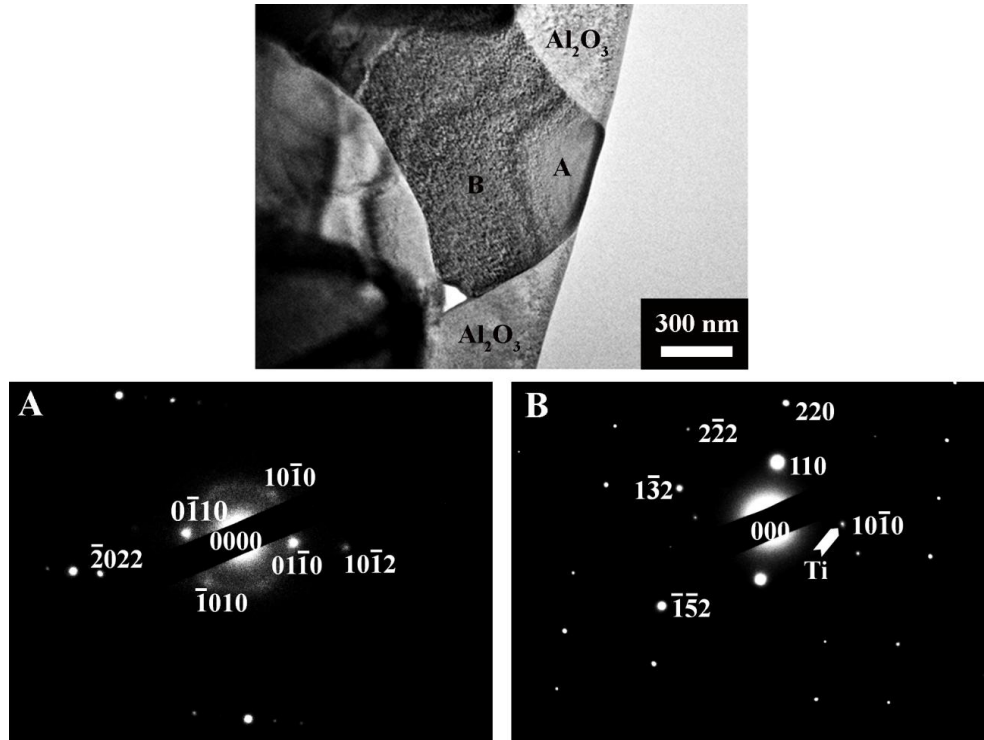


Figure 2.6 TEM micrograph of the Al_2O_3 /20% Ti composite and corresponding selected-area electron diffraction patterns of regions A and B.

Composite bulk density is shown as a function of Ti content in Figure 2.7. Each value plotted in Figure 2.7 represents an average of eight specimens. Theoretical density was calculated based on those of $\alpha\text{-Al}_2\text{O}_3$ (3.987 g/cm^3) and $\alpha\text{-Ti}$ (4.506 g/cm^3) by assuming rule of mixture of constituent phases. Bulk density increased with increasing Ti content, indicating that the addition of Ti and the existence of tertiary phases such as Ti–O (5.82 g/cm^3 as TiO) and TiAl_2O_5 (3.702 g/cm^3), where Ti–O is denser than Ti and Al_2O_3 , accelerated the densification of Al_2O_3 and improved the sintering density. However, the measured was higher than the theoretical density calculated assuming a mixture of $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Ti}$. This difference was attributed to the composition change during HPS process. In sintered Al_2O_3 /Ti composites, apart from Al_2O_3 and Ti phases, oxygen and

Aluminum diffused into Ti to form TiAl_2O_5 and complex Ti-O phases, such as TiO , Ti_2O_3 and $\text{Ti}_{0.67}\text{O}_{0.33}$ ^[24]. It is, however, hard to determine the precise quantitative contents of these reaction product phases (Ti-O and TiAl_2O_5). Therefore, in this study, theoretical densities were calculated only based on those of pure Al_2O_3 and Ti as mentioned before. For the same reason, the theoretical values including Young's modulus and Vickers hardness were calculated based on those of Al_2O_3 and Ti in the latter sections. Nevertheless, we have reason to believe that obtained composites all are highly densified with lower porosity, because relative density of monolithic Al_2O_3 in the present study was calculated to be 99.5%, and pores could be rarely observed at the polished surfaces by SEM investigation (see Figures 2.2 and 2.4).

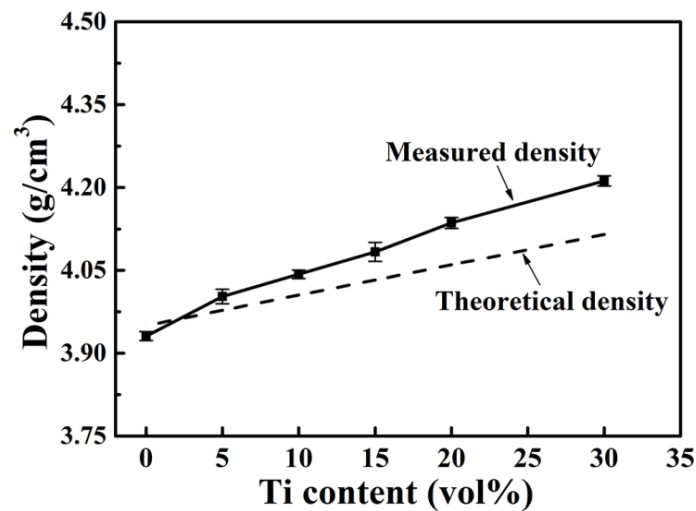


Figure 2.7 Bulk density of the $\text{Al}_2\text{O}_3/\text{Ti}$ composites as a function of Ti content. The theoretical density (dashed line) was calculated using the rule of mixtures by assuming the densities of $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Ti}$.

2.3.3 Mechanical properties

Figures 2.8 and 2.9 show the Young's modulus and Vickers hardness as functions of Ti content, respectively. The plotted data represent the averages of at least seven indentation measurements for each sample. Because the Young's modulus and Vickers hardness of Ti are relatively low (approximately 110 and 2 GPa, respectively) compared to those of α -Al₂O₃ (380 and 18 GPa, respectively), both Young's modulus and Vickers hardness decreased with increasing Ti content. However, the measured Young's modulus and Vickers hardness values were higher than the theoretical values predicted for mixtures of Al₂O₃ and Ti. This is attributed to the presence of TiAl₂O₅, which has been shown to be beneficial for improving hardness^[31]. The impurity effect of TiAl₂O₅ on Ti particles such as dissolving small amount of Al and/or oxygen elements was also considered to contribute to the increased Young's modulus and Vickers hardness.

There are two kinds of calculation methods for theoretical values of Young's modulus and Vickers hardness and the calculation for theoretical Young's modulus is shown in equation 2.4:

$$\text{Upper limitation: } E_U = (1-V_{Ti}) E_{Al_2O_3} + V_{Ti} E_{Ti}$$

$$\text{Lower limitation: } \frac{1}{E_L} = \frac{1-V_{Ti}}{E_{Al_2O_3}} + \frac{V_{Ti}}{E_{Ti}} \quad (2.4)$$

where $E_{Al_2O_3}$ and E_{Ti} is Young's modulus of Al₂O₃ and Ti while V_{Ti} is volume fracture of Ti. By calculation, measured Young's modulus of composites is even higher than calculated upper limitation value. Therefore, in this study, theoretical value means the upper limitation. The analysis for theoretical Vickers hardness is identical.

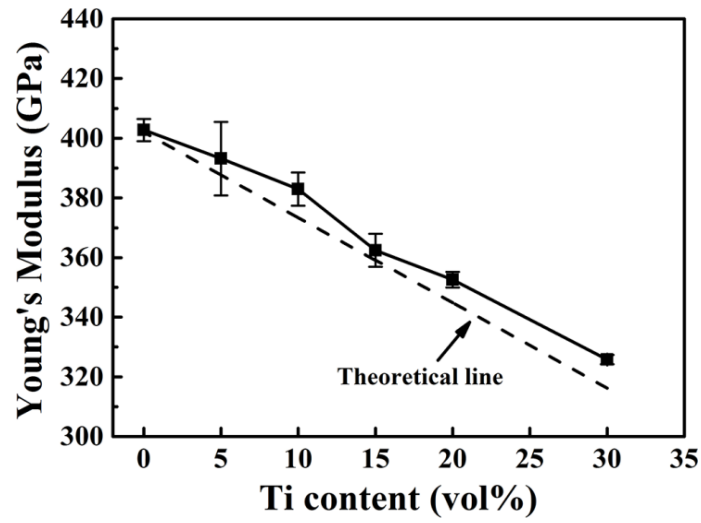


Figure 2.8 Young's modulus of the $\text{Al}_2\text{O}_3/\text{Ti}$ composites as a function of Ti content. The theoretical Young's modulus (dashed line) was calculated using the rule of mixtures.

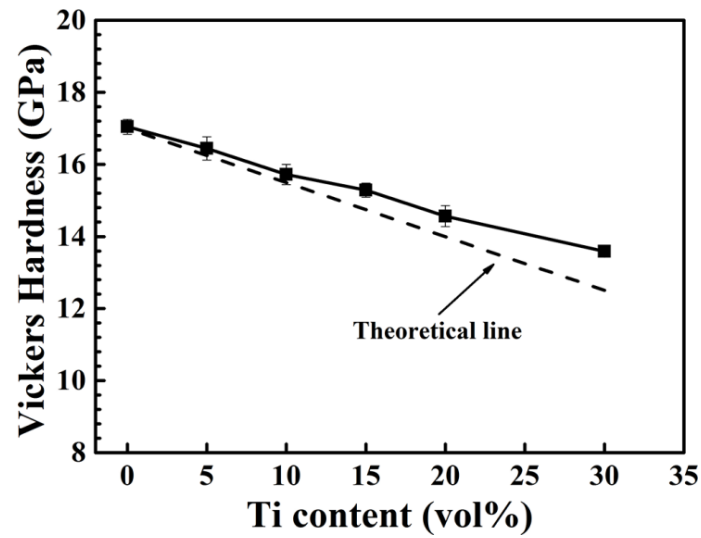


Figure 2.9 Vickers hardness of the $\text{Al}_2\text{O}_3/\text{Ti}$ composites as a function of Ti content. The theoretical hardness (dashed line) was calculated using the rule of mixtures.

Figure 2.10 shows flexural strength and fracture toughness as a function of Ti content. Flexural strength measured by the four-point bending test of composites decreased monotonously with the increase in Ti content, showing that Ti particles dispersed into Al_2O_3 matrix had no effect on improving the flexural strength. In current study, flexural strength of Al_2O_3 was measured to be 588 ± 39 MPa and the value of Ti was reported as approximately 400 MPa^[32]. The decreased flexural strength of $\text{Al}_2\text{O}_3/\text{Ti}$ composites was ascribed to lower flexural strength of Ti than that of Al_2O_3 . Furthermore, large particle size of Ti was considered to be another reason accounting for the low flexural strength of $\text{Al}_2\text{O}_3/\text{Ti}$ composites. The flexural strength of ceramics was reported to be inversely proportional to grain size of constituent phase^[33]. When the size of dispersed second phase is in nanometer scale, owing to the formation of sub-grain boundary and the inhibition of matrix grain growth, composites exhibit high strength^[34]. However, in current study, the dispersion of large Ti particles did not prevent the grain growth of Al_2O_3 matrix during sintering. Both Ti particles and Al_2O_3 grains were in micrometer-size, and Ti particle size increased with the increase in Ti content (approximately 2 μm) as shown in Figure 2.4 and discussed before. These facts resulted in increase in the size of fracture origin; in the present system, it might correspond to the grain size of large Ti because of its lower strength than Al_2O_3 and weak interface between Al_2O_3 and Ti, as discussed in the later part. Thus flexural strength of $\text{Al}_2\text{O}_3/\text{Ti}$ composites was decreased with the increase in Ti content.

On the other hand, all the composites displayed higher fracture toughness than monolithic Al_2O_3 . Fracture toughness increased with increasing Ti content up to 20 vol% (maximum fracture toughness = 4.21 ± 0.17 MPa $\cdot\text{m}^{1/2}$). Further increasing the Ti content to 30 vol% resulted in a slight decrease in fracture toughness.

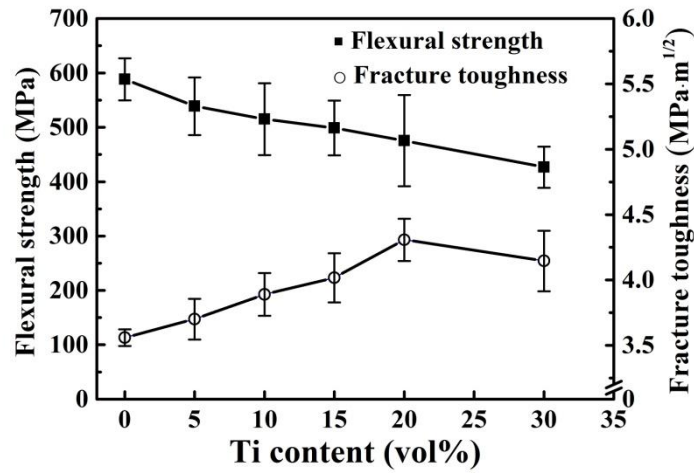


Figure 2.10 Flexural strength and fracture toughness of the $\text{Al}_2\text{O}_3/\text{Ti}$ composites determined by the four-point bending test (strength) and the indentation fracture method (toughness; 98 N, 15 s) as a function of Ti content.

To evaluate the toughening mechanism of the fabricated composites, the crack propagation behavior was investigated. Figure 2.11 shows SEM micrographs of the cracks induced by Vickers indentation. Figure 2.11(a) clearly shows that cracks propagated through the composites by deflection and were partly bridged by the Al_2O_3 particles and some Ti particles. The cracks also passed inside of Ti particles, resulting in the plastic deformation of Ti particles [indicated by the arrow in Figure 2.11(b)]. The interfaces between Al_2O_3 and Ti are weaker than pure Al_2O_3 grain boundaries; thus, cracks propagated along $\text{Al}_2\text{O}_3/\text{Ti}$ interfaces, resulting in intergranular fracture. Residual stress related to the mismatches in the coefficients of thermal expansion ($\alpha_{\text{Al}_2\text{O}_3} = 8.71 \times 10^{-6}/\text{K}$, $\alpha_{\text{Ti}} = 7.14 \times 10^{-6}/\text{K}$) and Young's modulus ($E_{\text{Al}_2\text{O}_3} = 380 \text{ GPa}$, $E_{\text{Ti}} = 116 \text{ GPa}$) between the Al_2O_3 matrix and Ti particles might have accumulated at the grain boundaries and/or $\text{Al}_2\text{O}_3/\text{Ti}$ interfaces^[35]. In this case, compressive stress perpendicular

to the Ti/Al₂O₃ interface while the tensile stress parallel to the interface is regarded to be formed during the cooling down process of sintering. Such local residual stress is known to affect the interactions between cracks and microstructures^[36]. In the present composites, when cracks reached Ti particles, the direction of crack propagation changed so that the cracks passed through the Ti particles. This resulted in the transgranular fracture of Ti particles. The toughening mechanism can be further clarified from the features of the fracture surfaces, as discussed below.

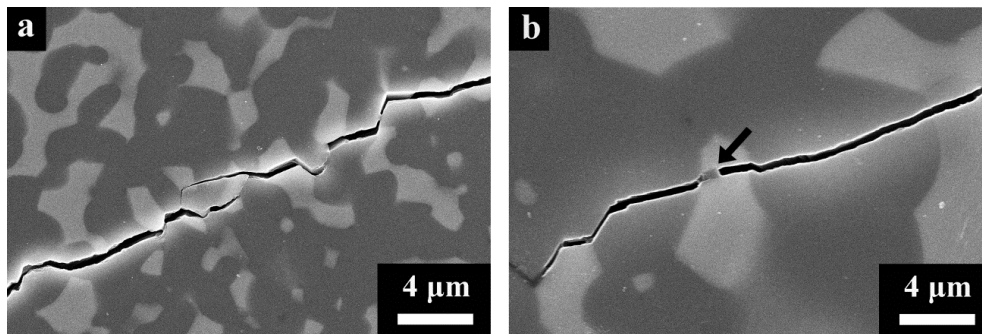


Figure 2.11 SEM micrographs showing the propagation pathways of cracks introduced on the surface of the Al₂O₃/20 vol% Ti composite by Vickers indentation (98 N).

Figure 2.12 shows the fracture surfaces of monolithic Al₂O₃ and the composite containing 20 vol% Ti. The inset in Figure 2.12(b) shows transgranular fracturing in a Ti particle. In contrast, the fracture of monolithic Al₂O₃ was completely intergranular [Figure 2.12(a)]. After the addition of Ti, the fracture mode became a mixture of trans- and intergranular, with transgranular being dominant [Figure 2.12(b)]. This change in fracture mode was considered to reflect a strengthening in interfacial bonding and increase in fracture toughness^[9]. This result differs from the report of Meir^[14], who found that cracks mostly propagated along the weak Ti/Al₂O₃ interface, and all samples

displayed lower fracture toughness than monolithic Al_2O_3 . In addition, the formation of small amount of interfacial reaction products contributed to the improved fracture toughness by deflecting the path of crack propagation and absorbing the propagation energy via pinning effects^[37]. Stress-induced micro-cracks were considered as another possible toughening mechanism^[7]. In the $\text{Al}_2\text{O}_3/\text{Ti}$ system in this study, micro-cracks formed in the frontal process zone during cooling as a result of residual stress. As expected, micro-cracks were observed on the fracture surface of the $\text{Al}_2\text{O}_3/\text{Ti}$ composite [inset of Figure 2.12(b)], although they were not numerous. These micro-cracks deflected the propagation of primary cracks and absorbed elastic strain energy. This released crack tip energy and reduced stress concentration, thereby improving fracture toughness.

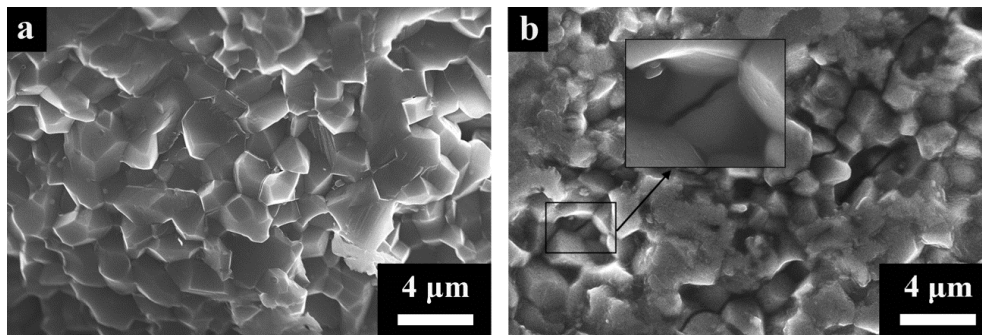


Figure 2.12 SEM micrographs of the fracture surfaces of (a) monolithic Al_2O_3 and (b) the $\text{Al}_2\text{O}_3/20$ vol% Ti composite. The inset in (b) shows a crack formed in the composite.

As motioned above, the small amount of TiAl_2O_5 can contribute to crack deflection and hence adsorbs crack propagation energy to increase fracture toughness owing to the “pinning effect” in spite that the intergranular micro-cracking in TiAl_2O_5 greatly

limits its fracture toughness^[31]. The content of formed TiAl_2O_5 was calculated by quantitative XRD analysis. The content of TiAl_2O_5 increased with the increase in Ti content. When Ti content was below 20%, mass percent of TiAl_2O_5 was calculated to be below 4% while it was 8% when Ti content was 30%. Thus, when Ti content is below 20%, pinning effect of small amount of TiAl_2O_5 is predominant, leading to increased fracture toughness than that of monolithic Al_2O_3 . On the other hand, with the further increase in the amount of TiAl_2O_5 , the effect of intergranular micro-cracking in TiAl_2O_5 cannot be ignored and becomes the leading factor. The slight decrease in fracture toughness observed upon increasing the Ti content to 30 vol% was thus ascribed to this effect. The results of this study demonstrate that the addition of 20 vol% Ti into Al_2O_3 is effective for improving fracture toughness.

2.3.4 Electrical properties

The electrical resistivity of the composites is shown as a function of Ti content in Figure 2.13. Al_2O_3 ceramics are highly insulating materials with resistivity over 10^{12} Ωcm . However, the electrical resistivity decreased with increasing Ti content. When the Ti content was below 10 vol%, the composites were still insulating. However, when the Ti content was 15 vol% or more, the resistivity decreased considerably, and the composite changed from an insulator to a conductor at room temperature. At Ti contents between 10 and 15 vol%, a sudden decrease of resistivity resulting in typical percolation behavior was observed (Figure 2.13). The percolation threshold volume, which is a characteristic property of the development of electrical conduction in an insulator matrix by the addition of a conductive phase, was calculated by the general effective media (GEM) equation^[38] to be 13.8 vol% for this system.

The observed change in electrical resistivity can be explained by the formation of conductive pathways (i.e., network formation). By dispersing an electrically conductive metal phase into the insulating ceramic matrix, a continuous conduction pathway was formed via the percolation of the dispersed phase, leading to an increase in electrical conductivity. In this study, the conductive Ti particles begin to contact each other as the Ti content increases, resulting in an interconnected Ti network through which electric current can pass. For Ti contents of 5 and 10 vol%, the Ti particles were not sufficient to form a continuous interconnected Ti network, as shown in the surface SEM images in Figures 2.4(a) and (b). When the Ti content increased to 15 vol% or more, an interconnected Ti network formed as a result of percolation [Figure 2.4(c)], and the electrical resistivity decreased. This is consistent with the calculated percolation threshold volume of 13.8 vol%. Further increasing the Ti content increased the probability of Ti–Ti contact in the composite, enhancing the conductive pathway. Accordingly, the electrical resistivity might further decrease. Nevertheless, 20 vol% Ti is considered to be the optimal Ti content based on the mechanical and electrical properties of the composites.

In addition, particle size of second conductive metal phase has great effects on electrical conductivity of composites and thus on percolation. Percolation threshold is the function of the ratio of matrix grain size relative to dispersed metal particle size $(R_{\text{matrix}}/R_{\text{particle}})^{[39]}$. With the increase in $R_{\text{matrix}}/R_{\text{particle}}$, percolation threshold decreases indicating that dispersed particle having smaller size is benefit for increasing $R_{\text{matrix}}/R_{\text{particle}}$ and thus decreasing percolation threshold. In this work, if nano-sized Ti particle could be obtained, a much smaller Ti content below 13.8% could change insulated Al_2O_3 into conductor.

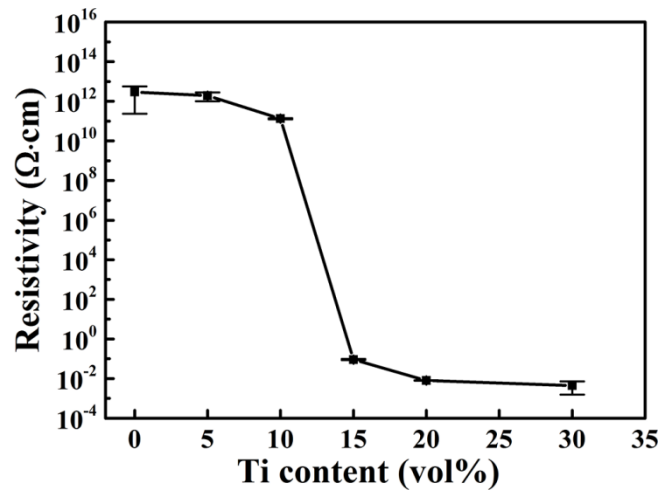


Figure 2.13 Electrical resistivity of the Al₂O₃/Ti composites (measured by the Van der Pavn method at room temperature) as a function of Ti content.

2.4 Summary

Al₂O₃/Ti composites with enhanced mechanical and electrical properties were successfully fabricated using Al₂O₃ and TiH₂ powders by HPS at 1500°C. The use of brittle TiH₂ as a raw material was advantageous for dispersing small-sized Ti particles into the Al₂O₃ ceramic matrix via in situ decomposition and sintering. As Ti content increased from 5 to 30 vol%, the Young's modulus and Vickers hardness values decreased; however, both values were higher than those predicted by the rule of mixtures. The dispersion of Ti had no effect on the enhancement of flexural strength of Al₂O₃ in this study, however, the fracture toughness of the composite containing 20 vol% Ti reached 4.21 MPa·m^{1/2}, which was 37% greater than that of monolithic Al₂O₃. The toughening was attributed to crack deflection, crack bridging, and the plastic deformation of Ti particles. The addition of Ti changed the primary fracture mode from intergranular (as for monolithic Al₂O₃) to transgranular. Compositing with Ti did not

increase strength and toughness simultaneously. It might be necessary to optimize preparation conditions to disperse finer and nanometer-sized Ti particles for further improvement of mechanical properties, especially fracture strength of $\text{Al}_2\text{O}_3/\text{Ti}$ composites. The addition of more than 15 vol% Ti changed Al_2O_3 from an insulator to a conductor at room temperature. The composite containing 20 vol% Ti exhibited a good balance of mechanical and electrical properties. The enhanced fracture toughness and electrical properties are expected to generate new applications of Al_2O_3 such as in electro-discharge machining, fracture sensing and electropotential-assisted crack healing.

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Combinative effects of Y_2O_3 and Ti on Al_2O_3 ceramics for optimizing mechanical and electrical properties

3.1 Introduction

Yttria (Y_2O_3) is widely used as a sintering additive to toughen Al_2O_3 ^[1,2,3]. In Al_2O_3 -based or Al_2O_3 -rich ceramics, Y_2O_3 is segregated to the grain boundaries of Al_2O_3 or Al_2O_3 -rich phases. When the amount of segregated Y_2O_3 exceeds its solubility (as reported, the upper limit of Y_2O_3 in $\alpha\text{-Al}_2\text{O}_3$ is less than 10 ppm^[4]), it reacts with Al_2O_3 to form a stable yttrium aluminum garnet ($\text{Al}_5\text{Y}_3\text{O}_{12}$, YAG) phase, which often enhances the fracture toughness, Vickers hardness, and high-temperature creep resistance of alumina ceramics^[5,6]. YAG particles in Al_2O_3 , serving as a reinforcing phase, are considered to homogenize stress field distribution^[7] and play an important role in crack deflection, which is an effective toughening mechanism^[2,8,9]. Recently, Al_2O_3 /YAG composites have been considered as a promising candidate for high-temperature structural applications owing to their excellent mechanical properties, good chemical resistance, and high stability in comparison with Al_2O_3 ^[10,11,12].

