Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 504631, 8 pages
http://dx.doi.org/10.1155/2013/504631

Research Article

Formation Behavior of Continuous Graded Composition in Ti-ZrO_2 Functionally Graded Materials Fabricated by Mixed-Powder Pouring Method

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Received 21 February 2013; Accepted 23 April 2013

Academic Editor: Lianjun Wang

A mixed-powder pouring method has been proposed to fabricate functionally graded materials (FGMs) with the desired compositional gradient. The experimental procedure involves preparation of mixed powders consisting of more than two types of particles with different size and/or density, which exhibit different velocities in suspension and sedimentation to form the green body under gravity conditions. The green body was sintered by a spark plasma sintering (SPS) method. The initiation of the particle settlement was precisely controlled by using crushed ice as the suspension medium. Ti-ZrO_2 FGMs were fabricated, in this study, using different sizes of ZrO_2 and Ti particles. Vickers hardness confirmed the compositional gradient in the fabricated FGMs. A numerical simulation was also carried out to analyze the particle movement inside the suspension medium during the formation process and predict compositional gradient in the FGMs.

1. Introduction

Functionally graded materials (FGMs) are the advanced composite materials characterized by spatial variations in composition and microstructure that change over the volume [1–5]. Due to this compositional gradient in materials and components, the functional properties of FGMs can be achieved [1–5]. The interface between materials is substantially eliminated; that is, the stress singularity is removed leading to minimizing thermal fatigue failure.

There are several effective techniques recently proposed to fabricate Ti-ZrO_2 FGMs [6–8]. Kinoshita et al. proposed a method developing compositional gradient using a slurry-pouring method [7, 8]. This method allowed particles to settle down under the gravitational force and the FGMs were successfully fabricated with large and continuous compositional gradients. However, it is difficult to control the initiation of particle settlement. In case of a centrifugal slurry-pouring method, the initiation of particle settlement cannot be controlled to completely nullify the effect of gravitational force.

In this study, to overcome this problem, we propose mixed-powder method, in which crushed ice is used as the particle suspension medium to control the particle sediment from the initiation to the end. In order to clearly understand behavior of particles in the suspension medium, also termed as a "buffer zone," the simulation was carried out in cases of different buffer zone lengths. We show that the desired gradient pattern from 100% Ti at one surface to 100% ZrO_2 at another can be obtained with the buffer zone of length 250 mm based on the simulation. Ti-ZrO_2 FGMs were experimentally fabricated using this new technique of mixed-powder pouring method. The simulation and experimental results are compared to verify the validity of the model and understand the effectiveness and usefulness of mixed-powder pouring method in the FGM fabrication.

2. Basic Theory and Simulation

The velocity of a spherical solid particle migrating in viscous liquid under the gravitational force can be described based on Stokes' law. In the simulation, the crushed ice was assumed to possess the characteristics of water, and the movement of solid particles is not affected by any other external forces

except for the resistance force by the suspension liquid and the gravitational force. The velocity of Ti and ZrO_2 particles migrating under the gravitational force in liquid can be expressed by the following equations:

$$v_{Ti} = \frac{(\rho_{Ti} - \rho_f)}{18\eta} d_{Ti}{}^2 g,$$
$$v_{ZrO_2} = \frac{(\rho_{ZrO_2} - \rho_f)}{18\eta} d_{ZrO_2}{}^2 g, \quad (1)$$

where ρ_{Ti}, ρ_{ZrO_2}, and ρ_f are the densities of Ti and ZrO_2 particles and the density of suspension liquid, d_{Ti} and d_{ZrO_2} are diameter of Ti and ZrO_2 particles, and η and g are viscosity of suspension liquid and acceleration due to gravity, respectively.

Figure 1 shows migration velocities of Ti and ZrO_2 particles under the gravitational force, where the densities of Ti and ZrO_2 particles are 4.5 Mg/m^3 and 6.05 Mg/m^3, respectively [8]. The velocities of the particles are calculated as a function of sizes and densities using (1).