On the other hand, dispersion of metal particles into ceramics has been extensively developed as an effective method to solve the brittleness of ceramics^[13,14,15]. In addition to the improved mechanical properties in comparison with those of monolithic ceramics, ceramic/metal composites have also shown new functions, such as electrical, optical, and magnetic properties, as well as machinability and superplasticity like metals. Ceramic/metal composites have been widely used as advanced structural parts in aircraft engine components,

cutting tools, and electrical conductors^[15,16,17,18,19]. Among these ceramic/metal composites, the compositing of Al₂O₃ and fine Ti might realize the incorporation of both high strength of Al₂O₃ and high fracture toughness of Ti. Since Al₂O₃ ceramic is widely used as structural components and Ti metal and its alloys are commonly used as dental implants and artificial joints^[20,21], Al₂O₃/Ti composites are considered as promising materials in a broadened application range for advanced structural parts, biomaterials, and electric devices. According to preliminary work, Al₂O₃/Ti composites were produced by a method based on the in-situ decomposition of titanium hydride (TiH₂) and sintering^[22].

Recently, I have reported the fabrication and multifunctions of Al₂O₃/Ti composites using the conventional hot-press sintering method^[23]. In the case of the Al₂O₃ composite containing 20 vol% Ti, fracture toughness was improved from 3.2 MPa·cm^{1/2} for monolithic Al₂O₃ to 4.3 MPa·cm^{1/2} for the Al₂O₃/20%Ti composite. Electrical resistivity was reduced monotonically from 3.0×10^{12} Ωcm from monolithic Al₂O₃ to 4.4×10^{-3} Ωcm from the Al₂O₃/30%Ti composite. This result suggests that the synergy of mechanical and electrical properties can be realized in one composite system.

In spite of the improved fracture toughness and excellent electrical conductivity, interfacial reaction between Al₂O₃ and Ti is not avoided completely. When TiH₂ was used as sintering material, although no Ti–Al alloys or intermetallic compounds (such as, Ti–Al and Ti₃Al) were detected, the formation of Ti–O phases and TiAl₂O₅ compounds were identified in sintered composites. These unfavorable reaction products filled up grain boundaries and weakened the bonding force^[24,25,26]. In particular, the presence of TiAl₂O₅ restricts the increase in the fracture toughness due to intergranular micro-cracking^[27]. Therefore, it is necessary to further control the interfacial reaction for optimizing the mechanical properties. In addition to the adverse effects on mechanical properties, interfacial reaction also affects the

increase in electrical conductivity. The reaction of Ti with Al_2O_3 decreases the amount of conductive pathways formed by Ti particles and increased electrical resistivity, because the reaction products, such as Ti-O and TiAl_2O_5 , are usually electrically insulators. It is speculated that if the interfacial reaction between Al_2O_3 and Ti could be further inhibited, electrical conductivity of $\text{Al}_2\text{O}_3/\text{Ti}$ composites could be further increased.

As mentioned before, Y_2O_3 is reported as effective additives in preparing ceramics to improve mechanical properties by suppressing interfacial reactions, strengthening grain boundaries, refining grain size, increasing oxidation resistance, and accelerating densification^[26,28,29,30]. However, in the reported $\text{Al}_2\text{O}_3/\text{Ti}$ system^[26,30], Ti powder was used as a sintering material, while brittle Ti-Al intermetallic compounds existed. In addition, little attention has been paid toward the role of YAG phases, which is considered as a dominant factor for inducing improvement mechanism. In addition to these effects on mechanical properties, the addition of Y_2O_3 for increasing electrical conductivity is also expected. By inhibiting interfacial reaction between Al_2O_3 and Ti, the decrease in the amount of Ti particles reacting with Al_2O_3 is considered to contribute toward the further increase in the effective volume of conductive pathways (here Ti phase) and thus the further increase in electrical conductivity. Few studies have examined the electrical properties of the $\text{Al}_2\text{O}_3/\text{Ti}$ composite system. The effects of Y_2O_3 addition on the electrical properties of the system are rarely reported. In this regards, I have recently reported the effect of fine Ti particulate dispersion on mechanical and electrical properties of Al_2O_3 ceramic composites^[23]. It was revealed that the addition of Ti not only enhanced the fracture toughness but also enhanced the electrical conductivity, which implies that the appropriate addition of Ti can realize multifunctional ceramic composites. Nevertheless, interfacial reaction between Al_2O_3 and Ti formed a small amount of reaction products, such as TiAl_2O_5 , Ti-O or dissolution of O into Ti phases, which

affect the mechanical properties of the composite. Furthermore, the dispersion of Ti had no effect on the enhancement of flexural strength of Al_2O_3 . The strength decreased with an increase in Ti content due to the enlargement of both Al_2O_3 and Ti grains. One of the reasons of this phenomenon might be the interfacial reaction. Therefore, to improve the strength particularly, it is necessary to inhibit or control the reaction during sintering.

Therefore, in the proposed study, I have attempted to combine the toughening effects of both Y_2O_3 and Ti to further optimize mechanical properties and improve electrical conductivity. Since $\text{Al}_2\text{O}_3/\text{Ti}$ composites are Al_2O_3 -base ceramics, it should be expected that the addition of Y_2O_3 has a similar effect on Al_2O_3 within $\text{Al}_2\text{O}_3/\text{Ti}$ composites. For the purpose of optimizing mechanical and electrical properties of Al_2O_3 ceramics, $\text{Al}_2\text{O}_3/20\text{vol}\%\text{Ti}$ composite was chosen as matrix, because the composition exhibited the highest fracture toughness and sufficiently low electrical resistivity^[23]. Y_2O_3 with different contents ranging from 0 to 5 wt% were used as the additive to the $\text{Al}_2\text{O}_3/\text{Ti}$ composites. The effects of Y_2O_3 on microstructures, mechanical, and electrical properties were investigated. The relations between mechanical and electrical properties and Y_2O_3 content were discussed by analyzing the optimization mechanism of Y_2O_3 .

3.2 Experiment process

3.2.1 Preparation of composites

$\alpha\text{-Al}_2\text{O}_3$ powder (0.2 μm , AKP-53, Sumitomo Chemicals Co., Ltd., Tokyo, Japan), TiH_2 powder (5–10 μm , > 99%; Kojundo Chemical Laboratory Co., LTD., Tokyo, Japan), and Y_2O_3 particles (99.99%, Kojundo Chemical Laboratory Co., LTD., Japan) were used as sintering materials. Different mass percent of Y_2O_3 (0, 1, 2, 3, and 5 wt%) was mixed with Al_2O_3 and

TiH₂ powders by wet ball milling for 24 h in ethanol. The volume fraction of Ti in final products was fixed to 20 vol% and thus the volume fraction of Al₂O₃ and Y₂O₃ was 80 vol%. Dried mixtures were again ball-milled for another 12 h, followed by hot-press sintering under an applied pressure of 30 MPa at 1500 °C for 1 h (Hi-Multi 5000, Fuji Dempa Kogyo Co., Ltd., Osaka, Japan). The heating rate was 20 °C/min. All these processes were carried out in Ar atmosphere. The thermal etching procedure was conducted at 1350 °C for 1 h in Ar atmosphere to reveal the microstructural characteristics and grain size of the Al₂O₃ matrix.

3.2.2 Characterization of mechanical properties

Microstructures of specimens and elemental analysis were observed using scanning electron microscopy (FE-SEM; SU9000, Hitachi, Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX; X-Max100TLE, Horiba, Kyoto, Japan). Phase compositions were determined by X-ray diffraction (XRD; D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany) using CuK α radiation at 40 kV and 40 mA. The relative densities and porosity were measured by Archimedes' method in deionized water. Young's modulus was determined by the ultrasonic velocity data obtained using a digital storage oscilloscope (DSOX3052T, Keysight, Tokyo, Japan) and an ultrasonic pulser/receiver (Model 5072, PANAMETRICS, MA, USA). Vickers hardness was measured using a Vickers Hardness Tester (FV-310e, Future-tech Corp., Tokyo, Japan) with an applied load of 98 N and holding time of 15 s. Fracture toughness was calculated under the same conditions using the indentation fracture (IF) method based on the lengths of the observed cracks^[31]. More than 10 indentations were measured and averaged for each sample.

3.2.3 Characterization of electrical properties

Electrical resistivity was measured by the Van-der Pouw method using polished disks (diameter = 12 mm and thickness = 1.5 mm). This method is based on four-probe resistivity and Hall coefficient measurements, which were carried out using an electrical resistivity measurement system (Resitest 8310, Toyo Technica Corp., Tokyo, Japan) under an air atmosphere at room temperature. Three specimens and more than six measurements were conducted and averaged for each composite.

3.3 Results and discussion

3.3.1 Phase development and composition

The typical microstructure and distribution of added yttrium were confirmed by SEM and EDX analysis. Results are shown in Figure 1 and Table 1. Ti phase, which could be seen as the bright contrast particles, was typically at micrometer size and dispersed between Al_2O_3 grains that were dark ones [Figure 3.1(a)]. EDS analysis revealed that yttrium was only observed at grain boundaries. More specifically, yttrium only located at triple points formed by Al_2O_3 and Al_2O_3 [Point 1 and 2 in Figure 3.1(a)] or Al_2O_3 and Ti [Point 3 and 4 in Figure 3.1(b)]. All these analyzed regions contained Ti, Al, and O meaning that no monolithic Y_2O_3 phase existed. The corresponding phase was then identified by considering the composition and XRD analysis results as shown below.

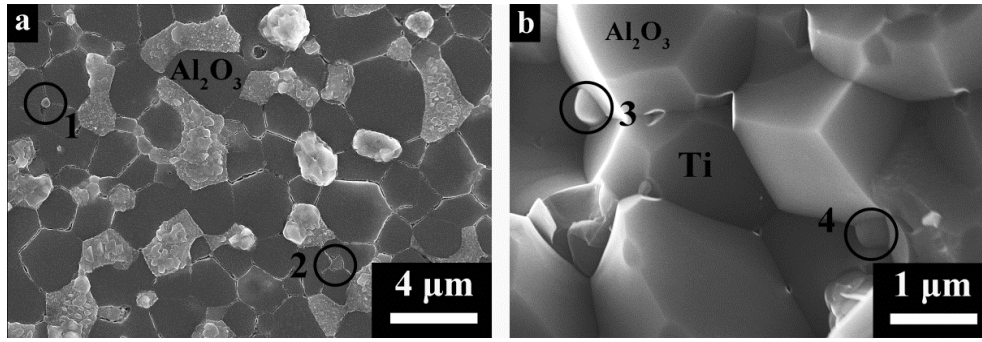


Figure 3.1 SEM micrographs of representative area in 2 wt% Y₂O₃ added Al₂O₃/20 vol% Ti composite, (a) top surface and (b) fracture surface. The circle marks with numbers represent the points of EDX quantitative analysis (Table 3.1).

Table 3.1 Chemical composition of the surface of the 2 wt% Y₂O₃ added Al₂O₃/20vol%Ti composite measured by EDX.

Point	Elements (mol%)				Possible phase
	Ti	Al	O	Y	
1	0.5	21.0	64.7	13.8	Y ₃ Al ₅ O ₁₂
2	0.3	22.6	63.4	13.7	Y ₃ Al ₅ O ₁₂
3	2.7	28.6	60.2	8.5	Y ₃ Al ₅ O ₁₂
4	5.7	27.8	61.2	5.3	Y ₃ Al ₅ O ₁₂

Figure 3.2 shows the XRD patterns of Y₂O₃ added composites. Yttrium aluminum garnet Y₃Al₅O₁₂ (YAG phases, PDF 00-033-0040) was identified in all samples after adding Y₂O₃, in addition to main phases of α -type Al₂O₃ and α -type metallic Ti, while no other compounds containing yttrium element were detected. Small reaction product that is considered as TiAl₂O₅ (PDF 00-026-0040) also existed. The size of YAG particles was about 200 nm (Figure 3.1). The content of YAG was increased by an increase in Y₂O₃. During sintering, the

solid-state reaction between Al_2O_3 and Y_2O_3 took place to form YAG. The free energy change ΔG of this reaction at 1500°C was calculated as -280 kJ/mol using the thermodynamic parameters equation^[32,33]. As mentioned above, YAG particles present at the grain boundaries affect the grain growth, microstructure, and residual stress distribution, thus influencing mechanical properties. Thus, it is expected that the existence of YAG particles would be the main factor for inducing reinforcement effect.

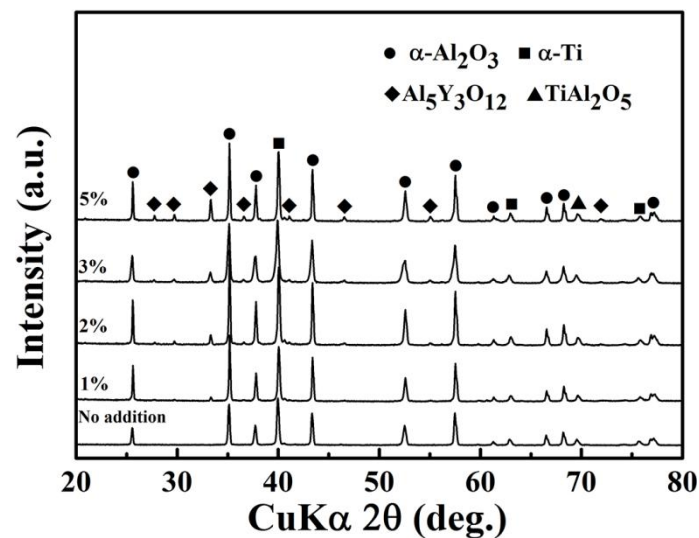


Figure 3.2 XRD patterns of $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composites with different contents of Y_2O_3 addition.

Since TiAl_2O_5 was detected in all Y_2O_3 added composites, the ratio of TiAl_2O_5 peak intensity relative to the sum of peak intensity of Al_2O_3 and Ti was chosen as characterization parameter to confirm whether Y_2O_3 addition weakened the interfacial reaction between Al_2O_3 and Ti. The result is shown in Figure 3.3 as a function of Y_2O_3 content. The most intensive peak of each phase was taken into calculation and peak information is list in Table 2. By increasing the Y_2O_3 content, the ratio value $I_{\text{TiAl}_2\text{O}_5}/(I_{\text{Al}_2\text{O}_3} + I_{\text{Ti}})$ decreased, which in turn,

resulted in a decrease in the amount of formed TiAl_2O_5 content. It was reported that the interfacial reaction took place during the sintering as a result of Al_2O_3 dissolution into Ti by diffusion^[34]. In the proposed study, Y_2O_3 present at the grain boundaries might act as a blocking site that inhibited the diffusion of Al_2O_3 into Ti. Accordingly, interfacial reaction between Al_2O_3 and Ti was reduced to a certain degree. As a result, bonding between Ti and Al_2O_3 might be strengthened.

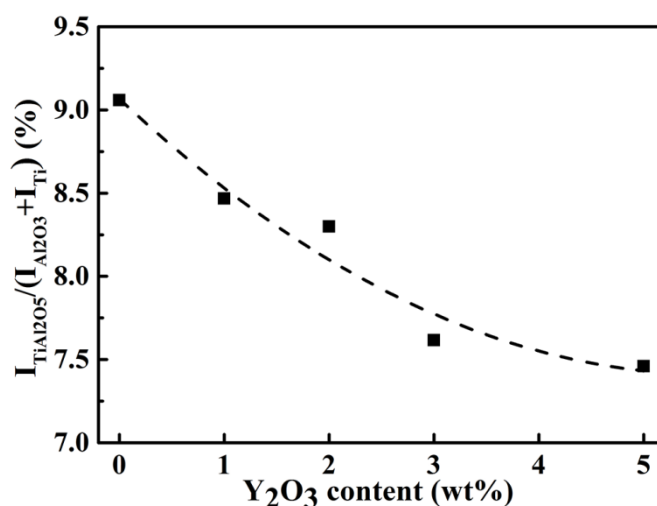


Figure 3.3 Change of ratio of TiAl_2O_5 peak intensity ($I_{\text{TiAl}_2\text{O}_5}$) relative to the sum of Al_2O_3 ($I_{\text{Al}_2\text{O}_3}$) and Ti (I_{Ti}) peak intensities by increasing Y_2O_3 content.

Table 3.2 Information of peaks taken into calculation.

Phases	2θ	(hkl)
Al_2O_3	35.130	(104)
Ti	40.171	(101)
TiAl_2O_5	68.482	(242)

3.3.2 Density and microstructure

Densities of the composites as a function of Y_2O_3 contents are shown in Figure 3.4. The densities of all Y_2O_3 added composites were higher than those of composites without Y_2O and increased by increasing Y_2O_3 content. Porosity decreased at the same time. During sintering, a solid-state reaction between Al_2O_3 and Y_2O_3 took place to form YAG. YAG phases and content have great effects on sintering and densification process^[40]. The higher density of YAG ($\rho = 4.55 \text{ g/cm}^3$) than that of both Al_2O_3 ($\rho = 3.9 \text{ g/cm}^3$) and Ti ($\rho = 4.5 \text{ g/cm}^3$) is considered as one of the reason for the increased bulk density. In addition, it is well known that the existed pores could act as stress concentration region, resulting in the degradation of mechanical properties, and thus flexural strength is closely related to porosity of ceramic^[35]. In the proposed study, the decrease in porosity is thought to contribute toward the improvement of mechanical properties, especially toward enhancing the flexural strength.

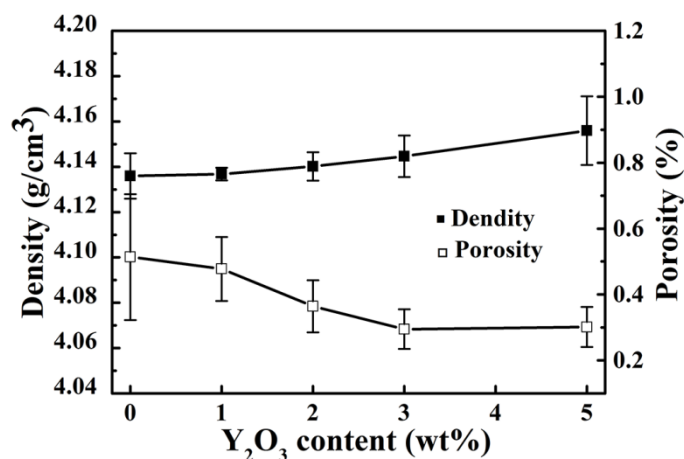


Figure 3.4 Densities and porosity of composites as the function of Y_2O_3 content for $\text{Al}_2\text{O}_3/20$ vol% Ti composite.

Microstructure was observed by SEM and EDS. Fracture surfaces of composites are shown in Figure 3.5. Inset in each graph shows transgranular fracturing in a Ti particle. All the composites showed dense structures having well bonding interface between each constituent grain. In all Y_2O_3 added composites, transgranular fracture was observed to be dominant. The existence of transgranular fracture indicates relatively high fracture toughness^[36]. According to the previous reports^[30,37], the interface between Al_2O_3 and Ti is weaker than that of monolithic Al_2O_3 due to weak bonding between Al_2O_3 and Ti. Cracks, thus, tend to propagate along weaker interface, resulted in intergranular fracture. In the current investigation, after adding Y_2O_3 , crack propagation along interface might become difficult owing to the reinforced interface by inhibiting interfacial reaction by the formation of YAG phases. Hence, cracks tended to propagate through Ti particles, resulting in the transgranular fracture of Ti particles as mentioned above.

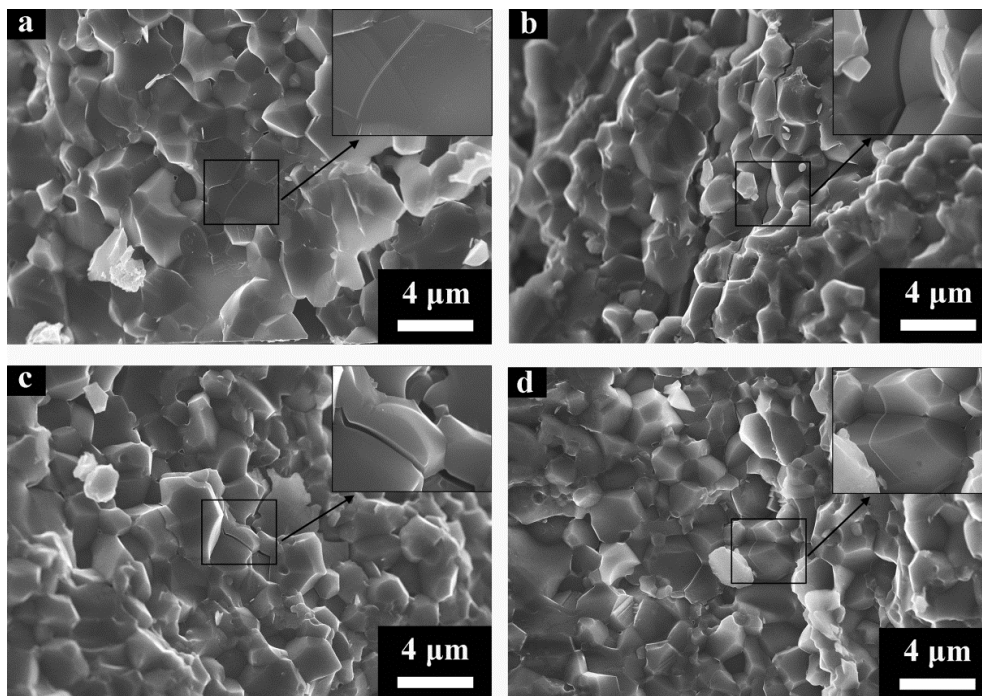


Figure 3.5 Fracture surface of Y_2O_3 added Al_2O_3 /20 vol% Ti composites having different Y_2O_3 content of (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, and (d) 5 wt%.

Thermally etched surfaces of composites with or without Y_2O_3 addition are shown in Figure 3.6. Based on EDX analysis, the bright and dark phases correspond to Ti and Al_2O_3 , respectively. As shown in Figure 3.6 (a), Ti particles were expanded and had complicated shape possibly due to some surface reaction of Ti and/or recrystallization during etching process. The interface between Al_2O_3 and Ti was blurry. After adding Y_2O_3 , homogenized Ti particles and more uniform microstructure were observed in Figure 3.6(b). The interface between Al_2O_3 and Ti was well revealed by thermal etching. Al_2O_3 matrix grain size was calculated by image analysis method using image J software. In Al_2O_3 /Ti composite without Y_2O_3 , Al_2O_3 grain size was calculated as $1.8 \pm 0.6 \mu m$. For Al_2O_3 /Ti system with 2wt% Y_2O_3 , Al_2O_3 average grain size was reduced to $1.5 \pm 0.6 \mu m$. YAG particles and content strongly influence grain growth^[2,40]. After adding Y_2O_3 , a pinning effect for grain growth of Al_2O_3 took place at grain boundaries due to the formation of YAG particles. Grain boundary diffusion was thus inhibited^[38]. As a result, the growth of both Al_2O_3 grains and Ti particles were restricted. The decrease in grain size further affected microstructures, leading to a refined one. Effective reinforcement is expected to be realized by the refined microstructure of both Al_2O_3 matrix and Ti dispersion having homogeneously distributed Ti phases owing to the addition of Y_2O_3 .

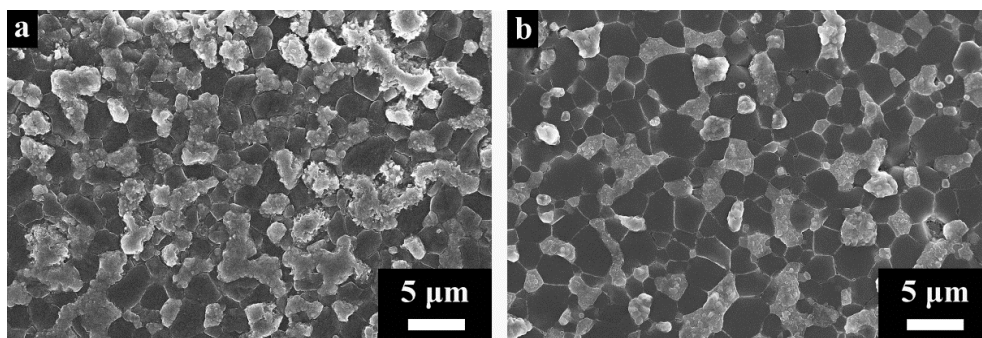


Figure 3.6 SEM micrographs of thermally etched samples for (a) without Y_2O_3 and (b) with 2 wt% Y_2O_3 addition.

3.3.3 Mechanical properties

Young's modulus, Vickers hardness, and fracture toughness of the composites are shown as a function of Y_2O_3 content in Figures 3.7 and 3.8. These data were the averages of at least seven measurements for each sample. The variation of Young's modulus, hardness, and fracture toughness showed the same trend with the increase of Y_2O_3 content. The values reached the maximum when Y_2O_3 addition content was 2 wt% for all the case. In this case, Young's modulus, Vickers hardness, and fracture toughness were 358 GPa, 15.4 GPa, and $4.6 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. These values for the $Al_2O_3/20\text{vol}\%\text{Ti}$ composite without Y_2O_3 addition were 352 GPa, 14.5 GPa, and $4.3 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. These results imply that the addition of Y_2O_3 exhibited an improvement in the mechanical properties of the proposed composites. As discussed before, the composite contained slight amount of YAG phase. The reinforcing effect from YAG phase, showing superior high hardness and fracture toughness, is thus mainly considered to account for the improved mechanical properties. The introduction of YAG is an effective method for increasing hardness and fracture toughness of Al_2O_3 , in spite of relatively low Young's modulus of YAG^[39]. However, Young's moduli of Y_2O_3 added composites having refined microstructure, strengthened bonding force, and dense structure were all higher than that of composite without Y_2O_3 . In addition, the existence of YAG phases changing the distribution of stress field and causing crack deflection was thought to be the effective factors on the increased fracture toughness. This could be interpreted from the crack propagation behavior as discussed below.

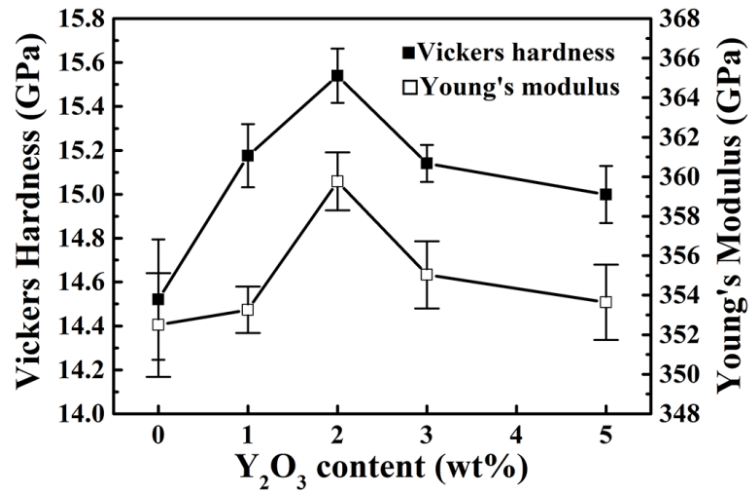


Figure 3.7 Vickers hardness and Young's modulus of Y_2O_3 added Al_2O_3 /20 vol% Ti composites as a function of Y_2O_3 content.