As seen in Figure 1, it is obvious that the velocity of ZrO_2 particles is higher than that of Ti particles, when the particle size is the same, due to larger density of ZrO_2 particles. On the other hand, if the mixed powder contains the ZrO_2 particles of smaller size and Ti particles of larger size, then Ti particles can have higher velocity than that of ZrO_2 particles in some specific conditions [8, 9].

The velocity of the particles is also greatly influenced by the resistance by the suspension liquid. Using Brinkman's viscosity equation [10], the resistance force by the viscous liquid to the migrating particles is calculated in the simulation. The viscosity of suspension liquid containing solid particles with spherical shape can be written as follows:

$$\eta = \frac{\eta_0}{(1 - V/V_{max})^{5/2}}, \quad (2)$$

where η, η_0, V, and V_{max} are the apparent viscosity of the liquid containing solid particles, the viscosity of the suspension liquid without particles, the volume fraction of solid particles and the maximum containable volume fraction of solid particles, respectively. The V_{max} depends on the packing fraction of solid particles in liquid. The maximum volume fraction of spherical solid particles is between 52% for simple cubic packing and 74% for close packing.

In this study, the formation behavior of graded composition in Ti-ZrO_2 FGMs using mixed-powder pouring method under gravity is simulated. The length of the suspension medium, that is, the buffer zone, of 250 mm, is used in the simulation. The buffer zone is divided into subzones with the equal length as shown in Figure 2. The particle movement velocity along the gravitational force direction is calculated in each zone. Correspondingly, the volume fraction of the two kinds of powders at any arbitrary zone, n, is also simulated. The volume fraction of particles, V_n', at zone n is calculated using the formula following:

$$V_n' = V_n - \frac{v_n}{a} V_n + \frac{v_{n-1}}{a} V_{n-1} D_{n-1}, \quad (3)$$

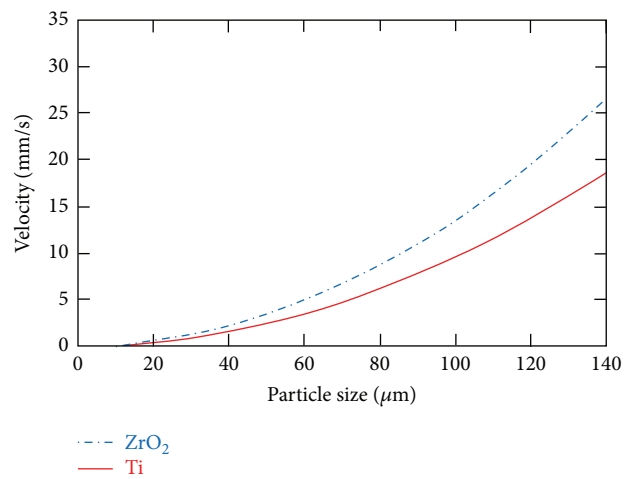

Figure 1: Variation in particle velocity for different size and density.

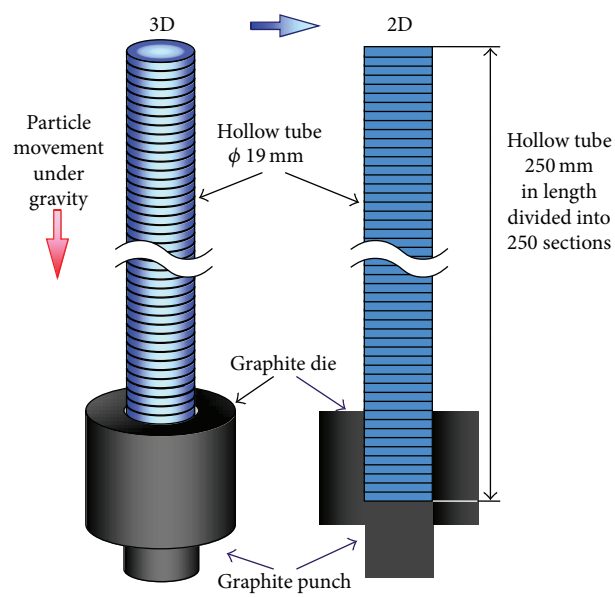

Figure 2: Classification of buffer length in zones.

where V_n, v_n, a, and D_n are the prior volume fraction of particle, movement velocity of a particle, width of each zone, and the ratio of volume fraction of zones n and $n + 1$, respectively.