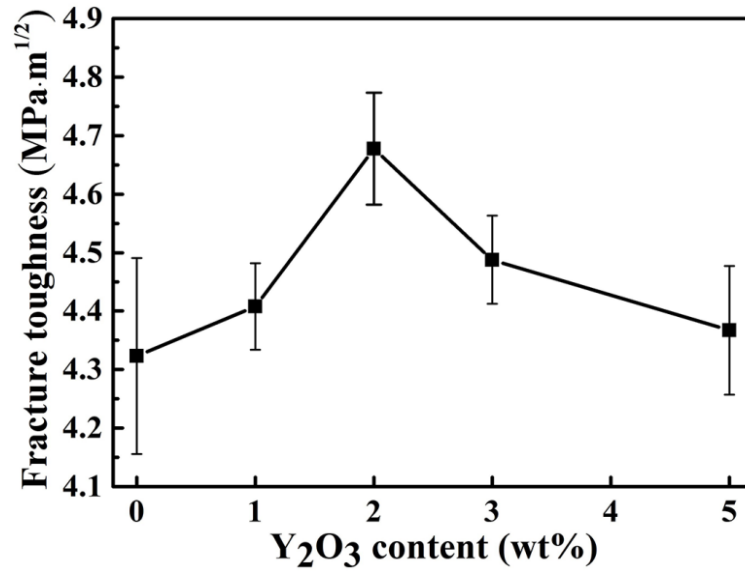


Figure 3.8 Fracture toughness of Y_2O_3 added Al_2O_3 /20 vol% Ti composites as a function of Y_2O_3 content.

Figure 3.9 shows the SEM micrographs of the crack introduced by Vickers indentation. Obvious crack deflection and transgranular fracture were observed for the composites without Y_2O_3 addition. Crack bridging and plastic deformation of Ti was also confirmed as minor phenomena^[23]. After adding Y_2O_3 , the transgranular fracture that was also observed in Figure 3.5 was a result of the reinforced interface. Crack deflection is the main reason accounting for increased fracture toughness.

Two aspects inducing crack to deflect were taken into consideration. At first, crack deflection was due to the existence of hard YAG particles. In the absence of Y_2O_3 , interface between Al_2O_3 and Ti was weaker than that of monolithic Al_2O_3 . Cracks propagated mostly along the heterogeneous interface without distinct deflections^[40]. Since YAG is harder than both Al_2O_3 and Ti, cracks couldn't pass through YAG particles and changed to go around them when cracks came close to them. As a result, crack propagation path was deflected and further propagation became difficult.

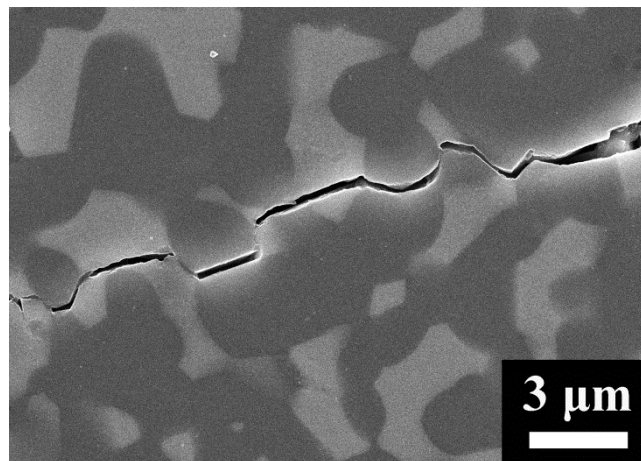


Figure 3.9 SEM micrograph of crack propagation path in 2 wt% Y_2O_3 added Al_2O_3 /20 vol% Ti composite.

In addition, crack deflection is ascribed to the change of stress distribution in $\text{Al}_2\text{O}_3/\text{Ti}$ composites caused by YAG. It is considered to the present residual stress at the grain boundaries and/or $\text{Al}_2\text{O}_3/\text{Ti}$ interface related from the mismatches of coefficients of thermal expansion ($\alpha_{\text{Al}_2\text{O}_3} = 8.71 \times 10^{-6}/\text{K}$, $\alpha_{\text{Ti}} = 7.14 \times 10^{-6}/\text{K}$) and Young's modulus ($E_{\text{Al}_2\text{O}_3} = 380$ GPa, $E_{\text{Ti}} = 116$ GPa) between Al_2O_3 and Ti. In the area of compressive stress, crack propagation tended to deflect. In the area of tensile stress, cracks tend to propagate along a straight line^[2]. These effects are regarded as one of the mechanisms for crack deflection in Ti-dispersed Al_2O_3 composite, which can contribute toward the enhanced toughness^[23].

When small amount of another phases having different thermal expansion coefficient with matrix locate at grain boundaries, a new residual stress field may be created and change the whole stress distribution state of the materials^[41]. In the proposed study, because YAG phase was formed after addition of Y_2O_3 , such an additional residual stress field might be created. YAG particles were subjected to compressive stress due to the lower thermal expansion coefficient of formed YAG ($\alpha_{\text{YAG}} = 6.9 \times 10^{-6}/\text{K}$) than that of Al_2O_3 . Such distribution of stress should affect the variation of crack propagation path.

In the proposed study, with 1 and 2 wt% Y_2O_3 addition, YAG phases might change the residual stress distribution and then make cracks reaching close to compressive stress area, and crack deflection was invisible. On the other hand, in the case of composites containing more than 3 wt% Y_2O_3 , decreased fracture toughness was ascribed to the strengthened interface. According to Tuan et. al.^[17], intermediate bonding strength between ceramic matrix and metal phases benefits for improving fracture toughness of ceramic/metal composites. Too weak or too strong bonding force can limit the contribution from ductility of metal phase on toughening, which are thus also the case for the present $\text{Al}_2\text{O}_3/\text{Ti}$ composite system containing high amount of Y_2O_3 addition. Therefore, based on the results above, the addition of 2 wt%

Y_2O_3 was optimized for reinforcing bonding force and improving fracture toughness.

To compare the optimization effects among Y_2O_3 , Ti and combination of Y_2O_3 and Ti on the performance of Al_2O_3 , density and mechanical properties of monolithic Al_2O_3 , Ti-dispersed Al_2O_3 composite, Y_2O_3 -doped Al_2O_3 and Y_2O_3 doped $\text{Al}_2\text{O}_3/\text{Ti}$ composite are listed in Table 3. The results were concluded as follows.

In the case of Y_2O_3 added Al_2O_3 , Young's modulus and Vickers hardness were almost the same as those of monolithic Al_2O_3 while they showed great increase in fracture toughness. In $\text{Al}_2\text{O}_3/\text{Ti}$ composite, although Young's modulus and Vickers hardness were low, relatively high fracture toughness was obtained. Among these material systems listed in Table 3.3, Y_2O_3 added $\text{Al}_2\text{O}_3/\text{Ti}$ exhibited the highest fracture toughness as well as moderate Young's modulus and Vickers hardness. It was concluded that the addition of Y_2O_3 is more effective than metal Ti in improving mechanical properties of Al_2O_3 .

However, compositing with metal Ti can realize multifunctionality, i. e., electrical conductivity, can be added to insulator ceramics such as Al_2O_3 , which cannot be achieved by the addition of only Y_2O_3 ^[30]. Ceramics with controlled electrical conductivity can be machined by electrical discharge machining, providing a new route for advanced ceramic processing. Hence, the effects of Y_2O_3 addition on electrical properties of $\text{Al}_2\text{O}_3/\text{Ti}$ composites were investigated and results are discussed in the following section.

Table 3.3 Density and mechanical properties of Al₂O₃ and its composites with different combination of added phases.

Materials system	Density (g/cm ³)	Young's Modulus (GPa)	Vickers hardness (GPa)	Fracture toughness (MPa·m ^{1/2})
monolithic Al ₂ O ₃	3.93±0.01	402±3.7	17.1±0.2	3.58±0.07
2wt% Y ₂ O ₃ -Al ₂ O ₃	4.16±0.02	400±2.7	17.5±0.4	4.33±0.28
Al ₂ O ₃ /20vol%Ti	4.14±0.01	352±2.4	14.5±0.3	4.32±0.17
2wt% Y ₂ O ₃ -Al ₂ O ₃ /20vol%Ti	4.14±0.01	360±1.5	15.5±0.1	4.68±0.10

3.3.4 Electrical properties

The electrical resistivity of these composites is shown as a function of Y₂O₃ content in Figure 3.10. The electrical resistivity of these composites monotonically increased with an increasing in the Y₂O₃ content. However, this increase in resistivity was unexpected. After adding 5 wt% Y₂O₃, the electrical resistivity of the Al₂O₃/20vol% Ti composite changed from 8.04×10^{-3} to 1.11×10^{-2} Ωcm, which still maintained high conductivity.

When electrically conductive Ti phase was dispersed into insulating Al₂O₃ matrix, Ti particles tended to touch each other to form continuous conduction pathway according to the percolation of dispersed Ti phase. Electric current can continuously pass through these interconnected Ti networks, leading to an increase in electrical conductivity, which changed Al₂O₃ ceramic body from insulator into conductor.

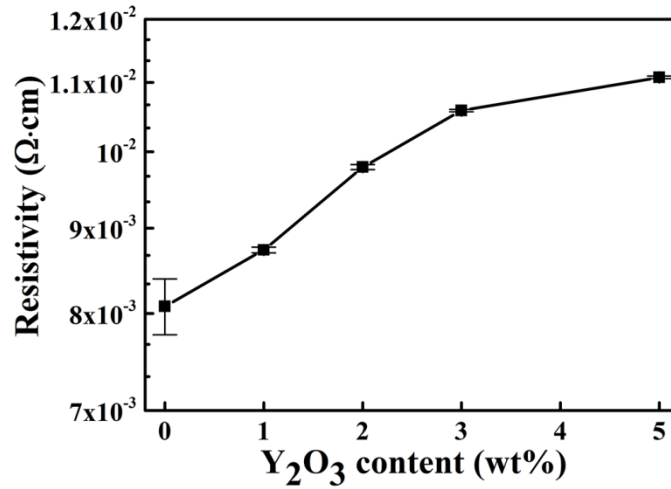


Figure 3.10 Electrical resistivity of Y₂O₃ added Al₂O₃/Ti composites as the function of Y₂O₃ content.

Our previous study revealed that the percolation threshold volume of fine Ti particles in Al₂O₃, where Ti was dispersed to Al₂O₃ by ball milling and followed sintering, was 13.8 vol%^[30]. Therefore, the composites containing large amount of Ti exhibited good electrical conductivity. In the case of Al₂O₃/20%Ti without Y₂O₃, electrical resistivity was $8.04 \times 10^{-3} \Omega\text{cm}$, which was $3.0 \times 10^{12} \Omega\text{cm}$ for monolithic Al₂O₃. After adding Y₂O₃, a small amount of YAG phase was formed. The YAG is insulator material, and particular YAG exists in grain boundaries (Figure 3.1); continuous Ti network was interrupted and thus conductive pathways were decreased. As a result, the electrical conductivity was consequently reduced.

However, within 5 wt% Y₂O₃ addition, the increase in electrical resistivity was negligible and composites could still have sufficiently low resistivity and hence were regarded as good conductors. This result implies that the balanced mechanical and electrical properties might open new applications of ceramic-based composites such as electro-discharge machinable ceramics.

3.4 Summary

The optimization effects of Y_2O_3 on mechanical and electrical properties of $Al_2O_3/20vol\%Ti$ composites due to the formation of YAG phases were studied. Y_2O_3 accelerated densification process and relatively dense composites were obtained. All Y_2O_3 added composites showed higher Young's modulus, Vickers hardness, and fracture toughness. The optimal Y_2O_3 content for the balanced mechanical and electrical properties in the proposed system was 2 wt%. The addition of Y_2O_3 prevented interfacial reaction, strengthened interface, inhibited Al_2O_3 matrix grain growth, and refined microstructure. The reason for the increased fracture toughness was mainly considered as the result of crack deflection. Due to the formation of insulated YAG, the addition of Y_2O_3 increased electrical resistivity of composites; however, this increase was negligible. When Y_2O_3 content was not more than 5 wt%, composites can be considered as conductors. The composite containing 2 wt% Y_2O_3 exhibited a good balance of increasing mechanical and electrical properties. After combining with dispersed metallic Ti particles, Al_2O_3 became a potential multifunctional ceramic. This multifunction was further improved by incorporating Y_2O_3 , making Al_2O_3 a promising materials in wide application fields.

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Surface morphology modification of ceramic-based composites for photocatalytic activity via simple chemical and heat treatments

4.1 Introduction

When metal particles are imbedded in ceramic substrates such as aluminum oxide (Al_2O_3) ceramics (which are used for hip implants^[1]) to form ceramic-based ceramic/metal composites, the combined advantages of ceramic and metal make these composites promising multifunctional materials with excellent mechanical properties^[2,3,4]. In our previous study, because of its good physicochemical consistency, titanium (Ti) was chosen as a second metal phase with which to toughen brittle Al_2O_3 ^[5]. The results showed that the fracture toughness of an $\text{Al}_2\text{O}_3/\text{Ti}$ composite containing 20% Ti as assessed by fracture volume was 37% higher than that of monolithic Al_2O_3 . I have measured the bending strength to be 475.6 MPa higher than that reported for metallic Ti^[6]. Other reports have also indicated that $\text{Al}_2\text{O}_3/\text{Ti}$ composites exhibit improved fracture toughness over that of Al_2O_3 and increased hardness and bending strength over those of Ti metal^[7,8,9]. A study of electrical conductivity showed that the electrical resistivity decreased monotonically from $3.0 \times 10^{12} \Omega\text{cm}$ for monolithic Al_2O_3 to $4.4 \times 10^{-3} \Omega\text{cm}$ for a composite of Al_2O_3 and 30% Ti^[5]. These excellent properties make Al_2O_3 ceramics possible materials for multifunctional applications.

Based on the performance of Ti metal, $\text{Al}_2\text{O}_3/\text{Ti}$ composites are considered to be promising ceramic-based composites for exhibiting photocatalytic activity. Therefore, with titanium dioxide (TiO_2) layers on their surfaces, $\text{Al}_2\text{O}_3/\text{Ti}$ composites are expected to act as environmental purification materials that exhibit both excellent mechanical properties and

photocatalytic activity.

Nowadays, to develop Ti metal and Ti-based alloys for artificial and implants, the materials are often treated with sodium hydroxide (NaOH) and heat to obtain bioactive surface layers to increase the surface roughness and specific surface area^[10,11,12,13,14]. After NaOH treatment, a nanometer-scale porous oxide layer has been found to form on the surface of Ti and its alloys, and TiO₂ with different crystalline phases appears on the surface after heat treatment^[15,16,17]. With the surface morphology controlled at nanometer scale and with high specific surface area, Ti after treatment with NaOH and heat has been reported to be effective in methylene-blue decomposition under visible light^[13].

Recently, because of its good chemical stability, high oxidizability, and non-toxicity, TiO₂ photocatalysts have been applied extensively to water purification, environmental cleaning, and the decomposition of organic pollutants^[18,19,20,21]. However, most of the reported TiO₂ photocatalysts were in the form of suspended powder. When used to deal with organic pollutants, suspended TiO₂ powder diffuses easily into water, thereby causing a secondary pollutant. Because it is difficult and costly to separate photocatalysts from aqueous solution, increasing attention is being paid to immobilized TiO₂ photocatalysts^[22,23,24]. Compared with powdered photocatalysts, immobilized photocatalysts can be used continuously and require no additional catalyst separation.

It is believed that NaOH treatment has the same effects on Ti within Al₂O₃/Ti composites which could generate a nano-porous layer on Ti surface to induce photocatalytic ability. When Al₂O₃/Ti composites are used for photocatalysis, being based on Al₂O₃ they have crucial advantages over Ti metal, such as higher bending strength, better wear behavior, high-temperature oxidization, corrosion resistance, good chemical stability, and low elastic modulus^[25,26,27,28,29]. However, to the best of our knowledge there have been no reports to date on using simple chemical treatments to form bioactive surfaces on ceramics or ceramic-based

composites for photocatalytic activity.

In the present study, to provide photocatalytic ability for multifunctional applications, I attempted to generate nano-porous surfaces at nanometer scale on $\text{Al}_2\text{O}_3/\text{Ti}$ composites to make them suitable as photocatalysts via subsequent chemical and heat treatments. To obtain a complete nano-porous surface layer over the entire surface of an $\text{Al}_2\text{O}_3/\text{Ti}$ composite, I exerted strict control over the NaOH concentration, treatment temperature, and time. Our preliminary study led us to treating a composite of Al_2O_3 and 20 vol% Ti, which showed the highest fracture toughness. The photocatalytic activity [in the form of the degradation efficiency of Rhodamine B (RhB)] of this treated $\text{Al}_2\text{O}_3/\text{Ti}$ composite was investigated, and factors which most affect its photocatalytic efficiency and why were considered.

4.2 Materials and methods

4.2.1 Samples preparation

$\text{Al}_2\text{O}_3/\text{Ti}$ composites were fabricated using mixtures of titanium hydride powder (TiH_2 , 5–10 μm , 99% up; High purity chemicals, Japan), corresponding to 20% of Ti in volume fraction in the final composite, and $\alpha\text{-Al}_2\text{O}_3$ powder (0.2 μm , AKP-53; Sumitomo Chemicals Co., Ltd., Japan) by hot-press sintering under an applied pressure of 30 MPa at 1,500°C for 1 h in an argon atmosphere. The heating rate was 20°C/min. The hot-pressed samples were machined into plate specimens with dimensions of 15 mm $\times$ 15 mm $\times$ 1.5 mm. These specimens were polished with diamond paste to 2 μm , washed in an ultrasonic cleaner with ethanol and high-purity water, and then dried in an oven at 60°C.

4.2.2 Surface treatment

The surface treatment of the composites was conducted in 20 mL of NaOH solution for

different times from 0.5 to 24 h. To study the effects of NaOH soaking conditions on the surface structure of the $\text{Al}_2\text{O}_3/\text{Ti}$ composites, the NaOH concentrations of 5 and 10 M and the treatment temperatures of room temperature and 60°C were chosen. The NaOH solution containing the sample was shaken in a bio-shaker (BR-23FP; Taitec, Japan) at 80 rpm. After soaking, the sample was removed from the NaOH solution and washed gently several times with high-purity water. For simple HCl or water treatment, composites after NaOH treatment and water washing were immersed in 10 mL of 0.5-mM HCl solution at 25°C or water at 80°C for shaken for 24 h in the bio-shaker at 80 rpm. All samples treated with NaOH and HCl or water were dried in ambient. After drying, the specimens were heated at 400°C, 500°C, or 600°C for 1 h in an electric furnace (Isuzu; Seisakusho Co., Ltd, Japan) in air at a rate of 5°C/min and then allowed to cool with the furnace to investigate how the heating temperature affected the surface morphologies of the treated composites.

4.2.3 Analysis of sample surface

The structures of the sample surfaces were studied by means of a field-emission scanning electron microscope (FE-SEM) (SU9000; Hitachi, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX) (EDX; Horiba, Japan). Phases were measured by a thin-film X-ray diffractometer (TF-XRD) (D8 Advance; Bruker Ltd., USA) using $\text{CuK}\alpha$ radiation at 40 kV and 40 mA. The glancing angle of the incident beam was set to 1° relative to the sample surface, and the chemical state of each sample was assessed by means of X-ray photoelectron spectroscopy (XPS) (JPS-9010MX; JEOL)

4.2.4 Evaluation of photocatalytic activity

The RhB degradation efficiency was used to evaluate the photocatalytic activity. One hot-pressed sample was divided into four pieces and each piece was in the size of 15 mm × 15

mm × 1.5 mm. After subjected to NaOH, HCl, and heat treatments, these pieces were immersed in 30 mL of 5-mg/L RhB solution and irradiated using an ultraviolet (UV) light source (Supercure-204S; San-ei Electric, Japan) under ambient conditions. Before being exposed to UV light, the solution was stirred in the dark for 1 h to reach adsorption–desorption equilibrium. The change in RhB concentration was examined by means of a UV–visible (UV-VIS) spectrophotometer (UV mini 1240; Shimadzu, Japan) by measuring the UV absorbance at 553 nm.

4.3 Results

4.3.1 Surface structures after NaOH treatment

Figure 4.1 shows micrographs of surface morphologies observed by FE-SEM of Al₂O₃/Ti composites [Fig. 4.1(a)] and hot-pressed monolithic Al₂O₃ treated by 5-M NaOH at 60°C for 24 h [Fig. 4.1(b)]. The bright and dark phases in Fig. 4.1(a) correspond to Ti and Al₂O₃, respectively. No porous layer was visible on the surface of the NaOH-treated Al₂O₃, indicating that NaOH treatment does not affect Al₂O₃.

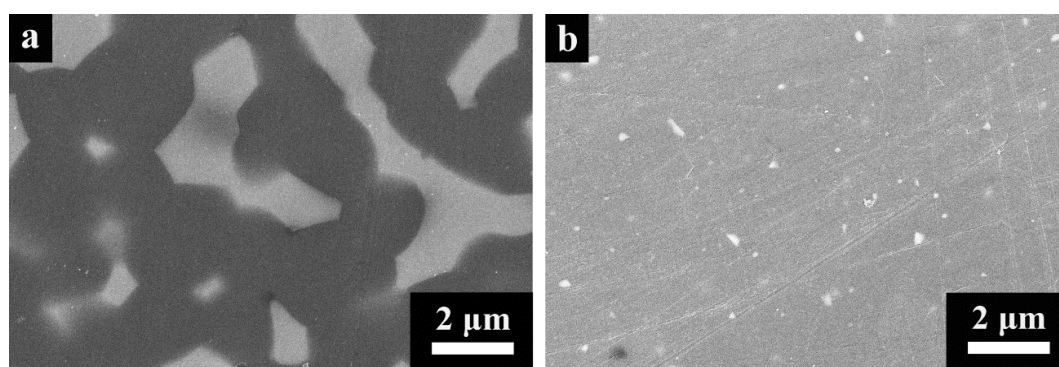
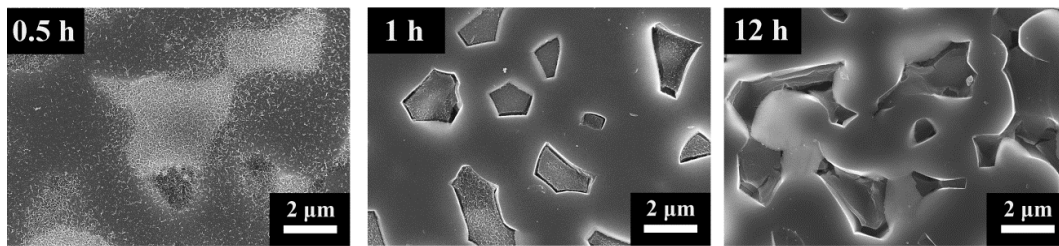


Figure 4.1 FE-SEM micrographs of surface morphologies of (a) untreated Al₂O₃/Ti composites and (b) Hot-pressed Al₂O₃ subjected to 5M-NaOH treatment at 60 °C for 24 h.

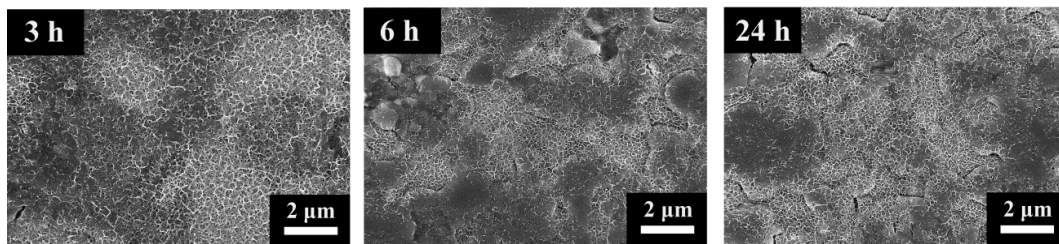
Figure 4.2 shows some representative micrographs of $\text{Al}_2\text{O}_3/\text{Ti}$ composites subjected to NaOH treatment at different NaOH concentrations and temperatures for various times from 0.5 to 24 h. The inset is a high-resolution micrograph of the Ti surface. In all the NaOH-treated composites, the Al_2O_3 phase is clearly distinguishable. At the higher NaOH concentration of 10 M and with treatment at room temperature, after 1 h the nano-porous structure had formed only on the Ti surface while a complete surface layer remained [Fig. 4.2(a)]. Extending the treatment time to 1 h, it was found that the porous layer formed on the Ti surface was partially removed and a bare interface between the surface of Al_2O_3 and Ti was revealed. After treatment for 24 h, no porous structure was visible and the formed porous layer had been removed completely.

In the case of 5-M NaOH, when treated at room temperature for 3 h or at 60°C for 1 h, the entire composite surface regardless of Al_2O_3 or Ti was covered with a complete nano-porous layer devoid of cracks or defects. When treated the composites for the longer time of 24 h, a nano-network was still formed on the entire surface, but now the $\text{Al}_2\text{O}_3/\text{Ti}$ interface was exposed and obvious Ti collapse was observed. After treatment with 5-M NaOH at 60°C for 1 h, the formed continuous fibrous networks were less than 20 nm in diameter.

10 M NaOH–RT



5 M NaOH–RT



5 M NaOH–60 °C

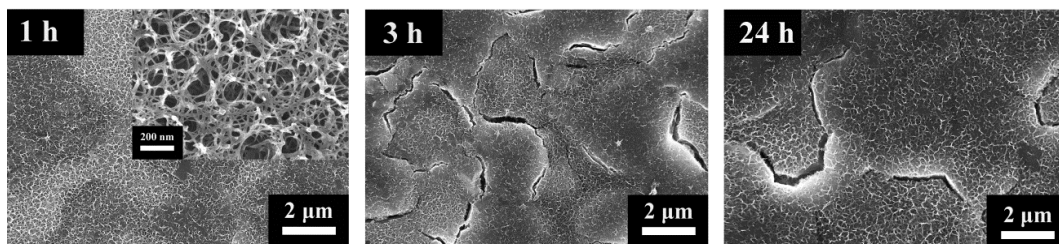


Figure 4.2 Representative FE-SEM micrographs of surface morphologies of 5M or 10M-NaOH treated $\text{Al}_2\text{O}_3/\text{Ti}$ composites for different time at various temperatures.