Figure 3 shows the flowchart for calculation of the velocity of particles inside the suspension zone and the volume fraction of the particles in each zone. The input parameters required for calculation are as follows: the densities of the particles used in the mixed-powder pouring method, the density and viscosity of water (suspension medium) of 0.998 Mg/m^3 and 0.89 mPa·s, respectively, particle size range, and the number of zones or sections in the suspension medium. The maximum packing factor is set at 0.52 in the calculation process.

The initial volumes of two particles are calculated. In case of Ti particles of a size range of 90–150 μm, the initial volumes

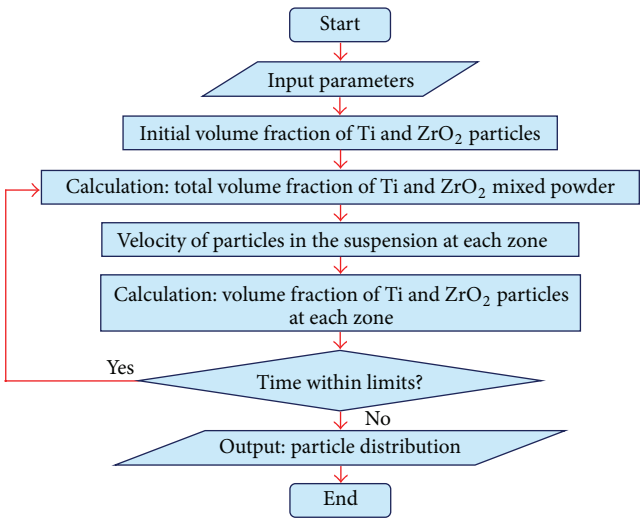

Figure 3: Calculation process of particle distribution in FGMs.

of 90 μm and 150 μm sized Ti powder are taken as 25% each, and the rest 50% of initial volume is assumed to be the average of 90 μm and 150 μm, that is, 120 μm. The velocity of particles at each zone is calculated based on Stoke's law. From the velocity of the particles, the volume fraction of particles is calculated using (3). This process is repeated in the specified limited time and the final particle distribution is obtained.

3. Materials and Methods

For the mixed-powder pouring process, homogeneously mixed powders of Ti and ZrO_2 with a volume ratio 1 : 1 were prepared. Ti particles have an angular shape, and ZrO_2 particles have a spherical shape. The details of prepared homogeneous mixture with different particle sizes are described in Table 1. In all the samples shown in Table 1, the average size of ZrO_2 particles is larger than that of Ti particles.

3.1. Preparation of SPS Specimen. A graphite die with an inner diameter of 20 mm and a height of 40 mm was used. carbon sheet was placed along the inner wall of the graphite die. A bottom punch was fitted tightly to one end of the graphite die as shown in Figure 4. A hollow tube with a length of 220 mm made of plastic was fitted and sealed to another end of the graphite die. The height of the total suspension, that is, the length of the hollow tube along with the graphite die is 250 mm. The crushed ice with a volume of 78.5×10^{-6} m^3 was prepared using the ice crusher.

The hollow tube was filled with the crushed ice as shown in Figure 4(a). Then, prepared homogeneously mixed powders were poured from the top of the crushed ice, as shown in Figure 4(b). The crushed ice was allowed to melt gradually under isothermal conditions at 40°C. Sedimentation of Ti and ZrO_2 particles proceeded along the hollow tube at the uniform temperature. The homogeneously-mixed powders poured on the top of crushed ice will move down along the hollow tube and settle down at the bottom of the graphite die. Sedimentation of the mixed powders depend on the densities and/or sizes of the particles. After settlement, a green body was obtained, as shown in Figure 4(c), which was sintered using SPS afterwards.