4.3.2 Surface structures after subsequent HCl or water treatment

Figure 4.3 shows surface micrographs of the composites after HCl or water treatment following 5-M NaOH treatment at 60°C for 1 h. The dashed line in each micrograph indicates the $\text{Al}_2\text{O}_3/\text{Ti}$ boundary, with the Al_2O_3 surface to the left. Figure 4.3 indicates that the subsequent HCl or water treatment did not remove the porous layer from the Al_2O_3 surface. As shown in Fig. 4.3(a) and (c), after HCl treatment, a nano-porous network remained on the surface and then changed into nano-rods after heating at 600°C. Meanwhile, after water

treatment at 80°C, a porous network structure also remained despite the network having widened, as shown in Fig. 4.3(b). After heating at 600°C, the fibrous network disappeared and the surface was covered instead by nano-particles, as shown in Fig. 4.3(d).

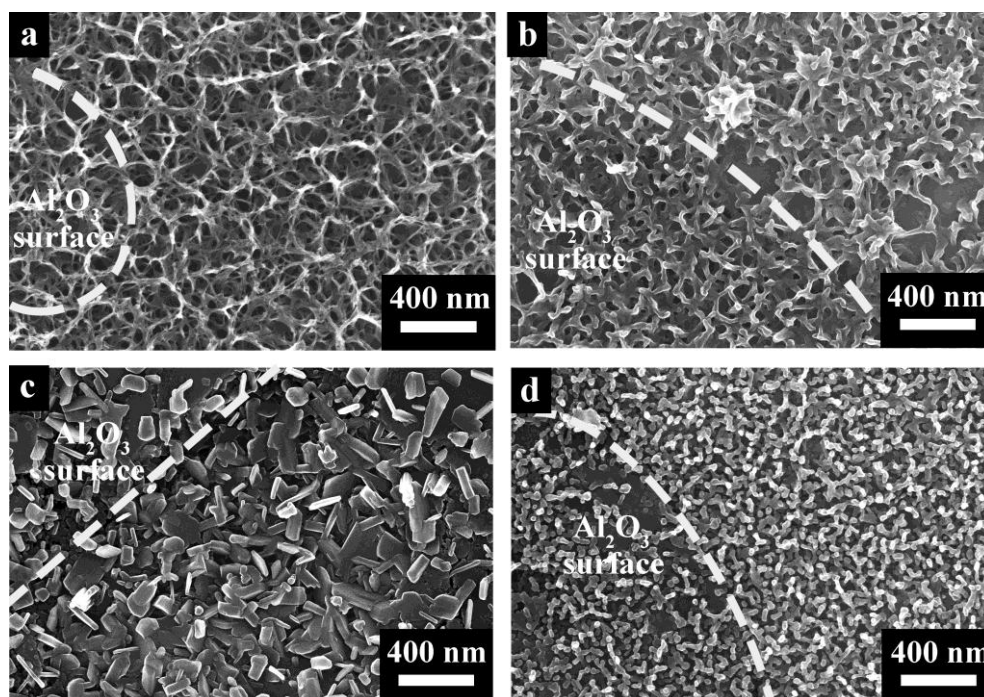


Figure 4.3 FE-SEM micrographs of surface structures of $\text{Al}_2\text{O}_3/\text{Ti}$ composites treated by (a) HCl at 25°C for 24 h (b) water at 80°C for 24 h, (c) HCl at 25°C for 24 h and heated at 600°C (d) water and heated at 600°C after 5M-NaOH treatment at 60°C for 1 h.

4.3.3 Surface phase compositions

Table 4.1 lists the EDX analysis results of untreated composites and those subjected to 5-M NaOH treatment at 60°C for 1 h with some follow-up processes. The detection area was $36 \mu\text{m} \times 28 \mu\text{m}$. After NaOH treatment, elemental Na was detected on the surface with the value of 2.5%. After subsequent HCl or water treatment and subsequent heat treatment, the Na^+ content dropped below the detection limit. The ratio of Ti to Al decreased after NaOH treatment and decreased further after treatment by HCl or water.

Table 4.1 EDX analysis results of chemical compositions of the surface of $\text{Al}_2\text{O}_3/\text{Ti}$ composites subjected to various treatments.

Treatment	Elements (mol%)				Relative ratio of Ti/Al
	Ti	Al	O	Na	
Untreated	12.4	24.3	65.3		0.42
NaOH	10.2	27.2	60.1	2.5	0.38
NaOH-HCl	10.2	27.8	61.9	0	0.37
NaOH-water	8.7	25.1	66.2	0	0.35
NaOH-HCl-heat	9.2	25.4	65.4	0	0.36
NaOH-water-heat	10.2	27.8	61.8	0	0.37

Figure 4.4 shows TF-XRD diffraction patterns of the treated composites. $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Ti}$ were detected in the untreated samples, whereas in those treated with NaOH, sodium hydrogen titanate, namely $\text{Na}_{2-x}\text{H}_x\text{Ti}_3\text{O}_7$ ($0 < x < 2$) was detected. After subsequent HCl treatment, the $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$ disappeared and titanate hydrogen, namely $\text{H}_2\text{Ti}_3\text{O}_7$, formed instead^[34,37]. After heat treatment at 600°C , this $\text{H}_2\text{Ti}_3\text{O}_7$ phase was converted into anatase and rutile. In the case of water treatment at 80°C for 24 h, anatase was detected and its content increased after heating at 600°C .

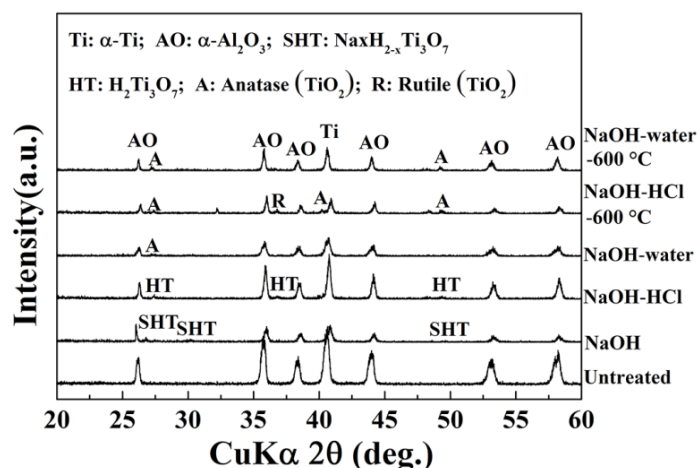


Figure 4.4 TF-XRD patterns of untreated or 5M-NaOH treated $\text{Al}_2\text{O}_3/\text{Ti}$ composites at 60°C for 1 h followed HCl or water treatment with or without heat treatment at 600°C . (Ti: α -Ti, AO: α - Al_2O_3 , SHT: Sodium hydroge titanate ($\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7$), HT: Hydrogen titanate ($\text{H}_2\text{Ti}_3\text{O}_7$), A: Anatase (TiO_2), R: Rutile (TiO_2)).

4.3.4 Effects of heat treatment temperatures on surface structures

To investigate how the heat-treatment temperature affected the photocatalytic activity, $\text{Al}_2\text{O}_3/\text{Ti}$ composites after NaOH treatment at 60°C for 1 h and subsequent HCL treatment at room temperature for 24 h were heated at different temperatures of 400°C , 500°C , and 600°C . Figure 4.5 shows the corresponding FE-SEM micrographs, which indicate that all samples after heat treatment exhibited good bonding between Al_2O_3 and Ti. The surface morphologies of the samples differed according to the heating temperature. At 400°C , a nano-porous structure remained on the surface after NaOH and HCl treatment. At 500°C , the surface morphology could still be regarded as being a porous structure at nanometer scale despite the change from nano-fibers to nano-particles. At 600°C , the nano-porous structure disappeared completely from the surface and was replaced by irregular 200-nm-long nano-rods.

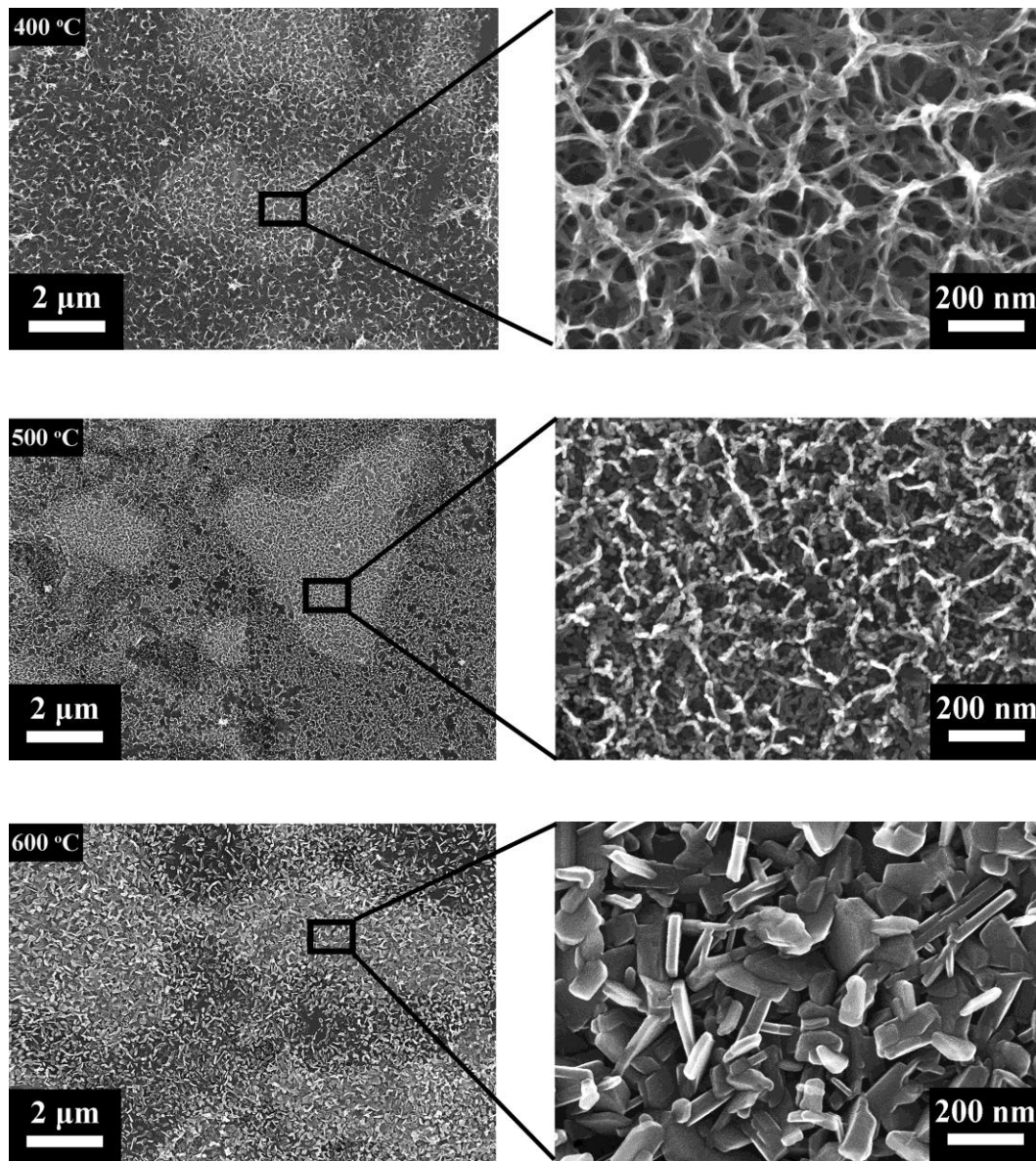


Figure 4.5 FE-SEM micrographs of surface structures of $\text{Al}_2\text{O}_3/\text{Ti}$ composites heat-treated at 400°C, 500°C and 600°C following 5M-NaOH treated at 60°C for 1 h and HCl treated at room temperature for 24 h.

4.3.5 Effects of heat treatment temperatures on surface phases

Figure 4.6 shows TF-XRD patterns of composites heated at 400°C, 500°C, and 600°C after 5-M NaOH treatment at 60°C for 1 h and subsequent HCl treatment at room temperature for 24 h, as well as XPS analysis results for the oxidation state of Ti in the sample heated at 600°C. Figure 4.6(a) shows that when composites were heated at 400°C, no new phases were detected apart from α -Al₂O₃ and α -Ti. However, crystalline anatase and rutile appeared on the surface at 500°C and 600°C. In Fig. 4.6(b), the peaks of Ti 2p located at 464.2 eV and 458.5 eV were attributed to Ti 2p_{1/2} and Ti 2p_{3/2}, respectively, for the normal state of Ti⁴⁺ in TiO₂.

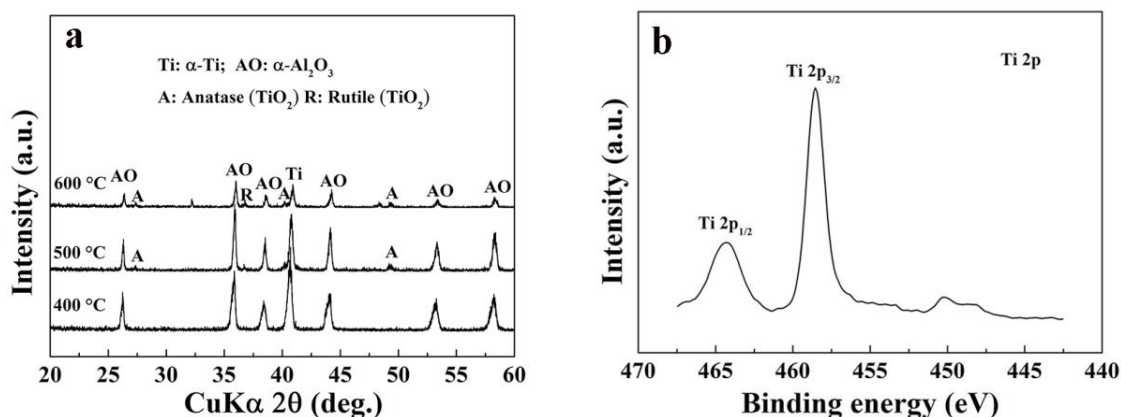


Figure 4.6 (a) TF-XRD patterns of Al₂O₃/Ti composites heat-treated at 400°C, 500°C and 600°C after 5M-NaOH treated at 60°C for 1 h and HCl treated at room temperature for 24 h (A: Anatase (TiO₂), R: Rutile (TiO₂)) (b) XPS spectra of the sample heated at 600°C.

4.3.6 Photocatalytic efficiency

The photocatalytic activity of Al₂O₃/Ti composites subjected to NaOH, HCl, and heat treatments was characterized by evaluating the efficiency of RhB degradation under UV light. Figure 4.7 shows the decrease in concentration of RhB immersed with Al₂O₃/Ti composites subjected to 5-M NaOH treatment at 60°C for 1 h, HCl treatment at room temperature for 24 h, heated at various temperatures, and irradiated with UV light. All the treated composites

exhibited photocatalytic activity. The RhB degradation efficiency increased with heat-treatment temperature. The sample heated at 600°C gave the highest photocatalytic efficiency. After UV exposure for 2 h, 14.5%, 17.5%, and 30.1% of the RhB was removed by the composites that had been heated at 400°C, 500°C, and 600°C, respectively.

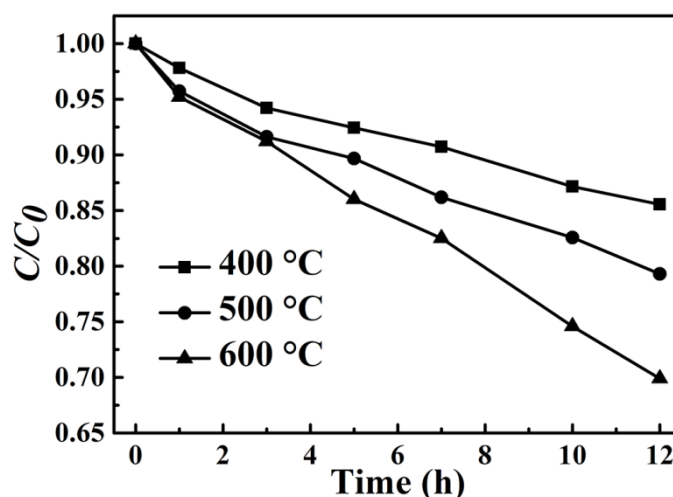


Figure 4.7 Degradation of RhB under UV light immersed with Al₂O₃/Ti composites heat-treated at 400 °C, 500 °C and 600 °C after 5M-NaOH treated at 60 °C for 1 h and HCl treated at room temperature for 24 h.

4.4 Discussion

4.4.1 Formation mechanism of titanate on composite

When Ti metal is treated with NaOH, HTiO₃·nH₂O forms and then combines with Na⁺ ions to form sodium hydrogen titanate, the formation mechanism of which has been clarified in detail^[30,31]. In the case of Al₂O₃/Ti composites, it should expect treatment with NaOH and heat to have the same effect on the Ti contained therein while having no effect on the Al₂O₃ matrix. However, under some strictly controlled treatment conditions, it was possible to

generate a bioactive layer over the entire surface of an $\text{Al}_2\text{O}_3/\text{Ti}$ composite regardless of Ti or Al_2O_3 to obtain the largest surface area for improving photocatalytic efficiency. Figure 4.1 confirms that NaOH treatment does not affect Al_2O_3 ceramics because of their high corrosion resistance when subjected to alkalis. Therefore, the nano-porous structure that forms on the Al_2O_3 surface was attribute to extension of the nano-network that forms on the Ti surface. I have considered the following possible mechanism for the formation of a nano-porous structure over the entire surface of an $\text{Al}_2\text{O}_3/\text{Ti}$ composite. When the composite is treated with NaOH, $\text{HTiO}_3 \cdot n\text{H}_2\text{O}$ forms on the Ti surface. With suitable treatment temperature and time, the $\text{HTiO}_3 \cdot n\text{H}_2\text{O}$ then migrates thermally to the surrounding Al_2O_3 surface. Consequently, $\text{HTiO}_3 \cdot n\text{H}_2\text{O}$ appears on the entire surface of the composite. The $\text{HTiO}_3 \cdot n\text{H}_2\text{O}$ then combines with Na^+ ions to form a porous layer of sodium hydrogen titanate. The connection between $\text{HTiO}_3 \cdot n\text{H}_2\text{O}$ and Al_2O_3 is weak, and the shaking speed should be limited; if the shaking is too vigorous, the NaOH solution might wash away the formed $\text{HTiO}_3 \cdot n\text{H}_2\text{O}$, thereby preventing a nonporous layer of sodium hydrogen titanate from forming. In our case, with a shaking speed of 120 rpm, no nano-porous layer was observed on the Al_2O_3 surface (results not shown).

4.4.2 Relationship of treatment conditions and formed titanate layer

In the present study, when treated a composite with 5-M NaOH at room temperature for 3 h or at 60°C for 1 h, a nano-porous network formed over its entire surface and there was good bonding between the Al_2O_3 and Ti. However, with longer treatment, the $\text{Al}_2\text{O}_3/\text{Ti}$ interface was bare. Because of the relatively weak Ti- Al_2O_3 bonding, the interface became etched with longer treatment, and the Ti phases separated from the Al_2O_3 matrix. It is concluded from Fig. 4.2 that the NaOH treatment time depends closely on the treatment temperature. Because the Ti in the $\text{Al}_2\text{O}_3/\text{Ti}$ composites was obtained from the decomposition of TiH_2 , it cannot neglect

the defect concentration, which might make the Ti in the $\text{Al}_2\text{O}_3/\text{Ti}$ composites more reactive when subjected to NaOH. To obtain a nano-porous structure over the entire surface of an $\text{Al}_2\text{O}_3/\text{Ti}$ composite while maintaining good bonding between the Al_2O_3 and Ti, it must exert strict control over the NaOH treatment conditions while Ti metal and Ti alloys are flexible in a wider range of treatment conditions. In the case of Ti metal and Ti alloys, with NaOH treatment at 60°C for even as long as 7 d, a nano-porous structure has been observed on the surface without obvious cracks or defects^[32]. For the following discussion, because $\text{Al}_2\text{O}_3/\text{Ti}$ composites subjected to 5-M NaOH at 60°C for 1 h form the most homogeneous nano-porous layers on their surfaces, all the NaOH treatments were conducted with 5-M NaOH at 60°C for 1 h.

4.4.3 Crystal morphology and composition

Because the Na^+ ions released from the sodium titanate that forms during NaOH treatment have adverse effects on living cells in the human body, it is necessary to remove Na^+ ions from the surface^[33,34]. It has been reported that simple water or HCl treatment is effective for removing Na^+ ions completely^[35,36,37]. In the present study, after immersion in HCl or water for 24 h, the change in surface morphology was different and became obvious after heat treatment at 600°C . The quite different surface structures shown in Fig.4.3 indicate that the surface morphology of a sample after heat treatment depends strongly on that before heat treatment. A relatively thin nano-fibrous network possibly turns into rods, whereas a broader network possibly turns into particles. After treatment with water at 80°C for 2 h, the remaining porous structure and the existence of anatase show the possibility of the formation of apatite, as reported by Uchida et al^[35]. Because surface roughness is considered not to affect the formation of apatite, which forms instead because of a positively charged surface^[34], composites treated with HCl (with or without heat treatment) are expected to exhibit the same

ability to form apatite after being immersed in SBF while non-porous surface structure disappeared after heat treatment.

Regarding photocatalytic ability, having removed the Na^+ ions, it might be able to convert the sodium titanate into sodium-free titania gel and then into anatase and/or rutile after heat treatment to increase the photocatalytic efficiency. According to our EDX and XRD analysis, the HCl and water treatments used in the present study could both remove Na^+ ions completely.

Because NaOH treatment does not affect Al_2O_3 , the decrease in the relative ratio of Ti to Al as given in Table 4.1 is considered to indicate that the NaOH treatment removed some of the Ti. When $\text{Al}_2\text{O}_3/\text{Ti}$ composites are treated with NaOH, the Ti metal might dissolve in the NaOH solution, thereby decreasing the elemental Ti content. The FE-SEM micrographs shown in Fig. 4.2 can be used to assess that hypothesis. For NaOH treatment times in excess of 3 h (room temperature) or 1 h (60°C), an obviously collapsed Ti surface suggested that some Ti was removed from the surface. It is considered that the NaOH treatment removed some Ti under all conditions. Nevertheless, because relatively little Ti was removed from those composites treated with NaOH for 3 h (room temperature) or 1 h (60°C), no obvious collapse was observed on the surface. More Ti was removed as the treatment time increased. To retain the maximum amount of elemental Ti and achieve a complete nano-porous layer on the surface for increased photocatalytic efficiency, strict control must be exerted over the temperature-based treatment time, which is consistent with the aforementioned conclusion. In addition, after immersion in HCl or water for 24 h, the further decrease in elemental Ti content was attributed to the removal of the sodium hydrogen titanate layer formed on the Al_2O_3 surface. We reason that the porous layer that forms on the Al_2O_3 surface after NaOH treatment is weakly bonded with the Al_2O_3 matrix. During the subsequent HCl or water treatment, it is that porous layer that is removed rather than the one formed on the Ti surface.

4.4.4 Effects of heat treatment on titanate layer

After the NaOH and HCl treatments, there was a nano-porous layer over the entire surface of a composite, as shown in Fig. 4.3(a). This surface with a nano-porous network structure remained when heated at temperatures up to 400°C but changed to nano-particles when heated at 500°C or nano-rods when heated at 600°C. In the case of Ti metal or its alloys, the homogeneous nano-porous structure remained unchanged even when heated up to 700°C^[34]. The differing levels of impurities and defects between (i) the Ti contained in Al₂O₃/Ti composites and (ii) Ti metal and its alloys might account for this phenomenon. Upon HCl treatment, Na⁺ ions are released into the HCl solution and are replaced by H⁺ ions, leading to the formation of hydrogen titanate as shown in Fig. 4.4. Because of the dehydration of hydrogen titanate and the formation of amorphous TiO₂, no new phases were detected upon heating the samples at 400°C. Increasing the heat-treatment temperature to 500°C or 600°C, the amorphous TiO₂ was converted to crystalline anatase and rutile. The XPS analysis shown in Fig. 4.6(b) further confirms the existence of TiO₂, which is consistent with the TF-XRD analysis results. Given their different surface areas and crystalline phases, these different surface structures are expected to affect the photocatalytic activity.

4.4.5 Photocatalytic activity of surface modified Al₂O₃/Ti composites

Increasing the heat-treatment temperature changes both the surface morphology and phases. Therefore, was investigated how the heat-treatment temperature affects the photocatalytic activity of samples. The first effect that I have considered is that on specific surface area. As shown in Fig. 4.5, when heated the NaOH- and HCl-treated samples at different temperatures, their surface morphologies differed, leading to different surface areas. Photocatalysts with higher surface area exhibit greater photocatalytic ability. With the change of surface morphology from nano-porous to nano-rods by increasing the heat-treatment temperature

from 400°C to 600°C, the surface area decreases. Next, I have considered the effect on the crystalline phases. Among the three different crystalline phases of TiO₂ (i.e., anatase, rutile, and brookite), anatase-type TiO₂ exhibits the highest photocatalytic activity. When samples are subjected to NaOH and HCl treatments followed by heating at 400°C, although the remaining nanometer-scale porous structure gives these samples the highest surface area, the crystalline phases of samples heated at 400°C are amorphous. When samples were heated at 600°C, the presence of anatase improved the photocatalytic ability despite the decreased surface area. From this, it is concluded that compared with the surface area, the crystalline phases of TiO₂ affect the photocatalytic activity more.

By the NaOH, HCl, and heat treatments, we confirmed the photocatalytic activity of Al₂O₃/Ti composites. Nevertheless, the RhB decomposition efficiency was not too high. A crucial factor is the small amount of formed TiO₂. In evaluating the photocatalytic activity, because of the limited experimental conditions, four pieces of specimen plates sized 15 mm × 15 mm × 1.5 mm were used. By image analysis using the Image J software, the percentage area of Ti on the surface was calculated to be 25%. Then the amount of TiO₂ (be it amorphous, anatase, or rutile) formed on the surface after heat treatment was calculated as approximately 0.1 mg. This minimal TiO₂ content greatly limits the efficiency of RhB degradation under UV light. Possible ways to increase the amount of TiO₂ are to increase the Ti content in Al₂O₃/Ti composites and increase the thickness of the formed active surface layer, both of which would improve photocatalytic efficiency.