3.2. Fabrication of FGMs. The SPS was carried out under the pressure of 30 MPa at the sintering temperature of 1200°C. After sintering, disc-shaped Ti-ZrO_2 sample of FGMs with 20 mm in diameter and 10 mm in height was obtained. To carry out microstructural investigation, the specimen was cut into a cuboid shape with dimensions of $10 \times 8 \times 5$ mm^3 using a microcutter. Scanning electron microscope (SEM) and energ y dispersive X-ray spectroscopy (EDX) were used to observe the microstructure and evaluate the composition distribution of the fabricated FGMs, respectively. Further, Vickers hardness test was conducted on the FGM samples to study the mechanical property and confirm the gradient in the composition of the fabricated FGMs.

4. Results and Discussion

4.1. Compositional Gradients Obtained by Simulation. Figures 5(a), 5(b), and 5(c) show the calculated volume fraction distributions of Ti and ZrO_2 in samples A, B, and C, respectively. The abscissa in Figure 5 is the position in the direction of gravity normalized by the length of composite; that is, 0 and 1 represent the top and bottom surfaces of the FGMs, respectively. It can be seen from Figure 5 that Ti and ZrO_2 distributions across the normalized position have yielded large compositional gradient within the FGMs. According to the simulation, with increase in normalized position 0 to 1, the volume fraction of Ti decreases and ZrO_2 increases, which results in a largely graded microstructure. It can be also seen in the figures that the particle distribution becomes homogeneous between normalized positions 0.6 and 0.65.

4.2. Microstructure and Compositional Gradient of Ti-ZrO_2 FGMs. Photographs of Ti-ZrO_2 FGMs samples #A, #B, and #C are shown in Figures 6(a), 6(b), and 6(c), respectively. As shown in these figures, continuous compositional gradients may form within these samples.

Figures 7(a), 7(b), and 7(c) are the SEM images the FGMs samples #A, #B, and #C, respectively. The four SEM images in each column show the graded structure of Ti and ZrO_2 across the normalized position, that is, from top to bottom of the fabricated FGMs. From the four figures, it can be seen that the concentration of spherical particles increases gradually from top to bottom.

The concentrations of Ti and ZrO_2 at each region were analyzed by EDX, and the volume fraction distributions of Ti and ZrO_2 in Ti-ZrO_2 FGMs were obtained as shown in Figures 8(a), 8(b), and 8(c). It can be seen from these figures that the volume fraction of Ti is close to 100% between the normalized positions of 0 and 0.2 in all the samples. The composition of Ti decreases and that of ZrO_2 increases continuously and gradually, to become nearly homogeneous between normalized positions of 0.6 and 0.65. The volume fraction of ZrO_2 reaches close to 100% between the normalized positions 0.8 and 1, as shown in Figures 8(a) and 8(b). Therefore, it is found that the mixed-powder pouring

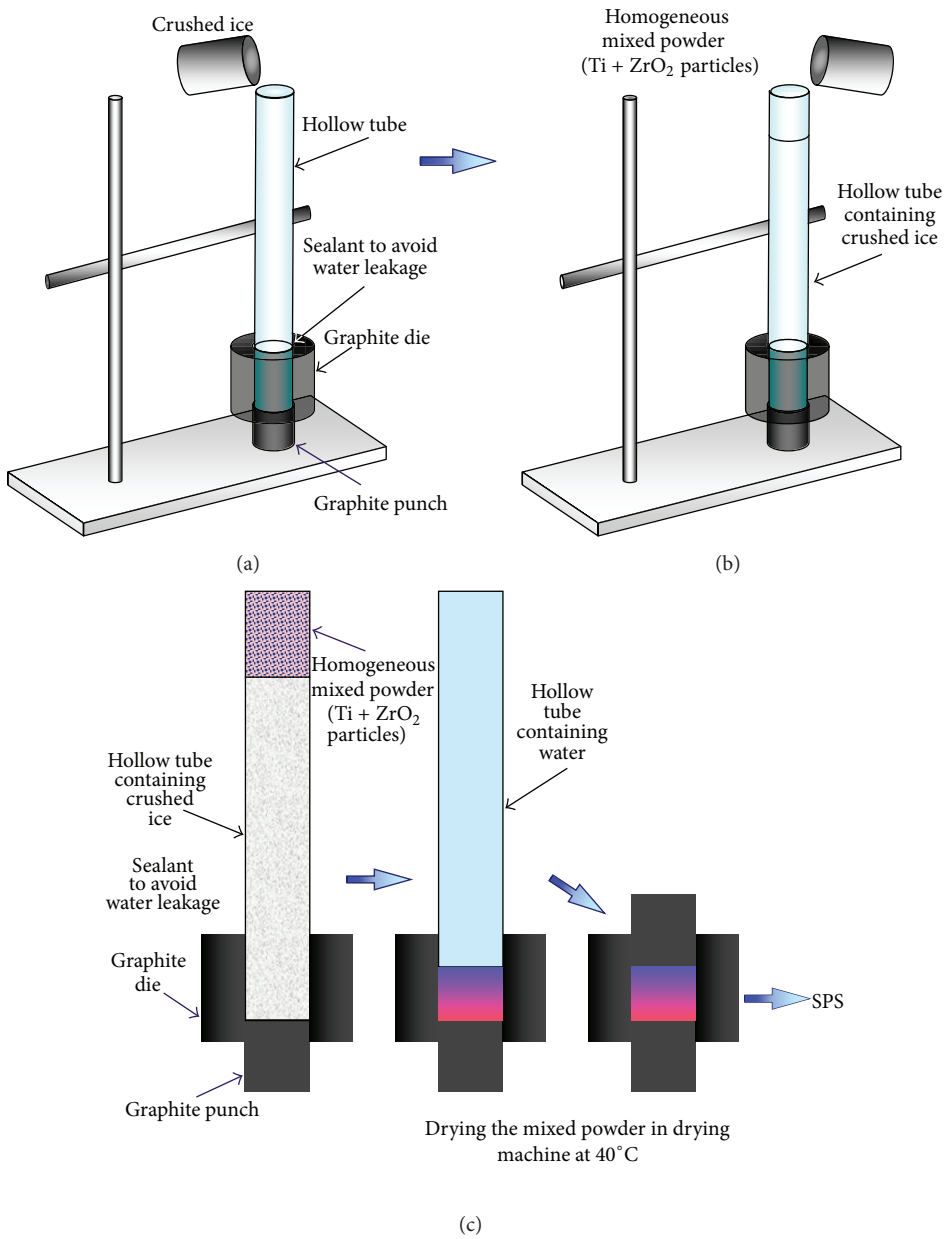

Figure 4: Experimental setup: (a) pouring crushed ice into hollow tube, (b) pouring homogeneous Ti-ZrO_2 mixed powder into hollow tube containing crushed ice, and (c) process involved in preparation of green body.

Table 1: Samples prepared in this study.

Particle	Density	Mass	Sample A	Sample B	Sample C
ZrO_2	6050 kg/m^3	9.51 g	75–106 μm	38–75 μm	106–150 μm
Ti	4500 kg/m^3	7.07 g	63–90 μm	45 μm pass	90–150 μm

method is an effective fabrication technique for FGMs with large and continuous compositional gradient. However, from the results shown in Figure 8(c), it can be observed that the volume fraction of ZrO_2 fails to reach 100% near the normalized position 1 where the large compositional gradient is not observed because of small migration speed difference between Ti and ZrO_2 particles. The larger buffer zone is necessary, for obtaining the larger compositional gradient in sample #C.