4.5 Summary

The surface morphologies, phases, and photocatalytic activity of Al₂O₃/Ti composites subjected to NaOH, HCl, and heat treatments were investigated. The results show that the

NaOH treatment conditions are dictated mainly by the NaOH concentration, treatment temperature, and time. To achieve (i) good bonding between the Al_2O_3 and Ti and (ii) a homogeneously formed porous active layer at nanometer scale, it is determined that the NaOH treatment should be soaking in 5-M NaOH at 60°C for 1 h. Both HCl and water treatment removed Na^+ ions completely. The surface morphologies of the heated composites depended strongly on those before heat treatment. After the NaOH, HCl, and heat treatments, all the $\text{Al}_2\text{O}_3/\text{Ti}$ composites exhibited photocatalytic activity in degrading RhB under UV irradiation. Those $\text{Al}_2\text{O}_3/\text{Ti}$ composites that were heated at 600°C for 1 h after NaOH and HCl treatments showed the highest photocatalytic activity despite the decreased surface roughness, indicating that the type of crystalline phase has more effect on the photocatalytic efficiency than does the surface morphology. Having confirmed their photocatalytic activity, Al_2O_3 ceramics are expected to be promising materials for multifunctional applications, not just for structural components. However, the present research was focused mainly on finding the optimal treatment conditions for inducing photocatalytic activity in $\text{Al}_2\text{O}_3/\text{Ti}$ composites, and only the RhB degradation efficiency was evaluated. Future work should involve a further complete characterization of the photocatalytic performance.

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Electrochemical assisted room-temperature crack healing of ceramic-based composite

5.1 Introduction

Ceramics such as Al_2O_3 demonstrate excellent wear behavior, high-temperature resistance, and chemical stability^[1,2,3]. However, they are brittle by nature; thus, surface cracks and/or defects are easily introduced during machining processes or during operations when ceramics are used in practical applications as structural components. Ceramics are sensitive to these surface cracks. When cracks occur, fracture strength and reliability are considerably reduced^[4,5] because the cracks function as fracture initiation sites upon stress concentration at the crack tips. Lapping and precise polishing are necessary to remove these harmful cracks and prolong service life; however, these processes result in low fabrication efficiencies and high machining costs.

Two approaches have been developed to eliminate these surface cracks. The first approach is to improve fracture toughness to increase crack resistance during subsequent machining processes and operations. This approach has long been extensively investigated as a method to overcome the brittleness of ceramics. The second approach is to introduce self-crack-healing ability into ceramics to eliminate existing surface cracks and recover lost mechanical strength and reliability. Methods to reduce the brittleness of ceramics include that of Sekino et al.^[6,7], who reported that metal-dispersed Al_2O_3 materials showed increased fracture toughness. However, despite

the increased fracture toughness, surface cracks still could not be avoided completely during machining and/or operation. Therefore, self-crack-healing ability is an important method to eliminate surface cracks to improve fabrication efficiency as well as to repair damaged ceramic parts by recovering their strength and, hence, their reliability and service lifetime.

Because of the high chemical and thermal stability of ceramics, self-healing in monolithic ceramics is intrinsically difficult. Currently, as far as we know, high-temperature heat treatment is the only method reported to realize self-crack-healing in ceramics. In these cases, the ceramics had been composited with other phases such as SiC and Ni. The ability of these ceramic-based composites to recover their mechanical strength through self-crack-healing after a high-temperature treatment has been extensively studied^[8,9,10,11,12,13,14,15]. The mechanism of heat-induced crack healing is attributed to the re-sintering of cracks by secondary sintering^[16], followed by filling of the cracks by reaction, diffusion of the constituent elements, and oxide formation^[11,17,18]. However, thermal healing at high temperatures is not an ideal solution because it often leads to unexpected further reaction of the constituent phases, excess grain growth by secondary sintering, and resultant phase changes. In addition, the thermal treatment can only be applied to standalone ceramic parts, which limits the scenarios in which the recovery process can be practically applied. Decreasing the healing temperature for recovering the mechanical properties of ceramics is thus a challenge.

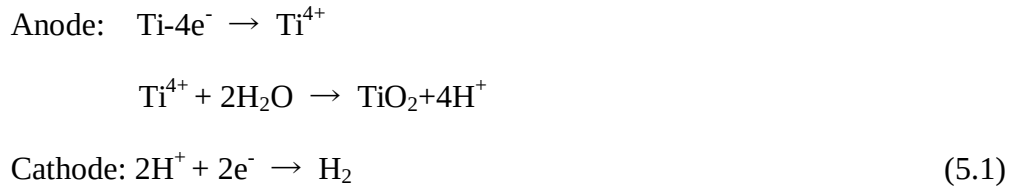
A self-healing function at room temperature has been reported for polymer composites^[19,20,21,22] and for some sol-gel-derived composite coatings such as silica/clay coatings^[23]. However, to our knowledge, the literature contains no report of the healing

of cracks in dense and hard ceramics at low temperatures, especially at room temperature. Here, the concept of room-temperature crack healing of a ceramic-based composite was introduced. Without applying a thermal treatment, I demonstrate a process to heal cracks electrochemically at room temperature by forming oxides, resulting in the recovery of the fracture strength in a ceramic composite containing a metal phase.

Electrochemical approaches such as electropulse and cathodic deposition have been used to heal damage in conductive metals at relatively low temperatures and show strong potential in restoring the performance of damaged materials^[24,25]. As one such electrochemical technique, anodic oxidation is known to be an effective method that can be conducted at room temperature to form metal oxides, e.g., aluminum oxides by anodizing an Al metal^[26] and titanium oxides by anodizing a Ti metal^[27].

To apply anodization to a ceramic, two problems should be solve in advance. First, the insulating ceramic should be made conductive. To this end, appropriate amounts of metal phases with appropriate particle sizes should be imbedded into the ceramic matrix. Second, the embedded metal particles should be converted into oxides through anodization. Dispersing metal particles into a ceramic matrix has been reported to not only increase the fracture toughness of the matrix but also provide other functions related to, for example, optical and electrical properties^[28,29,30]. In our previous study, I dispersed fine metallic Ti particles with a size of a few micrometers into an Al₂O₃ ceramic matrix, resulting in electrically conductive Al₂O₃/Ti composites^[31]. When 20 vol% Ti was added to the electrically insulating Al₂O₃ ($\sim 10^{12} \Omega \cdot \text{cm}$), the electrical resistivity of the composite decreased drastically to $8.04 \times 10^{-3} \Omega \cdot \text{cm}$, and the percolation threshold volume was calculated to be 13.8 vol%. Given this excellent

conductivity, I hypothesized that the Ti particles dispersed within the Al₂O₃/Ti composites could be anodized to form titanium oxides, which might heal cracks. I further hypothesized that the electrical current would not affect the insulating Al₂O₃ ceramic matrix. The relative reactions during anodizing metal Ti are given in equation 5.1. Although anodic oxidation has been widely used for surface modification of metals^[32,33,34] and research on the anodic oxidation of titanium or titanium alloys to prepare TiO₂ nanotubes or nanoporous structures has long been a topic of intensive research interest, I here report, for the first time, that anodization could be used to heal cracks in ceramic-based composites at room temperature.



In the current study, our objective was to heal cracks at room temperature to recover the mechanical strength of Al₂O₃ ceramics. The crack-healing behavior in Al₂O₃/Ti composites induced by anodization under the control of the electrolytic current and anodization time was investigated. The crack-healing ability was characterized by the change in surface morphology and by the recovery of the flexural strength at room temperature. I speculate on the application prospects of our Al₂O₃/Ti composites.

5. 2 Experimental procedures

5.2.1 Preparation of Al₂O₃/Ti composites samples

The details of the preparation method of Al₂O₃/Ti composites was explained in the chapter 2 as well as the previous work^[31]. Briefly, α -Al₂O₃ (0.2 μ m, AKP-53, Sumitomo Chemicals Co., Ltd., Japan) and TiH₂ (5–10 μ m, 99% up, Kojundo Chemical Laboratory Co., Ltd., Japan) with a volume percent of 20% (hereafter denoted as 20Ti) and 30% (30Ti) in finally sintered composites were mixed by wet ball milling for 24 h in ethanol. Dried mixtures were ball milled for another 12 h, followed by hot press sintering under an applied pressure of 30 MPa at 1500 °C for 1 h. The heating rate was 20 °C/min. All processes were conducted under the protection of argon gas. Obtained sintered bodies were cut into rectangular bars with dimensions of 24 mm $\times$ 3 mm $\times$ 2 mm by electrical discharge machining and then ground and mirror polished. Their electrical resistivities were measured to be 8.04×10^{-3} Ω cm for 20Ti and 4.06×10^{-3} Ω cm for 30Ti.

5.2.2 Anodizing processing

Cracks on the center of the polished surface were introduced by Vickers indentation using a Vickers hardness tester (FV-310e, Future-tech Corp., Japan) with an applied load of 29.4 N (20Ti-29.4) or 98 N (20Ti-98) on 20Ti. In the case of 30Ti, the applied load was 29.4 N (30Ti-29.4). The crack-healing procedure via anodization was carried out at room temperature in 1 M H₃PO₄ electrolyte solution using Pt as a cathode and composites as anodes. The oxidized area was 22-mm long, 3-mm wide, and 2-mm thick. A schematic of the anodizing apparatus and a plate-shaped sample is presented in Figure

5.1(a). The distance between the anode and cathode was controlled as 15 mm. The anodization process was conducted by the galvanostatic method. Three current densities were applied in the present study; the three sets of anodization conditions labeled as A1, A2, and A3 are shown in Figure 5.1(b). Among these conditions, A1 is a three-step anodization process at low current density, A2 is a three-step anodization process at high current density, and A3 is a one-step anodization process. After crack healing under various anodization conditions, samples were redefined on the order of composite load used to introduce indentation–anodization conditions; for instance, the notation 20Ti-29.4-A1 means that the indentation was induced in the $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite under an applied load of 29.4 N and that cracked composite was healed under condition A1. The detail information was given in table 5.1.

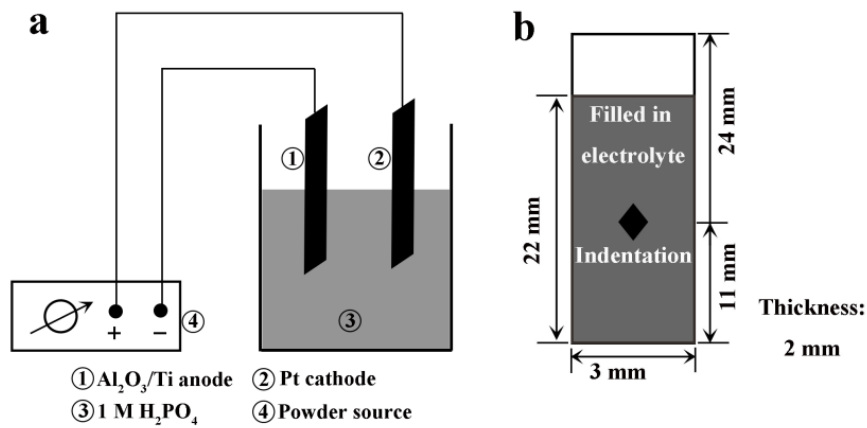


Figure 5.1 (a) Schemadic diagram of anodization apparatus and
(b) a sample in plate shape.

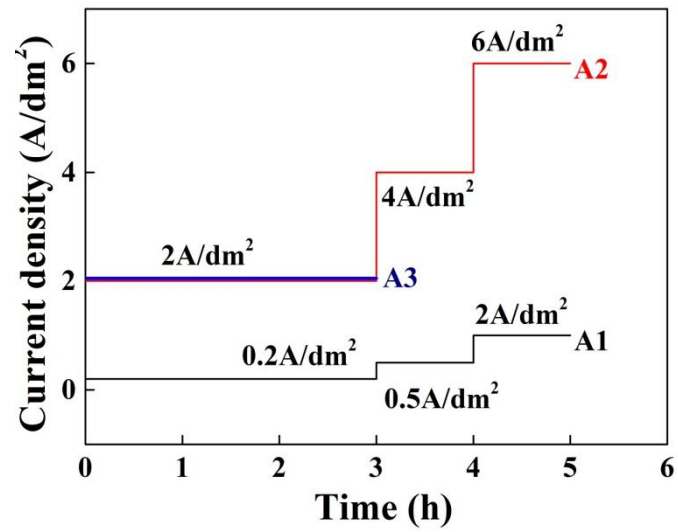


Figure 5.2 Crack-healing anodization condition applied in current study.

Table 5.1 Information and notation of samples used in current study.

Notation	composite	Load (N)	crack length (μm)	crack-healing condition
20Ti-29.4 or 98	$\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$	29.4 or 98	130	
30Ti-29.4	$\text{Al}_2\text{O}_3/30 \text{ vol\% Ti}$	29.4	130	
20Ti-29.4-A1, A2 or A3	$\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$	29.4	130	A1, A2 or A3
20Ti-98-A3	$\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$	98	370	A3
30Ti-29.4-A2	$\text{Al}_2\text{O}_3/30 \text{ vol\% Ti}$	29.4	140	A2

5.2.3 Characterization

Field-emission scanning electron microscopy (FE-SEM, SU9000, Hitachi, JAPAN) on an instrument equipped with an energy-dispersive X-ray spectroscopy (EDX, Horiba, Japan) system was used to observe the microstructures. The phase compositions of

crack-free and crack-healed composites with different anodization conditions were determined by X-ray diffraction (XRD; D8 Advance, Bruker Ltd., USA) using Cu $K\alpha$ radiation at 40 kV and 40 mA. The flexural strengths of crack-free samples and cracked samples before and after anodization were characterized using a three-point bending test by a universal testing machine (Autograph AGS-X, Shimadzu, Japan) with a cross speed of 0.5 mm/min and a span of 20 mm at room temperature.

5.3 Results

5.3.1 Effects of current density on crack-healing ability

Figure 5.3 shows one sample of electrical discharge machining of $Al_2O_3/20\%$ Ti composite indicating that with excellent electrical conductivity, it is possible to process complex shapes of ceramic materials which applies an easy and fast way for ceramic machining. “ISIR” is the abbreviation of “The Institute of Scientific and Industrial Research”.



Figure 5.3 One sample of electrical discharge machining of $Al_2O_3/20\%$ Ti composite.

Figure 5.4 shows one of the possible current pathways in $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite and surface morphologies after anodized under condition A2. Before anodization, dark and bright phases in Figure 5.4(a) correspond to Al_2O_3 and Ti respectively. For Ti particles which connect with surroundings, a complete pathway was formed. Electrical current can pass through this pathway. Only particles existed at conductive pathways could be oxidized. On the other hand, for the isolated Ti particles, due to the absence of complete pathway, electrical current cannot pass through these particles. After anodized under condition A2 shown in Figure 5.4(b), dark phases and bright phases are still corresponded to Al_2O_3 and Ti, while relatively brighter phases are corresponded to titanium oxides. It was found that on the surface, some Ti particles were oxidized while some Ti particles remained unchanged.

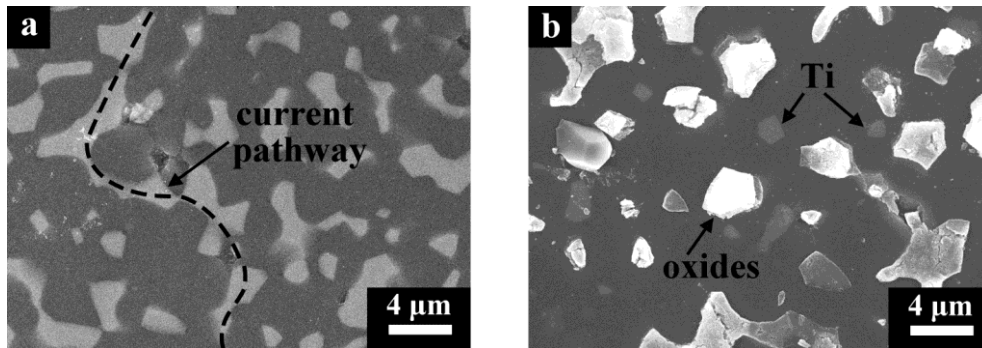


Figure 5.4 SEM micrographs of $\text{Al}_2\text{O}_3/20 \text{ vol\%Ti}$ composite surface morphologies
(a) One possible current pathway before anodization (b) surface morphologies after anodization under condition A3.

The effects of current density on crack-healing ability were investigated in 20Ti and FE-SEM micrographs are shown in Figure 5.5. In all of the SEM micrographs shown in this text, dark phases and bright phases correspond to Al_2O_3 and Ti before anodization,

whereas relatively brighter phases correspond to titanium oxides after anodization (Figure 5.4). As shown in Figure 5.5(a), before the crack-healing process, under an applied indentation load of 29.4 N, an obvious indentation and a crack with a length of 140 μm appeared on the surface. Two kinds of fractured Ti particles are observed: transgranular-fractured Ti particles (cross marked as point 1 in Figure 5.5(a) on both sides of the crack and intergranular-fractured Ti particles [cross marked as point 2 in Figure 5.5(a)] located along the crack propagation path. In the sample of 20Ti-29.4-A1 healed under a relatively low current density [Figure 5.5(b)], the indentation edges became blurred. Fractured metal Ti particles did not connect cracks completely after anodization. Along the propagation path of cracks, some positions without bridging by oxides were visible. When the crack-healing current density was increased to condition A2 [Figure 5.5(c)], the original indentation and cracks were vaguely visible, which means that the cracks were further healed. Under condition A3 of the one-step process [Figure 5.5 (d)], along the crack propagation path where Ti particles existed, the crack was bridged by the expanded oxides phases. The surface morphology observations revealed no obvious differences in crack-healing behavior between conditions A2 and A3. For all conditions under which the 20Ti composites were healed, the oxidized Ti particles retained their original shapes.

Figure 5.6 shows one of the complete cracks from indentation to crack tip in 20Ti-29.4-A2 which presented the change of crack propagation and the full crack-healing information.

Figure 5.7 shows two kinds of crack finish mode in 20Ti-29.4-A3. One is that crack was finished in Ti particle, as shown in Figure 5.7(a). The other is that crack was finished in Al_2O_3 matrix, as shown in Figure 5.7(b).

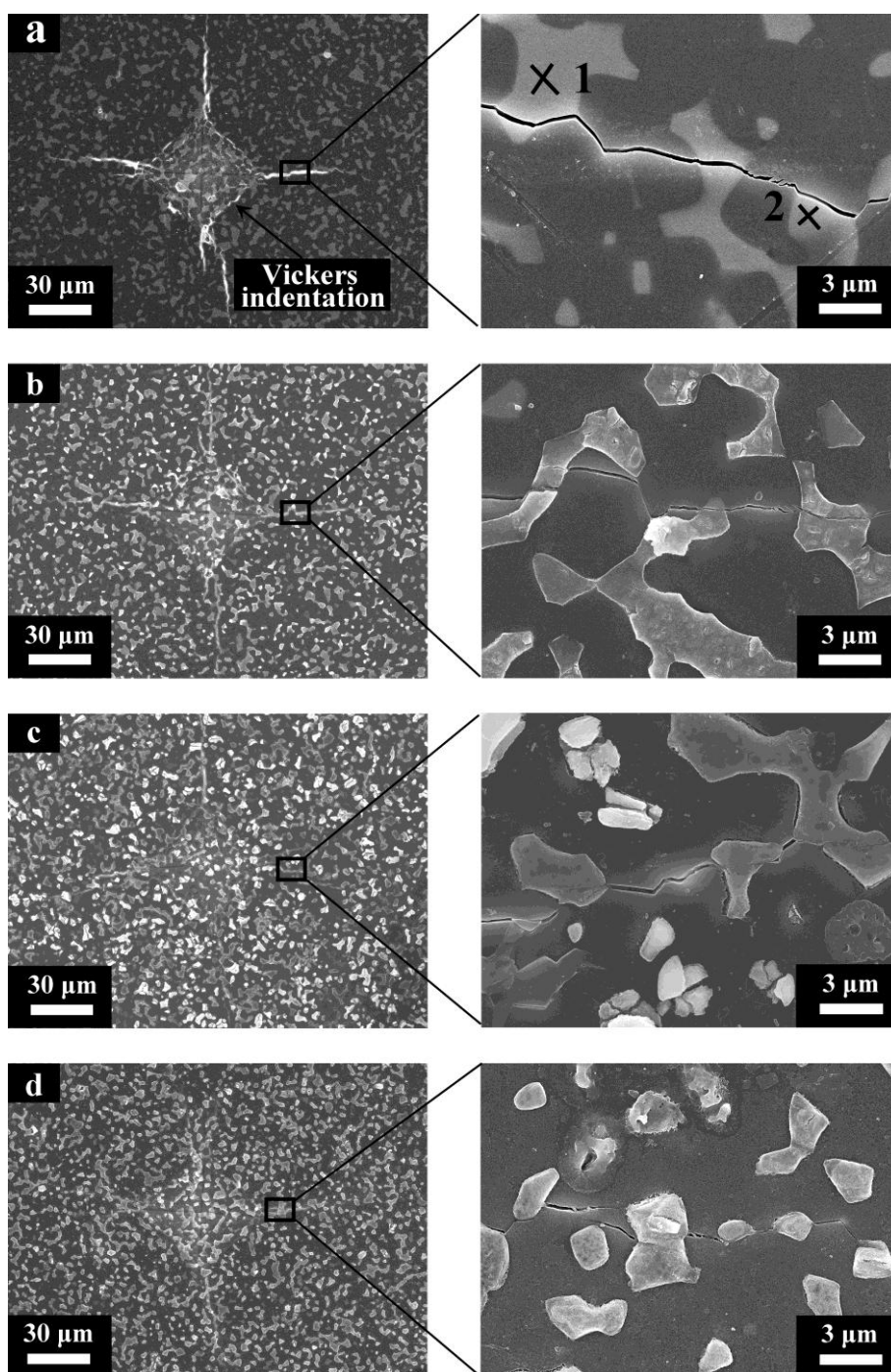


Figure 5.5 SEM micrographs of cracked $\text{Al}_2\text{O}_3/20\text{vol}\%\text{Ti}$ composites with a crack of 140 μm (a) before and after crack-healed under condition (b) A1 (c) A2 (d) A3.

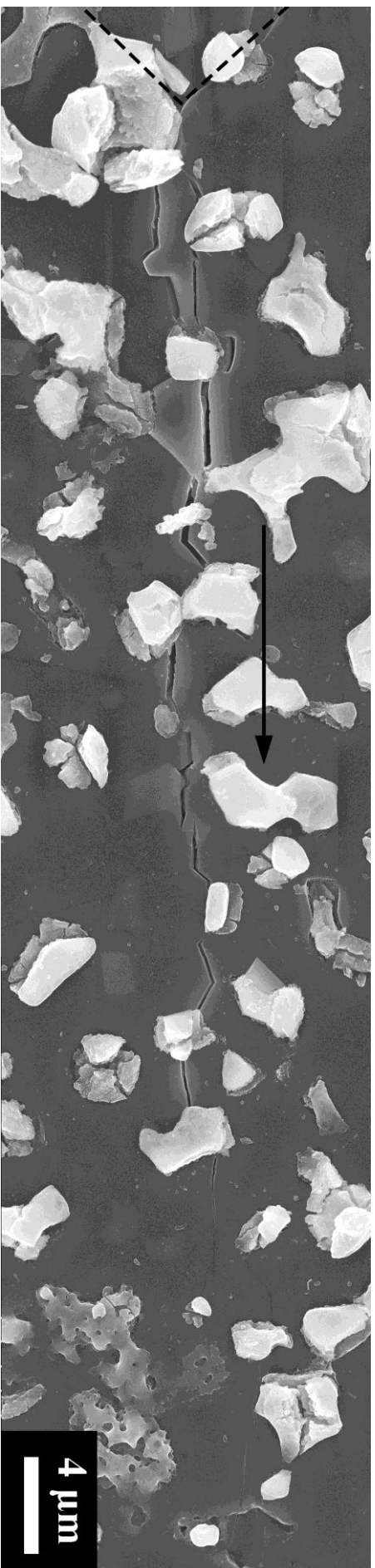


Figure 5.6
One of the full crack propagation path from indentation to crack tip observed in 20Ti-29.4-A2. Arrow means original crack propagation direction. Dotted line means indentation.

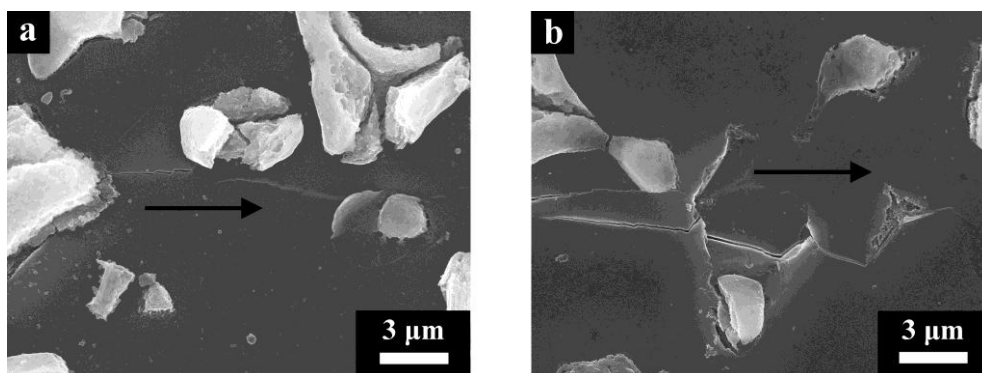


Figure 5.7 Two kinds of crack finish mode in 20Ti-29.4-A3 (a) crack finished in Ti particle (b) crack finished in Al_2O_3 matrix. Arrow means crack propagation direction.

In the XRD patterns in Figure 5.8, before anodization, peaks ascribed to α -type Al_2O_3 and α -type Ti were observed. After anodized under different conditions, the Ti metal particles were oxidized, and titanium oxides (TiO_2) of anatase and/or rutile were formed according to the anodization conditions. In 20Ti-29.4-A1 and 20Ti-29.4-A2, both anatase and rutile were detected, and the amount of TiO_2 increased at a higher current density. When composites were crack-healed under the one-step A3 process and with a shorter anodization time than that of the A2 process, anatase occurred, and rutile was not detected. After anodization, apart from Al_2O_3 , Ti, and titanium oxides, no other new phases were observed for any of the anodization conditions.

Figure 5.9 shows the results of the three-point bending strength of various samples measured at room temperature. For crack-free 20Ti composites, the average bending strength was 581.2 ± 42 MPa. After a crack was introduced in the 20Ti-29.4 composite, its bending strength was decreased by 38.8%. However, after healing, the bending strength of 20Ti-29.4-A1 recovered to 92.8% of the bending strength of the crack-free sample (20Ti). In both 20Ti-29.4-A2 and 20Ti-29.4-A3, bending strength was found to recover completely; meanwhile, the bending strength of 20Ti-29.4-A2 was slightly

higher than that of the crack-free samples.