Figure 9 shows the X-ray diffraction (XRD) pattern from the ZrO_2 surface in sample A. At the ZrO_2 surface, peaks for ZrO_2 (tetragonal) and no peak for Ti can be seen, which means that 100% ZrO_2 layer formed at one side. It is considered that FGMs with 100% ZrO_2 at one side and 100%

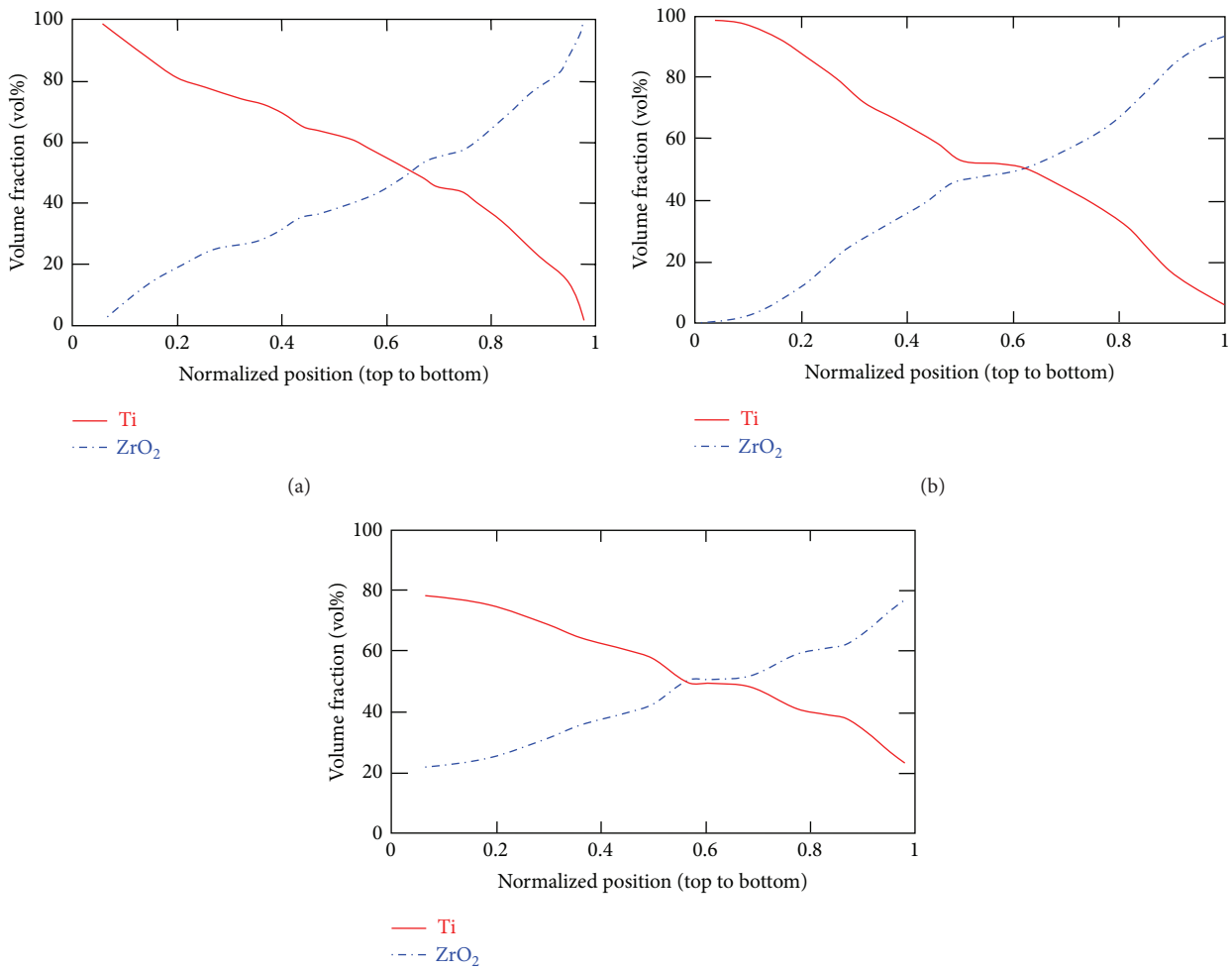

Figure 5: Calculated volume fractions of Ti and ZrO_2 in Ti-ZrO_2 FGMs, (a) sample A, (b) sample B, and (c) sample C.

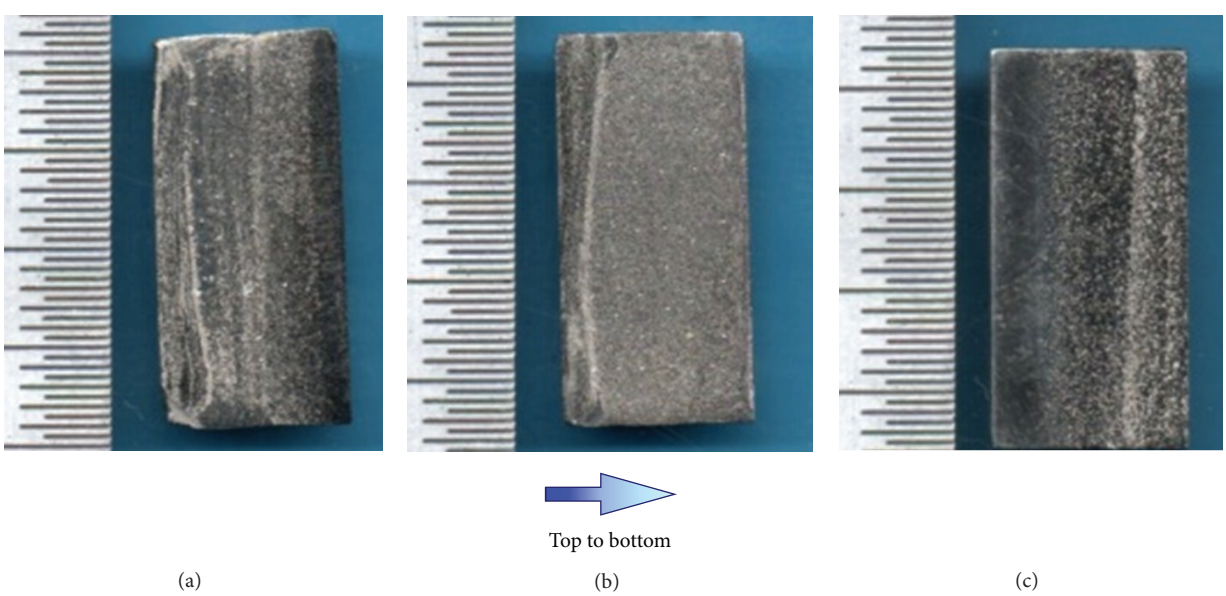

Figure 6: Photographs of Ti-ZrO_2 FGMs samples, (a) sample A (b) sample B, and (c) sample C.