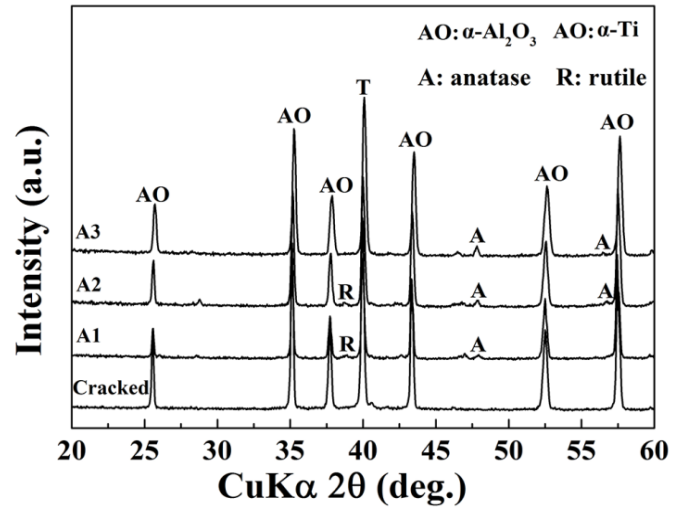


Figure 5.8 XRD patterns of cracked $\text{Al}_2\text{O}_3/30 \text{ vol\% Ti}$ composites before and after crack-healed under different conditions.

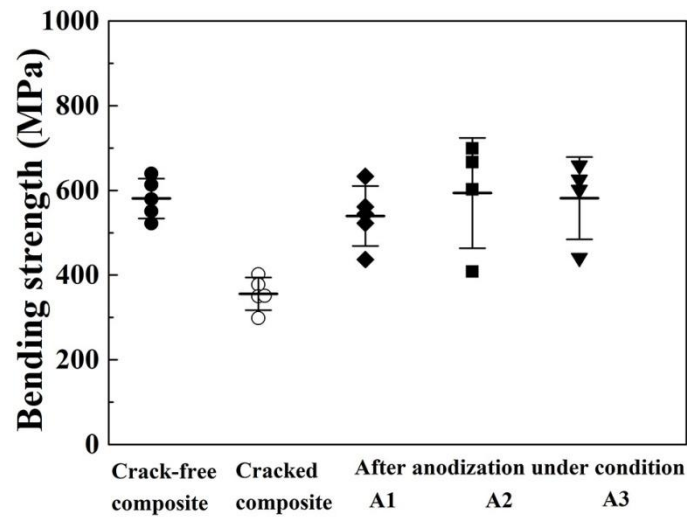


Figure 5.9 Three-point bending strength of $\text{Al}_2\text{O}_3/20\text{vol\%Ti}$ composites with a crack of 140 μm before and after crack-healed under condition A1, A2 and A3.

Fracture mode after three-point bending test was observed by SEM and Figure 5.10 shows two kinds of fracture modes in crack-healed $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composites under condition A3. Figure 5.10(a) indicates that composites fractured from crack-healed zone, while Figure 5.10(b) means that composites fractured outside the crack-healed zone.

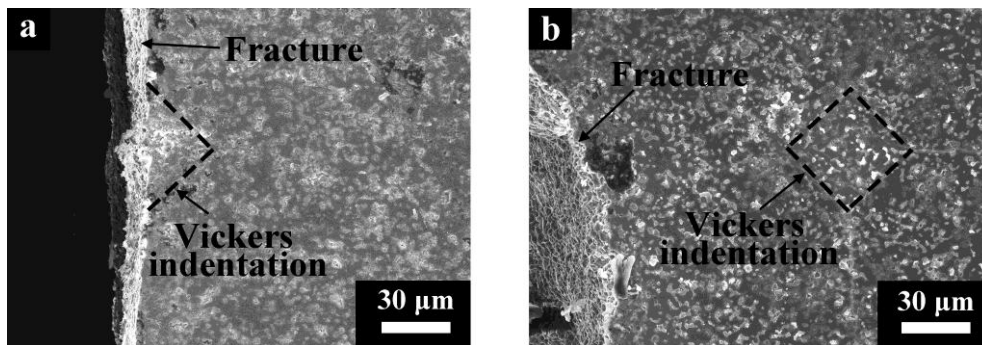


Figure 5.10 Fracture mode in crack-healed $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composites after bedding test (a) fracture initiated from crack (b) fracture initiated outside the crack-healed zone.

After each step in condition A2, the change in morphology of one representative Ti particle and element condition are investigated. In Figure 5.11, it was found that, with the further increase of current density, oxides were further expanded while remained the original shapes. After step1, expanded oxides filling crack was observed. After step2, oxide Ti particle was expanded again. After last step, crack was filled by oxide completely. Table 5.2 indicated that increased relative content of oxygen element after each step was observed.

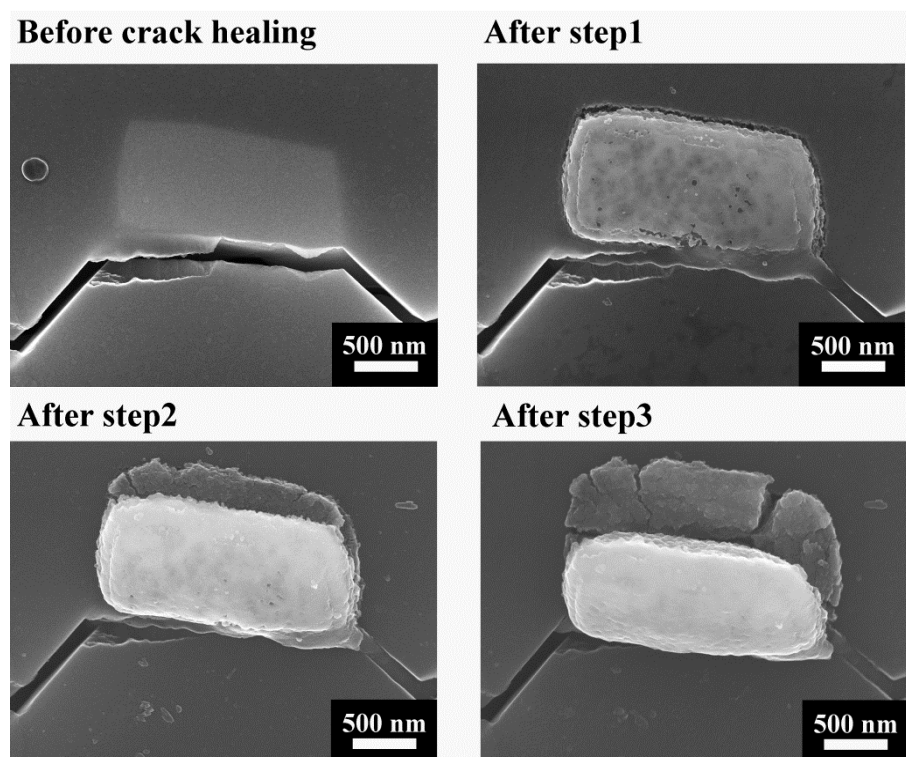


Figure 5.11 The change in morphology of one representative Ti particle observed in $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite during anodization process under condition A2.

Table 5.2 Chemical composition of the surface of the $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite measured by EDX before and after anodization after each step within A2.

Samples	Elements (mol%)			O/Al
	Ti	Al	O	
Before anodization	12.3	25.6	62.1	2.42
After step1	17.3	23.7	59.1	2.49
After step 2	17.4	23.4	59.3	2.53
After step 3	11.3	18.7	70.0	3.74

5.3.2 Effects of crack size on crack-healing ability

Figure 5.12 shows the SEM micrographs of cracked 20Ti composites under an applied load of 98 N before and after crack healing under condition A3. In this work, two kinds of cracks introduced in 20Ti were studied. One crack type was introduced under an applied load of 29.4 N, which led to a 140- μm -long crack, as shown in Figure 5.5. The other crack was induced under a load of 98 N, which led to a 370- μm -long crack, as shown in Figure 5.12. The fractured Ti particles located at the region with a large crack open distance (COD), which was near the root of indentation cracks, did not connect with each other after anodization oxidation. With crack propagation, i.e., near the crack tip region, the COD became smaller, and oxides were connected completely, bridging the crack.

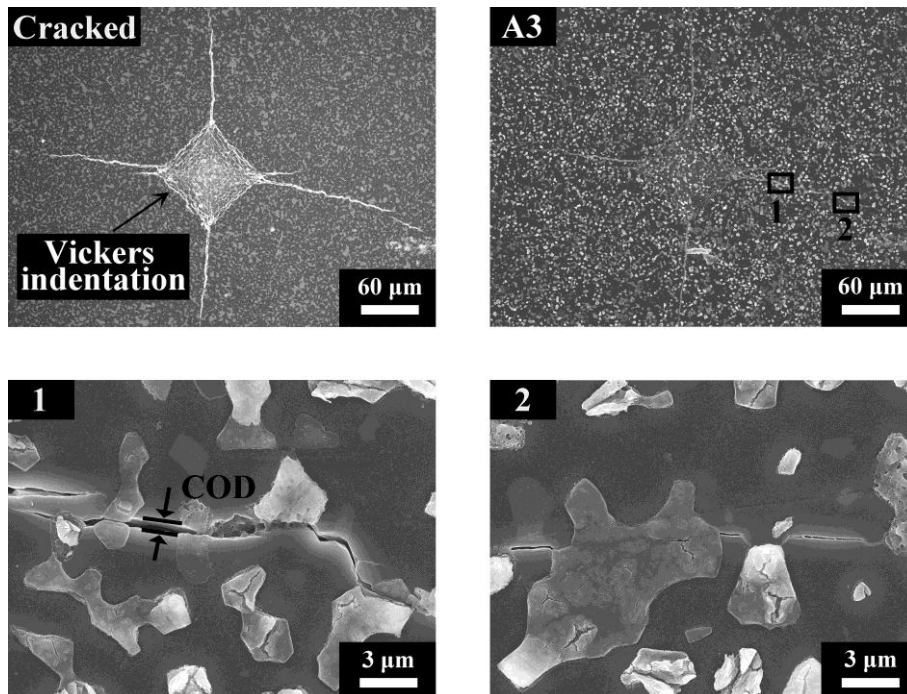


Figure 5.12 SEM micrographs of $\text{Al}_2\text{O}_3/20\text{vol}\%\text{Ti}$ composites with a crack of 370 μm and crack-healed under condition A3.

The bending strength of the aforementioned 20Ti samples with cracks of two different sizes before and after crack healing under condition A3 is shown in Figure 5.13. Compared with sample 20Ti-29.4-A3, sample 20Ti-98-A3 shows a more dramatic decrease in bending strength. After anodization, the bending strength of sample 20Ti-98-A3 recovered to 518.7 ± 71 MPa, with a recovery efficiency of 89.2% with respect to the crack-free sample, whereas the bending strength of sample 20Ti-29.4-A3 completely recovered after crack healing.

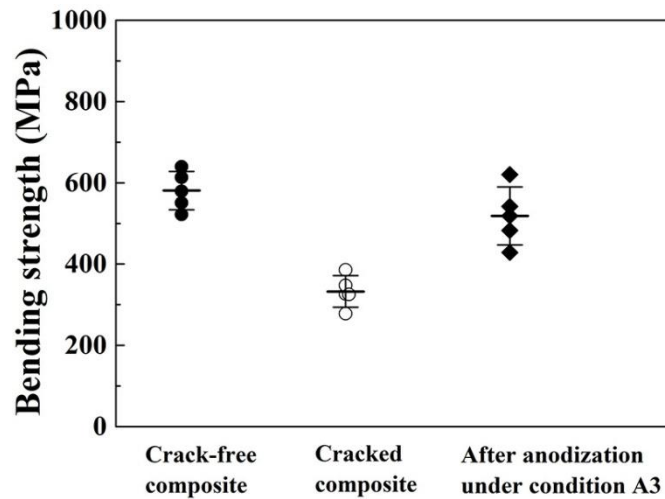


Figure 5.13 Three-point bending strength of $\text{Al}_2\text{O}_3/20\text{vol}\%\text{Ti}$ composites with different crack length before and after crack-healed under condition A3.

5.3.3 Effects of conductivity of composites on crack-healing ability

Figure 5.14 shows the crack-healing behavior in 30Ti. The crack length caused by a load of 29.4 N was 150 μm , which is slightly longer than that of sample 20Ti-29.4, as given in Figure 5.5. After anodization under condition A2, the indentation became blurry. From the magnified image in Figure 5.5(b), the same crack-healing behavior of crack bridging by the connection of oxides was observed. However, in the case of 30Ti,

oxidation became severe, and Ti particles did not retain their original shapes after anodization.

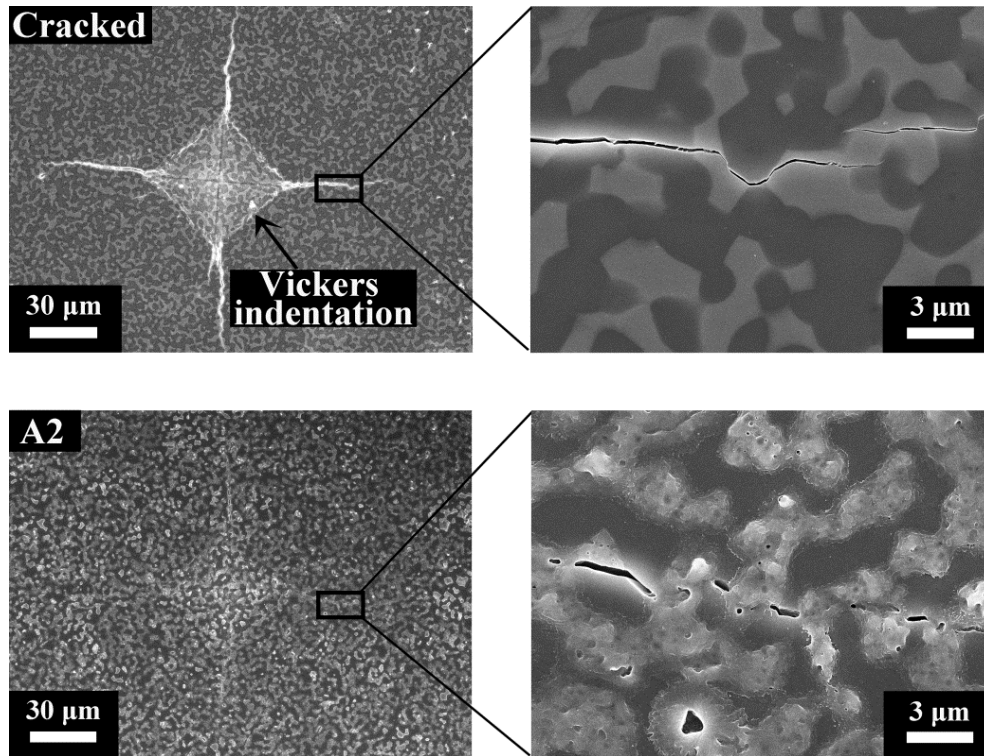


Figure 5.14 SEM micrographs of cracked $\text{Al}_2\text{O}_3/30\text{vol}\%\text{Ti}$ composites and crack-healed under condition A2.

XRD diffraction patterns showing in Figure 5.15 indicated that after anodization, apart from $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Ti}$, peaks ascribed to rutile and anatase were detected. The bending strength of cracked 30Ti with and without crack healing is shown in Figure 5.16. After the cracks were introduced, bending strength decreased from 550.8 ± 29 to 290.3 ± 48 MPa, corresponding to a 47.3% decrease. When composites were crack-healed under condition A2, the bending strength recovered to 519.8 ± 63 MPa and was 94.4% of the bending strength of sample 30Ti.

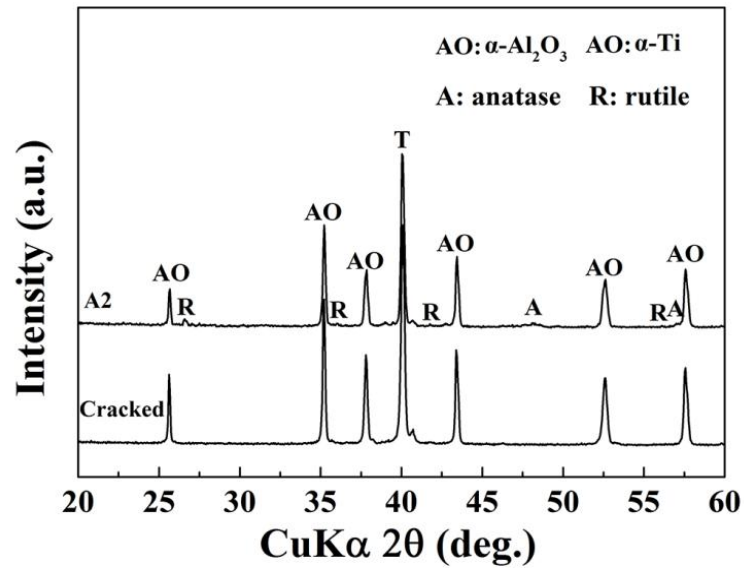


Figure 5.15 XRD patterns of cracked Al₂O₃/30 vol% Ti composites before and after crack-healed under condition A2.

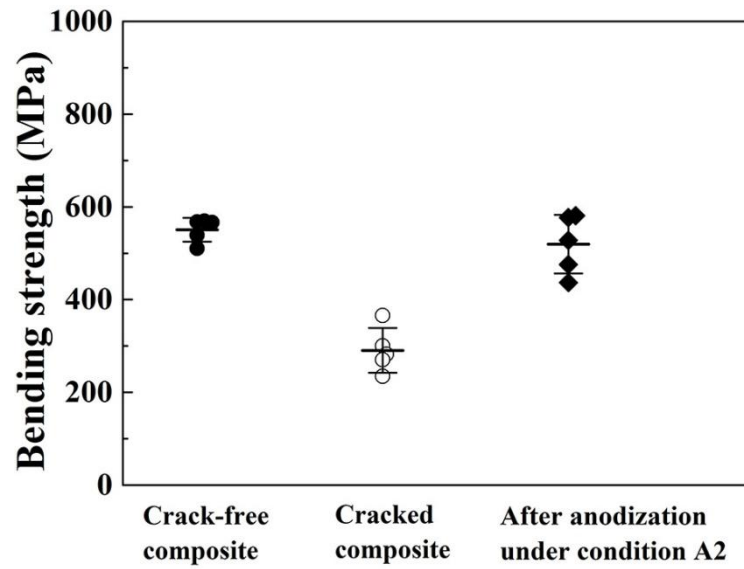


Figure 5.16 Three-point bending strength of Al₂O₃/30vol%Ti composites before and after crack-healed under condition A2.

5.4 Discussion

5.4.1 Crack-healing mechanism

From the results obtained above, a possible crack-healing mechanism was considered. Crack-healing behavior is ascribed to the bridge of crack by oxides with expanded volume. Crack healing procedure is divided into three steps and the Schematic graphs are shown in Figure 5.17. Firstly, when electrical current passes through cracked composites, current will concentrate in crack tip leading to a dramatic increase of current density in crack tip and thus oxidation starts from crack tip. With the oxidation of Ti particles associated with expanded volume, crack tip is healed see Figure [5.17(a)]. Secondly, with increased current density and prolonged anodization time, cracks are healed from crack tip to indentation gradually and all Ti particles distributed on the side of crack are oxidized and expanded to bridge the crack [see Figure 5.17(b)]. Finally, Ti particles distributed in all possible current pathways are oxidized [see Figure 5.17(c)]. Since anodization procedure is conducted at room temperature in current study, ion diffusion is negligible and oxidized Ti particles are isolated without complete oxides layer. In anodization induced crack-healing process, crack-healing behavior is ascribed to the bridge of crack by oxides with expanded volume.

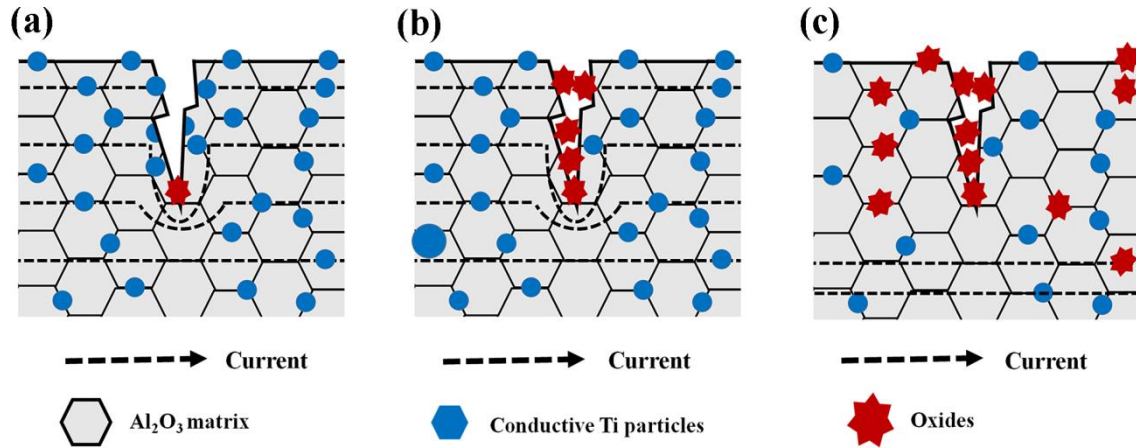


Figure 5.17 Schematic graphs of crack-healing mechanism induced by anodization.

Figure 5.18 shows a detailed example confirming the proposed crack-healing mechanism observed in the current research. Specifically, Figure 5.18(a) shows that a crack initiates from the Al_2O_3 matrix and passes through Ti particles, leading to intergranular-fractured Ti (marked as 1), or propagates along the interface between Al_2O_3 and Ti, leading to fractured Ti particles distributed along the two sides of the crack propagation path, leading to transgranular-fractured Ti (marked as 2). After the crack healed under condition A3 in Figure 5.18(b) when current was passed through the composite, metal Ti particles were oxidized, accompanied by an expansion of volume and the bridging of cracks by these oxides.

Notably, the mechanisms by which transgranular-fractured and intergranular-fractured Ti particles bridge cracks differ slightly. For intergranular-fractured Ti particles, oxides expand from two directions perpendicular to the crack propagation path toward the crack to connect each part and bridge the crack, as shown in Figure 5.18(c). For transgranular-fractured Ti particles, oxides expand from one direction perpendicular to the crack propagation path toward the crack, as shown in

Figure 5.18(d). That is, after anodization, crack bridging occurs via the connection of transgranular-fractured particles and the single expansion of intergranular-fractured particles.

In addition to bridging cracks, oxides were observed to also tend to fill cracks in the Al_2O_3 region, as shown in Figure 5.18(c) and Figure 5.18(d). The EDX analysis results presented in Figure 5.19 verify the existence of Ti at the crack between Al_2O_3 phases, demonstrating that the formed phase filled the crack even in the Al_2O_3 region. Oxides filling cracks is also considered to contribute to the recovery of bending strength, which should have the same mechanism when samples are healed at high temperatures^[8,9]. However, because crack-filling behavior is not a major phenomenon in current research, crack bridging is recognized as the major and effective crack-healing mechanism induced by anodization.

In addition, Figure 5.18(a) and 18(b) reveal that, in the case of 20Ti-29.4-A3, dispersed Ti particles retained their initial shapes after anodization under condition A3. The distance between Ti particles clearly decreased after anodization, indicating that, for Ti particles, the volume expanded but no change in shape occurred. The same conclusion was reached for other crack-healed composites 20Ti-29.4-A1 and 20Ti-29.4-A2. The unchanged particle shape further verified that no diffusion of elements occurs during the anodization procedure and that crack healing is caused by the expanded volume of oxides.

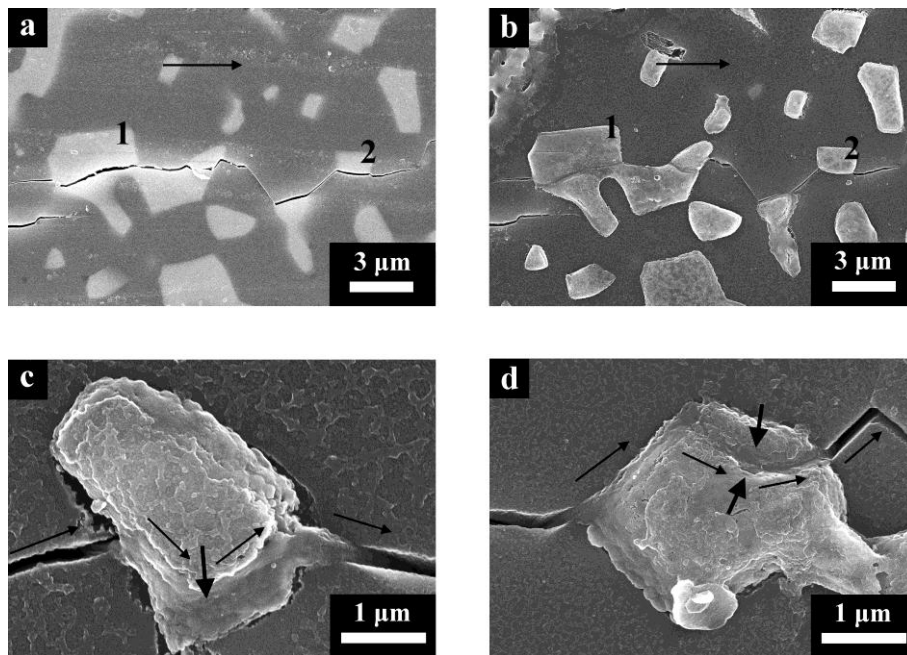


Figure 5.18 Crack-healing mechanism in $\text{Al}_2\text{O}_3/20\text{vol}\%\text{Ti}$ composites (a) cracked composite (b) crack-healed under condition A3 (c) a representative intergranular-fractured crack-healed particle (d) a representative crack-healed transgranular-fractured particle.

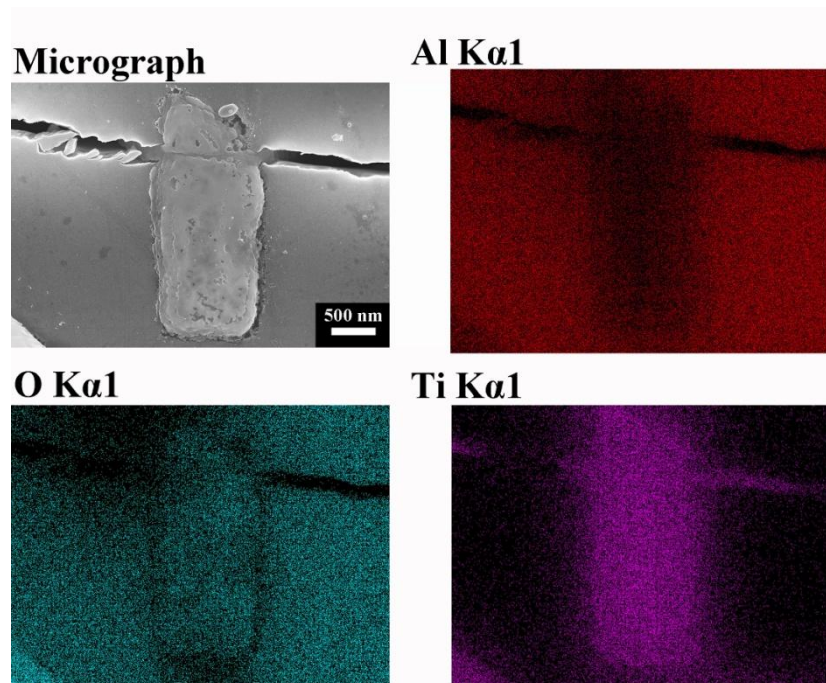


Figure 5.19 EDX analysis of a bridged Ti particle in crack-healed $\text{Al}_2\text{O}_3/20\text{vol}\%\text{Ti}$ composite under condition A3.

5.4.2 Strengthening mechanism

With respect to the strengthening mechanism in crack-healed composites, it is considered that crack healing by crack bridging and crack filling leads to the recovery of bending strength. In addition to the effect of crack healing, other reasons account for the recovery of the bending strength. When a crack was introduced into the ceramics' surface, because of the residual stress field near the indentation, the ceramics tended to fracture at the crack under the action of external forces, leading to a dramatic decrease in bending strength. However, anodization induced crack bridging caused a residual stress relaxation, resulting in increased mechanical strength. In addition, after the crack-healing process, oxides passivated the formed crack tips to eliminate the stress concentrations at the crack tips. With the relaxation of residual stress and the elimination of stress concentration, bending strength was increased accordingly. However, because of the different crack finish modes, the relaxation of the stress concentration at the crack tip is different, leading to different contributions to the recovery of the mechanical strength. This difference in contributions is regarded as the reason why, under the same anodization conditions, the measured bending strength of each sample differs.

On the other hand, in the case of crack filling, bending strength recovery was contributed to the decrease in crack length. Griffith's criterion for fracture of elastic body showing in Equ. (1)^[35] indicates the critical stress over which crack begins to propagate causing ceramics fracture. When cracked composites were healed by anodization, with the filling of crack by oxides, crack length decreased leading to the increase in critical stress. Under some action of external forces, crack propagation caused ceramics fracture became difficult. As a result, mechanical strength was

increased.

$$\sigma_f = \left(\frac{EG_c}{\pi c}\right)^{1/2} \quad (1)$$

Where σ_f is critical stress, E is Young' modulus and c is the half of crack length. Here, $G_c E = K_{IC}$ (fracture toughness) which could be regarded as constant. For crack-free 20Ti with three-point bending strength of 352 GPa (Figure 5.9), the critical crack length causing fracture was calculated to be $2c = 90.4 \mu\text{m}$. That means that if the crack length is below $90.4 \mu\text{m}$, cracked composites could show as high strength as crack-free ones.

In addition, in current study, it is considered that although the existence of cracks caused great decrease in bending strength, introduced cracks has no great effects on fracture toughness. This could be interpreted from the relationship between bending strength and fracture toughness since bending strength could be measured from 3-point bending test. In brittle materials, bending strength is inversely proportional to fracture toughness which could be presented as $\sigma_f K_{IC}^2 = \text{contant}$. It is indicated that when bending strength decreases or increases to 4 times, fracture toughness increased or decreases to 1/2. In this study, the greatest change in bending strength was given by 20Ti-98-A3 which shows 60% of bending strength with respect to the crack-free sample. After simple calculation, the increase in fracture toughness is below 20%. That is to say, the change in fracture in the whole crack-healing procedure is within 20%.

5.4.3 Effective factors on crack-healing ability

First of all, anodization current density has essential effects on crack-healing behavior. In the $\text{Al}_2\text{O}_3/\text{Ti}$ composites, in which electrically conductive Ti was dispersed into the insulating Al_2O_3 ceramic matrix, the conductive Ti particles are randomly distributed but contact each other to percolate, resulting in an interconnected Ti network through

which electric current can pass. This phenomenon is described in detail elsewhere^[31]. The obtained electrical conductivity implies that the $\text{Al}_2\text{O}_3/\text{Ti}$ composite was suitable for anodization. However, only interconnected Ti particles can form a completely continuous pathway [Figure 5.4(a)]; thus, electrical current passes through the composites via selected pathways, indicating that not all of the Ti particles could be oxidized. Therefore, some metal Ti particles remained in the composite after anodization. The XRD analysis results confirm the existence of the Ti metal. Because the crack-healing process was conducted at room temperature, thermal diffusion did not occur; therefore, the oxidized particles were isolated, and an oxide layer was not observed on the surface of the composite [Figure 5.4(b)].

In addition, with the formation of oxides, the resistivity of the composites increased. Thus, an increase in current density was required during the late anodization stage. In this study, a three-step process was applied with a progressively increasing current density, e.g., conditions A1 and A2. Under a relatively low current density, the expanded volume of the oxidized particles was found to be insufficient to bridge the crack; thus, the recovery efficiency of the bending strength was low. However, under conditions A2 and A3, the bending strength recovered completely and showed no obvious difference. Under a given current density, oxidation was considered to finish at the first stage within a short time. With increasing anodization time, further oxidation was difficult. Thus, a higher current density was required for further oxidation.

Under some current density, oxidation was considered to finish at first stage with a short time. Then further increase anodization time, oxidation is difficult to further take place. Thus current density should be improved to make second oxidation occur. Since crack was gradually healed, in the case of condition A2, the change in morphology of Ti

particles and element condition after each step turned out that it is important to increase current density during later anodization stage to cause further oxidation. Since oxidation associated with expanded volume of Ti particles located at crack propagation path is considered fully completed under relatively higher current density for a long time, the repeated anodization has no effects on further healing cracks and recovering bending strength.

In cracked composites, bending strength strongly depends on the fracture mod. When composites fracture from the crack, they exhibit low bending strength; by contrast, composites exhibit relatively high bending strength when the fracture occurs in the crack-healed zone^[14]. In the current study, in cracked composites, fracture initiated from the crack, leading to a dramatic decrease in bending strength. After the anodization-assisted crack-healing process, samples 20Ti-29.4-A2 and 20Ti-29.4-A3 fractured almost outside the crack-healed zone, which means that the crack was healed completely. Because microcracks cannot be eliminated completely after polishing, after anodization, with the healing of the microcracks, the bending strength of the crack-healed composites was possibly increased. The relatively higher bending strength of sample 20Ti-29.4-A2 is attributed to this effect. The recovered bending strengths shown in Figure 5.9 verify the crack-healing ability of the samples. However, some composites crack-healed under condition A1, which included a low current density, fractured from the crack. In this case, the crack was not healed completely, leading to an average recovered bending strength of 539.8 ± 70 MPa.

Different applied loads caused different lengths of cracks and different CODs, which strongly affect crack-healing ability. Sample 20Ti-29.4-A3, with a crack length of 140 μm , exhibits a higher recovery efficiency than sample 20Ti-98-A3, with a crack length

of 370 μm . Because Ti particles are dispersed on the surface and cracks do not always propagate along interfaces or pass through Ti particles to lead to intergranular-fractured or transgranular-fractured Ti particles, cracks also propagate along the Al_2O_3 matrix. In this case, cracks cannot be healed by anodization because of the absence of Ti species to form oxides. Because cation diffusion of oxidized Ti cannot occur at room temperature, oxides remain in their original location. For longer cracks, the possibility of propagation along the Al_2O_3 matrix is higher, thus leading to relatively lower crack-healing ability.

In addition to crack length, COD is also speculated to affect crack-healing ability. With a certain anodization current density and anodization time, the amount of oxide formed and, hence, the volume of oxides is limited. When the COD was large, the expanded volume of oxidized Ti particles was not sufficient to connect the crack. The upper limit of the COD that can be healed by crack bridging depends on the current density. In this study, when the current density was 3 A/dm^2 (Figure 5.12) and the COD was larger than 0.5 μm , part of the crack was not connected despite the formed oxides filling the cracks. However, when COD was less than 0.3 μm , the expanded oxides connected the crack. When the COD was between 0.3 and 0.5 μm , cracks were occasionally bridged by expanded oxides. For different crack sizes, the optimal anodization conditions must be experimentally determined.

Under the same crack-healing condition of A3, the crack-healing abilities of the 20Ti and 30Ti composites with different electrical resistivities differed. Sample 30Ti, with a higher electrical conductivity and greater Ti content than sample 20Ti, appears to be more effective in anodization; however, 20Ti, with a slightly lower electrical conductivity and lower Ti content, exhibits better crack-healing ability. These differences are attributed to the differences in fracture toughness. When a crack was

induced under the same load of 29.4 N, the decrease in bending strength differed. In the 20Ti composite of higher fracture toughness, crack propagation was difficult, leading to a crack 140 μm in length. In the case of the 30Ti composite of lower fracture toughness, the propagated crack was slightly longer (150 μm), which is responsible for the lowered bending strength. After anodization, although the degree of oxidation in 30Ti was greater, the recovery efficiency of bending strength was lower for the longer crack, as previously discussed for the effect of crack length on crack-healing ability. In addition, the higher fracture toughness of 20Ti indicates that, along the crack propagation path, the Ti particles tend to fracture into two parts by the transgranular fracture mode. Because transgranular-fractured Ti particles were located at the two opposite sides along the crack propagation path, the expanded fractured Ti particles connected cracks by contacting each part during the anodization process. Therefore, the transgranular-fractured Ti particles were more effective in bridging cracks than intergranular-fractured Ti particles. On the basis of the aforementioned results, it is concluded that, compared with conductivity, fracture toughness more strongly affects crack-healing ability under the same applied indentation load.

In addition, crack finish mode is considered to have effects on crack-healing ability, thus affects the recovery of bending strength. When crack was finished in Ti particles, after anodization, crack tip could be healed completely [see Figure 5.7(a)]. With the relaxation of stress concentration at crack tip, bending strength could be increased meaning a higher crack-healing ability. On the other, when crack was finished in Al_2O_3 matrix [see Figure 5.7(b)], since anodization has no effect on Al_2O_3 matrix, after crack-healing procedure, stress concentration at crack tip still remained. In this case, the contribution from crack tip passivation on improving bending strength is negligible

indicating a relatively low crack-healing ability. The effects of crack finish mode also explained why the same samples after crack-healed under the same condition had different bending strength.

5.5 Summary

In this study, I first applied an anodization process to heal cracks in ceramic-based composites at room temperature. Although heat treatment to induce self-crack-healing behavior for recovering mechanical properties such as the bending strength of ceramics and their composites is a promising solution when conducted at high temperatures, crack-healing ability induced by anodization provides an easy and fast method for healing surface cracks at room temperature. After the healing process, the bending strength of the samples was recovered completely. Notably, the key issue for realizing room-temperature crack healing in the present work lies in the development of ceramic-based composites with sufficient electrical conductivity because the dispersion of conductive-metal particles into insulating ceramics is critical to this approach. Ti metal and Al_2O_3 ceramic were used in the present work. However, this novel methodology based on electrochemical crack healing can be applied to other materials and/or ceramic-based composites. In a future work, I will attempt to heal ceramic-based composites using wet air as an electrolyte, which would potentially be applicable to ceramic parts under any conditions irrespective of the size and use of ceramics.

In summary, a room-temperature healing was achieved by electrochemical anodization to recover the mechanical strength of ceramic-based composites. The behavior of crack bridging, which was considered as the recovery mechanism in

cracked composites, was observed. Under certain anodization current density and time conditions, the complete recovery of the bending strength of cracked samples was confirmed. Nevertheless, the anodization conditions are not restricted to those mentioned in the present work. In addition to crack-healing ability, the electrical discharge machining process used here is also beneficial for machining brittle ceramics into complex shapes.

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Preparation of 1D TiO₂ nanorod on the surface of Al₂O₃/Ti composites by simple heat treatment for photocatalytic application

6.1 Introduction

Owing to wide band gap, unique ionic and electric properties, nano-structured TiO₂ have attracted comprehensive attention for their potential applications in photocatalysis, sensors, water splitting and photovoltaic cells^[1]. Recently, TiO₂ photocatalysis has been the most efficient alternatives and has caused great attention in water purification, environment cleaning and organic pollutants decomposition because of its good chemical stability, high oxidizability and non-toxicity^[2,3,4,5].

The morphologies and structures of TiO₂ have greatly effects on properties. Among all the structures of TiO₂, 0D TiO₂ nanoparticles have been caused great concern. Due to large surface area and broadened band gap, 0D TiO₂ nanoparticles show excellent performances in photocatalysis, hydrogen production and solar cells^[6,7]. However, the fast recombination of electrons and holes, slow charge carrier transfer and high recycling cost greatly limit their application as photocatalysis^[8]. 1D TiO₂ nanostructures including nanotube, nanorod, nanowire and nanosheet have been widely investigated due to their unique properties compared with 0D TiO₂ nanomaterials, such as direct electrical pathways and electron transportation. 1D TiO₂ nanomaterials not only have the properties of 0D materials but also show some other properties, such as unique

electronic properties, high specific surface area and even high mechanical strength^[9].

Among these 1D TiO₂ nanostructures, 1D TiO₂ nanorod has attracted great attention in solar cell and photocatalysis due to their superior electrical transport performance, excellent chemical stability, high refraction index, and cheap product cost^[10,11,12]. In addition, it was reported that 1D TiO₂ nanorod arrays are favor in prolonging the life of photogenerated charge carriers to provide them enhanced photocatalytic activity^[13].

Various methods have been developed to grow TiO₂ nanorod arrays on fluorine-doped tin oxide (FTO) glass substrate^[2], polymer substrates^[14] or metal sheets^[15]. These synthesis methods contain oxidation of Ti substrate^[16], solvothermal method^[17], Template-assisted method, sol-gel method^[18, 19] and hydrothermal synthesis^[20,21]. The hydrothermal method is the most used method because of the simple procedure and low production cost. Shen et al^[2] prepared TiO₂ nanorod arrays on FTO substrate by hydrothermal process and characterized their photodegradation efficiency of RhB under visible light. Wang^[22] et al synthesized C₃N₄ modified TiO₂ nanorod arrays by hydrothermal process on FTO substrate and realized the high visible light photoelectrochemical activity. Guo et al^[23] fabricated TiO₂ nanorod orienting perpendicular to the (001) facet on carbon fiber by hydrothermal synthesis and etching process with a diameter ranging from 10 to 30 nm.

Since TiO₂ could be obtained by oxidizing metal Ti, it is considered that TiO₂ nanorod might be achieved by simple heat treatment process in air or oxygen atmosphere on appropriate substrate. Peng et al^[16] successfully fabricated TiO₂ nanorod on titanium substrate by oxidizing Ti at 850 °C using dibutyltin dilaurate [(C₄H₉)₂Sn(OOC₁₁H₂₃)₂, DBTDL] as oxygen source which was carried in by an argon stream. In our previous report^[24], dispersing Ti particles into Al₂O₃ ceramic matrix

fabricated $\text{Al}_2\text{O}_3/\text{Ti}$ composites with high mechanical properties and electrical properties. During sintering, Al_2O_3 was found to decompose, diffuse into Ti which could be regarded as the source of oxygen like DBTDL. It is assumed that nanorod structure could be also formed on $\text{Al}_2\text{O}_3/\text{Ti}$ composite surface at suitable heat treatment temperature and time. Here, I tried to generate TiO_2 nanorod on the substrate of $\text{Al}_2\text{O}_3/\text{Ti}$ composites via simple heat treatment for photocatalytic application. If $\text{Al}_2\text{O}_3/\text{Ti}$ could be used as photocatalysis, as ceramic-based composites, there are some crucial advantages than metal Ti, such as high bending strength, better wear behavior, high-temperature oxidization, corrosion resistance, good chemical stability and low elastic modulus^[25,26,27,28,29].

In order to generate 1D TiO_2 nanorod on the surface of $\text{Al}_2\text{O}_3/\text{Ti}$ composites by simple heat treatment, the effects of various treatment conditions on the formation of nanorod were studied, including heating temperature and heating time. Photocatalytic activity (degradation efficiency of Rhodamine B) of heated $\text{Al}_2\text{O}_3/\text{Ti}$ composites was preliminarily characterized with the purpose of applying multifunctions on $\text{Al}_2\text{O}_3/\text{Ti}$ composites in addition of mechanical properties. A reasonable interpretation about the formation mechanism of nanorod was given in this text.

6.2 Experimental procedures

6.2.1 The preparation of $\text{Al}_2\text{O}_3/\text{Ti}$ composite substrate

$\text{Al}_2\text{O}_3/\text{Ti}$ composites were fabricated using the mixtures of titanium hydride powder (TiH_2 , 5-10 μm , 99% up, Kojundo Chemical Laboratory Co., Ltd., Sakado, Japan) corresponding to 20% of Ti in volume fracture in final composite and $\alpha\text{-Al}_2\text{O}_3$ powder

(0.2 μm , AKP-53, Sumitomo chemicals Co., Ltd., Japan) by hot press sintering method under an applied pressure of 30 MPa at 1500 $^{\circ}\text{C}$ for 1 h in Ar atmosphere. The detail preparation methos was described in chapter 2. Hot-pressed samples were polished with diamond paste to 2 μm and then washed in an ultrasonic cleaner with ethanol and high pure water following dried in an oven at 60 $^{\circ}\text{C}$. In order to make a comparison, pure Ti, Al_2O_3 /50 vol% Ti and Al_2O_3 /80 vol% Ti composites were also prepared as substrates in this work using the same preparation method.

6.2.2 Heat treatment

Published samples were heat treated at different temperature (400 $^{\circ}\text{C}$, 500 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$) for different time (1 h, 2 h, 3 h and 5 h) to search for the appropriate conditions for forming TiO_2 nanorod on the surface of Al_2O_3 /Ti composites. Heat treatment process was conducted in an electrical furnace (Isuzu, Seisakusho Co., Ltd, Japan) in air at a rate of 5 $^{\circ}\text{C}/\text{min}$ and cooled with the furnace.

6.2.3 Analysis of sample surface

The surface structures of heat treated samples were studied by a field-emission scanning electron microscopy (FE-SEM; SU9000, Hitachi, Japan) equipped with energy dispersive X-ray spectroscopy (EDX; Horiba, Japan). Phases were measured by X-ray diffractometer (XRD; D8 Advance, Bruker Ltd., USA) using $\text{CuK}\alpha$ radiation at 40 kV and 40 mA.

6.2.4 Evaluation of photocatalytic activity

The degradation efficiency of RhB was used to evaluate the photocatalytic activity of

composites after heat treatment at 400 °C, 500 °C and 600 °C. Four pieces of samples with the size of 15 mm×15 mm×1.5 mm were immersed into 30 mL of 5 mg/L RhB solution and irradiated using UV light source (Supercure-204S, San-ei Electric, Japan) under ambient conditions. Before UV light on, the solution was stirred in dark for 1 h to reach adsorption-desorption equilibrium. The concentration change of RhB was examined using an ultraviolet visible (UV-VIS) spectrophotometer (UV mini 1240, Shimadzu, Japan) by measuring the UV absorbance at 553 nm.

6.3. Results

6.3.1 Effects of heating time on surface morphology

Surface morphology of $\text{Al}_2\text{O}_3/20 \text{ vol}\%\text{Ti}$ composite before heat treatment shown in Figure 6.1 could be also observed in chapter 2. In Figure 1, dark phases correspond to Al_2O_3 matrix while bright phases correspond to Ti. Since heat treatment below 600 °C has no effects on Al_2O_3 surface, in current, the study of surface morphology change of composites was mainly focused on Ti surface.

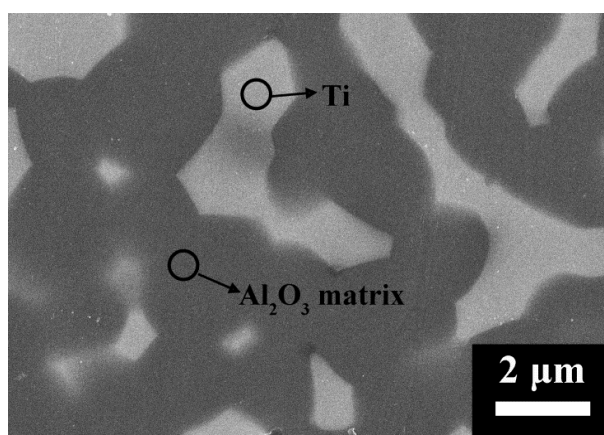


Figure 6.1 FE-SEM micrograph of $\text{Al}_2\text{O}_3/20 \text{ vol}\%\text{Ti}$ composite before heat treatment.

Figure 6.2 shows the change in surface morphology of $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite observed by FE-SEM when heated at 600°C for different time. These graphs were taken from the same sample. It could be found that when sample was heated at 600°C in air, metal Ti could be oxidized and the surface was changed. After heated for 1 h, particle morphology was observed on the Ti surface while some columnar structure was also observed. Increase heating time to 2 h, 1D TiO_2 nanorod began to turn out in spite of the small amount. Further increase heating time to 3 h, Ti surface was almost covered by nanorod while some particle structure could be still observed. After heated for 5 h, well ordered TiO_2 nanorod was completely formed on the whole Ti surface.

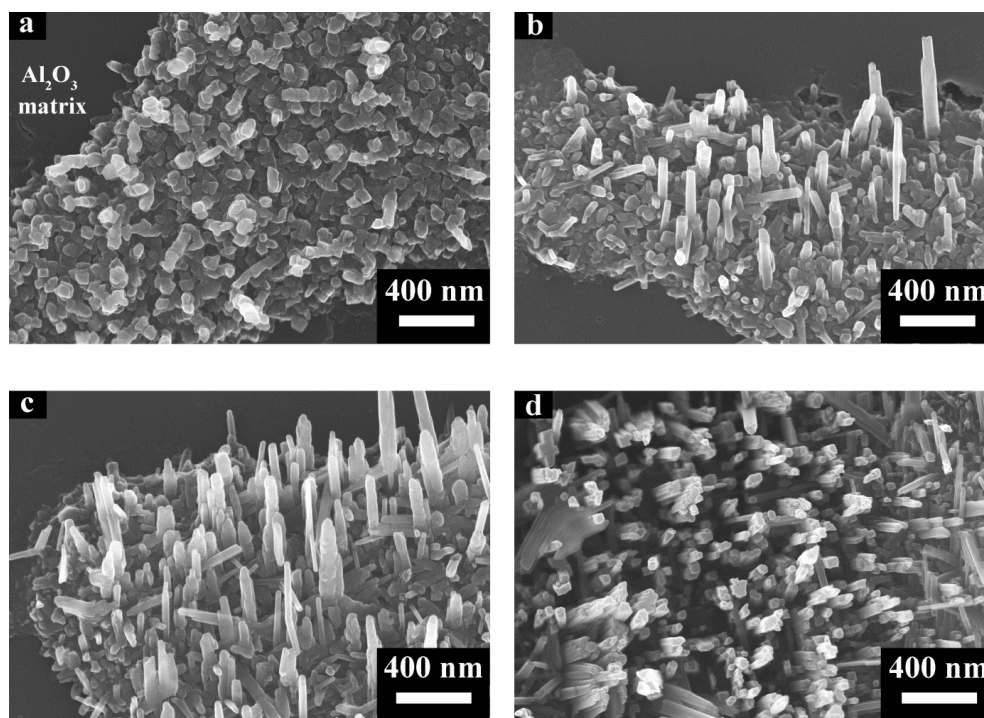


Figure 6.2 The change in surface morphology of $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite when heated at 600°C for (a) 1 h (b) 2 h (c) 3 h (d) 5 h.

In addition of well ordered nanorod arrays which were the main morphologies, some nanoflower-like arrays were also observed, as shown in Figure 6.3.

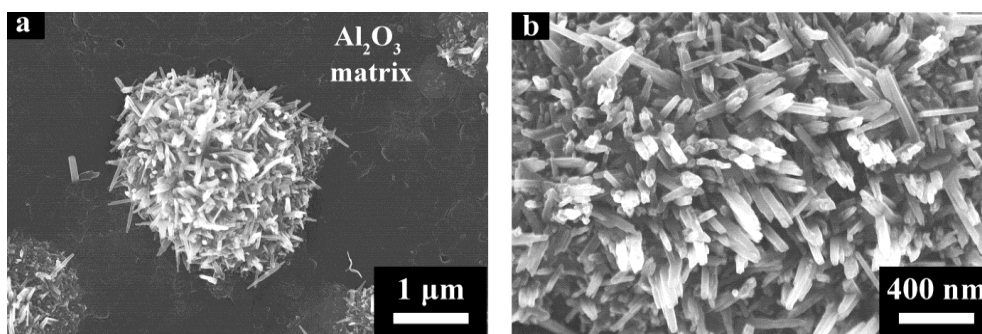


Figure 6.3 Nanoflower-like structure observed on $\text{Al}_2\text{O}_3/20$ vol% Ti composite after heat treatment at 600°C for 5 h

6.3.2 The effects of heat-treatment temperature on surface morphology

The effects of heat-treatment temperature on the formation of TiO_2 nanorod were studied and FE-SEM micrographs are shown in Figure 6.4. The cross marks with numbers in Figure 6.4(c) representing the points of EDX quantitative analysis was shown in Table 6.1. After heated at 400°C , nanoscale particles were formed on Ti surface. Increase temperature to 500°C , particle size became large while still in nanoscale level. After heated at 600°C for 5 h, nanorod structure was observed, like shown in Figure 6.2(d).

From the data list in Table 6.1, it was found that nanorod was composed of Ti and O as well as small amount of Al. Relative ration of O/Ti is over 2 indicating that in addition of TiO_2 , nanorod structure also composes other oxides, such Ti-Al-O compounds.

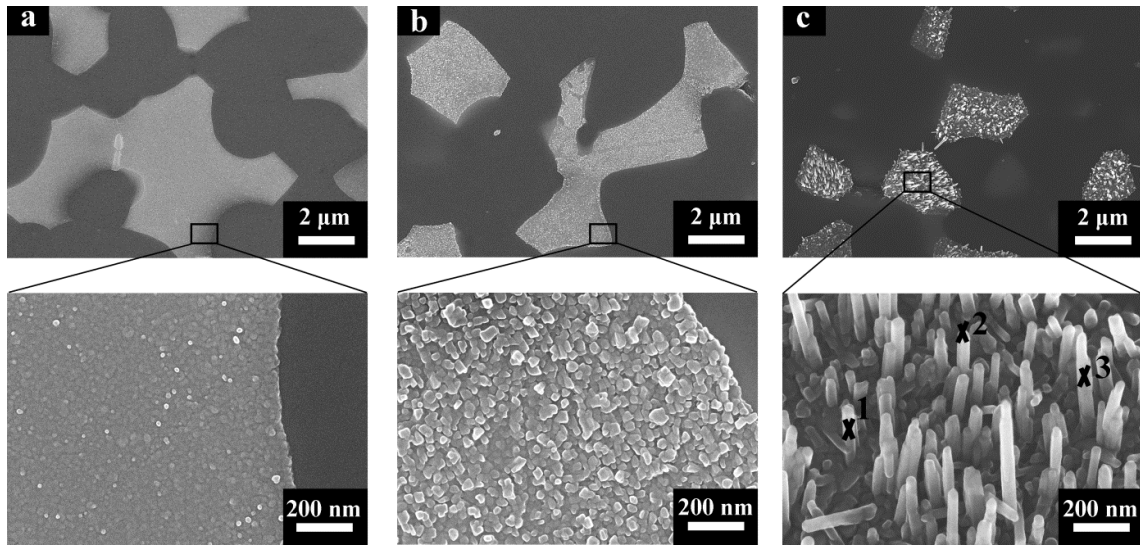


Figure 6.4 The change in surface morphology of $\text{Al}_2\text{O}_3/20\text{vol}\%$ Ti composite after heated for 5 h at (a) 400 °C (b) 500 °C and (c) 600 °C .The cross marks with numbers represent the points of EDX quantitative analysis (Table 6.1).

Table 6.1 Chemical composition of the nanorod formed on the surface of the $\text{Al}_2\text{O}_3/20\text{vol}\%$ Ti composite measured by EDX.

Point	Elements (mol%)			Relative ratio of O/Ti
	Ti	Al	O	
1	19.7	7.6	72.6	3.68
2	18.8	9.5	71.6	3.81
3	25.2	7.9	66.9	2.65

6.3.3 The effects of heat-treatment temperature on surface phase

XRD patterns of $\text{Al}_2\text{O}_3/20\text{ vol}\%$ Ti composites heat treated at 400 °C, 500 °C and 600 °C for 5 h were shown in Figure 6.5. It indicated that in the composite before heat treatment, the main phases were $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Ti}$. After heated at 400 °C for 5 h, there

is no change in phases. The formed TiO_2 was amorphous. Increasing heating temperature to 500 °C, rutile was detected and the content of rutile increased when heated at 600 °C.

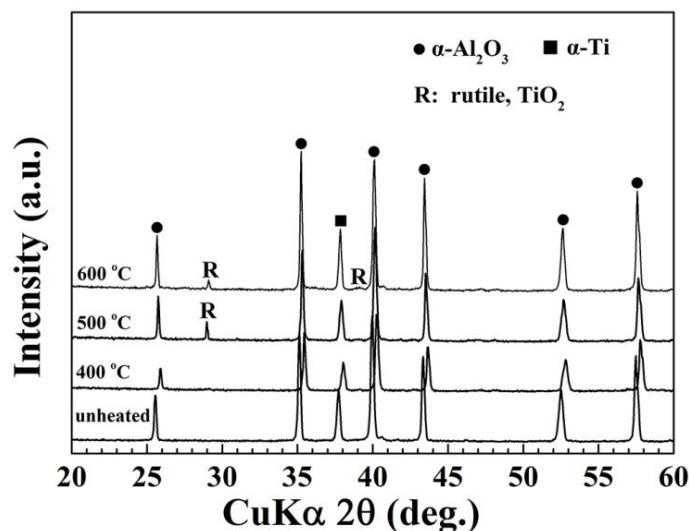


Figure 6.5 XRD patterns of $\text{Al}_2\text{O}_3/20 \text{ vol\%Ti}$ composites heat treated at 400 °C, 500 °C and 600 °C for 5 h.

6.3.4 The effects of matrix materials on the formation of nanorod

In order to confirm the effects of Al element on the formation of nanorod, matrix materials with different Al_2O_3 content were heated at 600 °C for 5 h and FE-SEM micrographs of the surface morphologies are shown in Figure 6.6. There is no nanorod structure was found on the matrix surface of pure Ti and $\text{Al}_2\text{O}_3/50 \text{ vol\% Ti}$ composite, while on the surface of $\text{Al}_2\text{O}_3/80 \text{ vol\% Ti}$ composite, some rod-like structure was observed.

Table 6.2 shows element compositions of $\text{Al}_2\text{O}_3/20\text{vol\% Ti}$ treated at different conditions observed by EDX analysis. It was found that, when composites were heated

at 600 °C, the ratio of O/Al increased with the increase of heating time indicating the increase in oxygen content. When composites were heated at different temperature for the same time of 5 h, in the case of 400 °C, the content of oxygen reacting with Ti is not enough. When heat treatment temperature increased to 500 °C and 600 °C, there is no obvious difference in the content of oxygen.

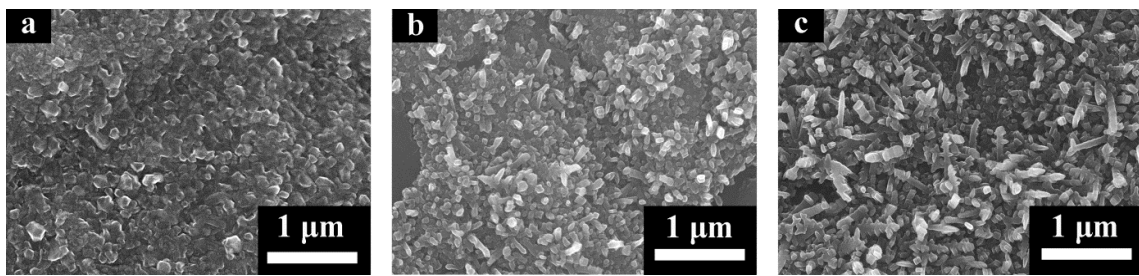


Figure 6.6 Surface morphologies of (a) pure Ti (b) Al_2O_3 /50vol% Ti composite and (c) Al_2O_3 /80vol%Ti composite after heat treatment at 600 °C for 5 h.

Table 6.2 Results of EDX analysis on the surface of Al_2O_3 /20vol% Ti composites heated at different temperature for 5 h or at 600 °C for different time.

Treatment conditions	Elements (mol%)			Relative ratio of O/Al
	Ti	Al	O	
Unheated	11.5	26.4	62.0	2.34
400°C-5 h	9.3	27.4	63.2	2.31
500°C-5 h	13.1	21.2	65.7	3.09
600°C-1 h	11.1	25.4	63.5	2.49
600°C-2 h	10.8	24.4	64.8	2.64
600°C-3 h	10.9	23.4	65.7	2.80
600°C-5 h	13.1	21.2	65.7	3.10

6.3.5 Photocatalytic efficiency

Photocatalytic activity of $\text{Al}_2\text{O}_3/20\text{vol}\%$ Ti composites heat treated at different temperature is characterized by evaluating the degradation efficiency of RhB under UV light and the result is shown in Figure 6.7. All heated composites exhibits photocatalytic activity. The degradation efficiency of RhB increased with the increase in heat treatment temperature of samples. After exposed to UV light for 12 h, the highest degradation efficiency of RhB is about 18% which is given by the sample heated at 600 °C. In addition, there is no obvious difference between samples heated at 500 °C and 600 °C in exhibiting photocatalytic ability.

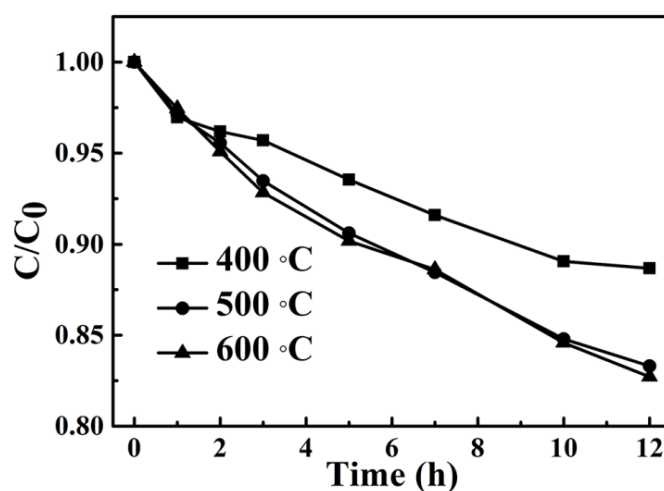


Figure 6.7 Degradation of RhB under UV light immersed with $\text{Al}_2\text{O}_3/20 \text{ vol}\%$ Ti composites heat-treated at 400 °C, 500 °C and 600 °C.

6.4. Discussion

6.4.1 Formation mechanism of nanorod

In the case of $\text{Al}_2\text{O}_3/20\text{Ti}$ composite, it is considered that there are two factors

determining whether nanorod structure can form or not. One is oxygen content reacted with Ti. And the other one is the diffusion of Ti. The former is related to heating time while the later depends on heat temperature. When $\text{Al}_2\text{O}_3/\text{Ti}$ composite was thermally heated, oxide film was firstly formed on Ti surface. Heating temperature has obvious effects on surface morphology of $\text{Al}_2\text{O}_3/\text{Ti}$ composite. At low temperature of 400 °C or 500 °C, the diffusion of Ti is too low to grow into nanorod. As a result, Ti surface was oxidized into nanoparticles. At higher temperature of 600 °C, the diffusion of Ti is enough to grow into nanorod while composite was heated for some time. Below one hour, in spite of the high diffusion of Ti, the content of oxygen reacting with Ti was little. After heated for two hours or more, oxygen was enough to react with Ti to make continuous oxidation of Ti and grow up into nanorod. The relative ration of O to Al shown in Table 6.1 indicates that at 600 °C, with the increase of heating time, oxygen content was increased since heat treatment was considered to have no effect on Al_2O_3 matrix and thus have no effect on Al content.

Besides, since metal Ti within $\text{Al}_2\text{O}_3/\text{Ti}$ composite was obtained from the decomposition of TiH_2 , it is thought that defect concentration in Ti was relatively higher. Thus the higher reactive activity of Ti with oxygen is also considered to contribute to induce the formation of nanorod. Because composites were heated in air atmosphere, the disorder of airflow determined the two different surface morphologies of well order nanorod arrays and disordered nanoflower-like structure. It is guessed that if the direction of air could be controlled, nanorod arrays will grow toward the same direction to formed well ordered nanorod structure.

In addition, the existence and the content of Al_2O_3 greatly affect the formation of nanorod. As shown in Figure 6.2 and Table 6.1, the composition of nanorod structure

not only includes Ti and O, but also includes little Al. During HPS process at high temperature, Al_2O_3 could decompose and diffuse into Ti to form titanium oxides or Ti-Al-O compounds as reported in our previous study^[24]. When composites were heat treated again in air, the existence of Al was considered as an essential element for promoting the generation of nanorod. The content of Al_2O_3 is also effective in forming nanorod structure. When composites were heat treatment in air atmosphere, the oxygen content is not enough to react with metal Ti to form nanorod structure. More oxygen was considered to come from Al_2O_3 . The study of different matrix materials shown in Figure 6.6 confirmed the necessity of Al_2O_3 in forming nanorod. In the absence of Al_2O_3 , nanorod didn't form on the surface of pure metal Ti [Figure 6.6(a)]. When Ti content was increased to 80 vol%, small amount of Al_2O_3 limited the formation of nanorod in spite that some rod-like structure was observed [Figure 6.6(c)].

6.4.2 Photocatalytic activity of heated Al_2O_3 /Ti composites

Photocatalytic activity of TiO_2 is related to crystalline phase and surface area. With the increase of heating temperature, both surface morphologies and phases of composites change resulting in different photocatalytic activity. First is the effect from specific surface area. When Al_2O_3 /20 vol% Ti composites were heated at different temperatures, surface morphologies were quite different leading to different surface area, as shown in Figure 6.2. With the change of surface morphologies from nano-particles to nanorod after heated from 400 °C to 600 °C, surface area increased leading to higher photocatalytic ability.

Second is the effect from crystalline phases. As shown in Figure 6.5, when samples were heated at 400 °C, amorphous along with low surface area made TiO_2 to exhibit

relatively low photocatalytic ability. When samples were heated at 500 °C, rutile occurred and the content of rutile increased when heated at 600 °C. Both high surface area and the existence of rutile made samples heated at 600 °C exhibit the highest photocatalytic ability. However, owing to the existence of rutile, composites heated at 500 °C and 600 °C have no obvious difference in showing photocatalytic ability although the former has lower surface area. It means that compared with surface area, rutile phase is more effective in affecting photocatalytic ability. Nevertheless, in current study, due to the small content of formed TiO_2 , the efficiency in decomposing RhB was not too high until irradiated under UV light for 12 h.

Since it was confirmed that nanorod could be formed on $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite powder, it is believed that high photocatalytic ability could be achieved when more $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite powder is used because powder could be mass produced.

6.5 Summary

1D TiO_2 nanorod was successfully generated on the surface of $\text{Al}_2\text{O}_3/\text{Ti}$ composite via simple heat treatment. The formation condition of the nanorod structure was strict which was only observed on the surface of $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composite after heat treatment at 600 °C in air atmosphere. When heating time was 5 h, Ti surface was completely covered with nanorod arrays. Two different Ti surface morphologies after heat treatment of well ordered nanorod arrays and disordered nanoflower-like structure were ascribed to the disordered airflow. With the formation of TiO_2 nanorod, $\text{Al}_2\text{O}_3/\text{Ti}$ composites employed as solar cell is expected. After the heat treatment, photocatalytic ability of $\text{Al}_2\text{O}_3/\text{Ti}$ composites was confirmed. Since powder could be mass produced, it

is believed that the photocatalytic ability could be further increased when more powder was used as photocatalyst rather than bulk composite.

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Conclusions

In the present study, ceramic/metal composites with improved mechanical properties and developed multifunctions were studied, which allowed ceramics to be employed in a broadened application range. When Al_2O_3 ceramic matrix was dispersed with fine Ti metal particles via controlled powder processing and sintering methods, fracture toughness was increased and electrical insulated Al_2O_3 ceramic was transferred into conductor. The enhanced fracture toughness and electrical properties have been expected to generate new applications of Al_2O_3 such as in electro-discharge machining, fracture sensing and electropotential-assisted room temperature crack healing. Based on the performance of metal Ti, $\text{Al}_2\text{O}_3/\text{Ti}$ composites were confirmed as potential structural components as engineering as well as bioactive materials and photocatalysis after chemical or simple heat treatment. Further, this study has successfully demonstrated the room-temperature crack healing ability for the present ceramic-based composites at first time in the world. The main conclusions obtained in this study are summarized as follows.

In chapter 2, $\text{Al}_2\text{O}_3/\text{Ti}$ composites containing 0–30 vol% dispersed fine Ti particles were fabricated using a hot-press sintering method at 1500°C from mixtures of Al_2O_3 and TiH_2 powders. During sintering, TiH_2 decomposed to form metallic Ti. The effects of the Ti content on the mechanical and electrical properties of the composites were then investigated. No Ti–Al intermetallic compounds were detected by X-ray diffraction, and energy-dispersive X-ray spectroscopy indicated the presence of Al–Ti–O solid solution

and Ti–O phases. The composites showed enhanced densification; the measured densities were higher than the calculated theoretical values. Microstructural observation revealed homogeneously distributed fine Ti particles dispersed in the Al₂O₃ matrix. The Ti particle size ranged from sub-micrometer to a few micrometers depending on the Ti content. The fracture mode of the composites was primarily transgranular, in contrast to the intergranular fracture mode of monolithic Al₂O₃. Although the flexural strength was decreased with increase in Ti content, the composite containing 20 vol% Ti displayed the maximum fracture toughness of 4.3 MPa·cm^{1/2}, which was 37% greater than that of monolithic Al₂O₃. The composites containing more than 15 vol% Ti exhibited drastic decreases in resistivity ($\sim 10^{-1}$ Ωcm), which were attributed to the formation of interconnected Ti networks at these Ti contents. The percolation threshold volume for electrical conduction in the present system was calculated to be 13.8 vol%. The results indicate that dispersing fine Ti particles into Al₂O₃ increased the fracture toughness and improved the conductivity of Al₂O₃.

In chapter 3, the combination of improvement effects of Y₂O₃ and Ti addition was attempted to Al₂O₃ ceramic. Al₂O₃-based composite containing 20 vol% of metallic Ti was chosen, and Y₂O₃ was used as effective additive to optimize mechanical and electrical properties of Al₂O₃/Ti composites. The effects of Y₂O₃ ranging from 1 wt% to 5 wt% on mechanical and electrical properties of Al₂O₃/Ti composites were studied. All Y₂O₃ doped Al₂O₃/Ti composites showed increased density. Microstructure observation revealed refined microstructure and decreased Al₂O₃ grain size. When Y₂O₃ content was 2 wt%, Vickers hardness, Young's modulus and fracture toughness of composite reached to the maximum, and the values were 15.2 GPa, 355.2 GPa and 4.5 MPa·cm^{1/2}, respectively. In all composites, ductile fracture mode, transgranular fracture, was visible.

The toughening mechanism coming from YAG was demonstrated. In addition, after adding Y_2O_3 , electrical resistivity of composites increased monotonically with the increase in Y_2O_3 content. Nevertheless, the increase was negligible and composites could be regarded as good electrical conductor within 5 wt% Y_2O_3 addition.

In chapter 4, a potentially novel ceramic-based composite was developed for photocatalytic activity. $\text{Al}_2\text{O}_3/\text{Ti}$ composites were treated with NaOH and heat to generate a nanometer-scale structure to induce an active surface layer for photocatalytic activity. Because NaOH treatment does not affect Al_2O_3 ceramics, to form a nano-layer over the entire surface of a composite whose surface contains both Al_2O_3 and Ti, strict control was exerted over the NaOH concentration, treatment temperature, and time. The results showed that $\text{Al}_2\text{O}_3/\text{Ti}$ composites were fully covered by nano-porous layers after being treated with 5-M NaOH at room temperature for 3 h and at 60°C for 1 h. After HCl treatment at 25°C or water treatment at 80°C for 24 h, Na^+ ions were removed completely and a nano-porous structure remained despite a widened network. However, composites heat treated at 600°C following HCl or water treatment had a different surface morphology. HCl treatment and heat treatment at temperatures of 400–600°C changed the surface structure from a nano-porous network to nano-plates. The photocatalytic activity of $\text{Al}_2\text{O}_3/\text{Ti}$ composites treated with NaOH, HCl, and heat was also investigated. Samples heated at 600°C exhibited the highest Rhodamine B degradation efficiency of 35% after exposure to ultraviolet light for 12 h.

In chapter 5, I proposed and demonstrated room-temperature crack-healing in ceramic-based composites. To proof this methodology, 20~30 vol% of fine titanium metal (Ti) homogeneously-dispersed electrically-insulating alumina (Al_2O_3) ceramic composite was designed and fabricated; resulted $\text{Al}_2\text{O}_3/\text{Ti}$ composites containing 20 ~

30 vol% of metal particles exhibited excellent electrical conductivity. Electrochemical anodization was employed to heal cracks induced in $\text{Al}_2\text{O}_3/\text{Ti}$ composites by forming titanium oxides for recovering fracture strength and reliability at room temperature. Bending strength of bare, crack-induced and electrochemically-healed composites was used to evaluate crack-healing ability, and the effects of anodization current density, crack size including crack length and crack open distance and conductivity of composites on crack-healing behavior were investigated and discussed. Results indicated that bending strength of crack-induced composites, which value was approximately 61% of crack-free composite, was completely recovered after crack-healing procedure at room temperature under appropriate anodization conditions. Crack bridging by expanded titanium oxides after anodization was considered as crack-healing mechanism. Transgranular-fractured Ti particles and intergranular-fractured Ti particles had different extension mode to bridge crack. Both crack length and crack open distance affected crack-healing ability. For Al_2O_3 -based composites containing 20 vol% and 30 vol% of Ti composites with different electrical conductivity and mechanical properties, fracture toughness was found to be more effective in affecting crack-healing ability; composites having higher fracture toughness exhibit higher crack-healing ability. By anodizing $\text{Al}_2\text{O}_3/\text{Ti}$ composites, I provide a new and convenient way to heal cracks for recovering fracture strength of cracked ceramics at room temperature.

In chapter 6, I applied a simple and easy way for fabricating TiO_2 nanorod for photocatalytic application on the surface of developed $\text{Al}_2\text{O}_3/\text{Ti}$ composites. It was found that by simple heat treatment, 1D TiO_2 nanorod was formed on the surface of $\text{Al}_2\text{O}_3/20$ vol% Ti composites after heating at 600 for 5 h in air atmosphere. Formation

mechanism was interpreted. Photocatalytic ability was examined by the degradation of RhB and found that $\text{Al}_2\text{O}_3/20 \text{ vol\% Ti}$ composites heated at 500 °C and 600 °C exhibited almost the same photocatalytic activity in spite of the different surface area. It means that compared with surface morphology, the existence of rutile phase was more effective in affecting photocatalytic ability.

In conclusion, $\text{Al}_2\text{O}_3/\text{Ti}$ composites with excellent mechanical and electrical properties have been successfully fabricated using the mixture of Al_2O_3 and TiH_2 powders by hot pressing sintering method (chapter 2). This basic materials design concept has realized to develop ceramic-based composite with various multifunctions due to the synergy of ceramic and metal properties (Figure 7.1). The mechanical properties were further improved by adding Y_2O_3 which weakened the interfacial reaction between Al_2O_3 and Ti (chapter 3). New functions of $\text{Al}_2\text{O}_3/\text{Ti}$ composites, such as photocatalytic application (chapter 4 and chapter 6) and anodization-assisted crack healing (chapter 5) were firstly attempted and hence confirmed. Samples used in studying the crack-healing ability were processed by electrical discharge machining method proving a simple way for advanced ceramic processing for complex shapes. These results indicated that compositing with metal particles is an effective and promising way to develop multifunctions in ceramics. Combining both characterizations of ceramic and metal, in addition to functions developed in this work, there are some other functions should be studied. e.g., with the change of electrical conductivity, $\text{Al}_2\text{O}_3/\text{Ti}$ composites could be used as fracture and/or stress-sensing. With the incorporation of both high strength of Al_2O_3 ceramic and high fracture toughness and better biocompatibility of metal Ti, $\text{Al}_2\text{O}_3/\text{Ti}$ composites are expected to be used as various engineering components including biomaterials with novel functions such as the

room-temperature crack-healing ability.

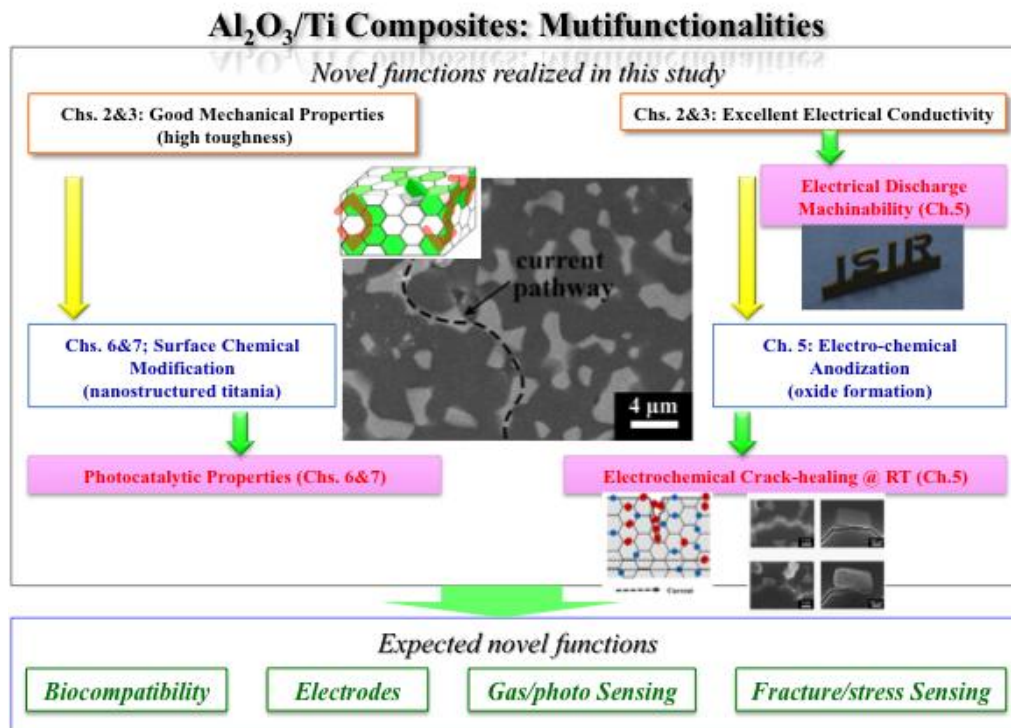


Figure 7.1 Schematic illustration of multifunctionalities realized in the present Al₂O₃/Ti composites in this study.

List of Publications

1. S. Shi, J. Gu, Y. Zhang, Preparation of supported TiO₂ ultrafiltration membranes, *Journal of Functional Materials*, **46** (2015) 10148-10152.
2. S. Shi, S. Cho, T. Goto, T. Sekino, Fine Ti-dispersed Al₂O₃ composites and their mechanical and electrical properties, *Journal of American Ceramic Society*, **101** (2018) 3181-3190.
3. S. Shi, S.H. Cho, T. Goto, T. Kusunose, T. Sekino, Combinative effects of Y₂O₃ and Ti on Al₂O₃ ceramics for optimizing mechanical and electrical properties, *Ceramic International*, (2018). DOI: <https://doi.org/10.1016/j.ceramint.2018.07.054>.
4. S. Shi, T. Goto, S.H. Cho, H. Hashimoto, S. Yin, S.W. Lee, T. Sekino, Formation of vertically grown 1D TiO₂ nanorods on the surface of Al₂O₃/Ti composites by simple heat treatment and their photocatalytic performance, *Journal of the Ceramic Society of Japan*, (2018), in press.
5. S. Shi, T. Goto, S.H. Cho, T. Sekino, Surface-morphology modification of ceramic-based composites for photocatalytic activity via simple chemical and heat treatments, *Journal of the Ceramic Society of Japan*, under review.
6. S. Shi, S.H. Cho, T. Goto, T. Sekino, Electrochemical assisted room-temperature crack healing of ceramic-based composite, *Acta Materialia*, under review.

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