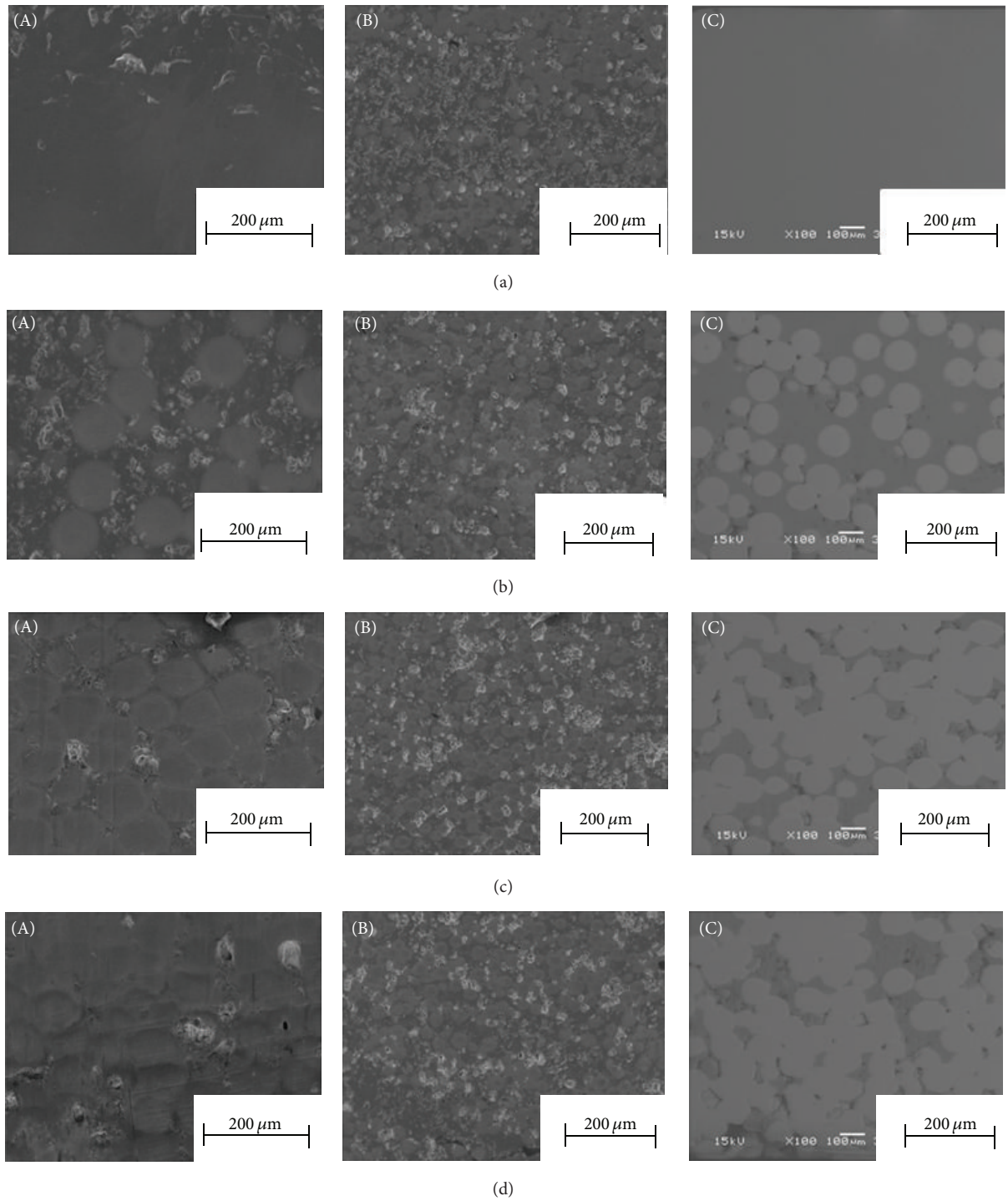

Figure 7: SEM photographs of microstructure of Ti-ZrO_2 FGMs for (A) sample A, (B) sample B, and (C) sample C. Photographs of (X-a), (X-b), (X-c) and (X-d) are taken at normalized position of 0.0 to 0.25, 0.25 to 0.5, 0.5 to 0.75, and 0.75 to 1.0, respectively.

Ti at another side can be obtained with a suitable selection of powder sizes and buffer zone length.

4.3. Hardness. The hardness values in Ti-ZrO_2 FGMs samples #A, #B, and #C are also shown in Figures 8(a), 8(b), and 8(c), respectively. The Vickers hardness (Hv) of Ti and ZrO_2 ranges between 200–300 and 1200–1300, respectively. It was concluded in [11] that SPS has the potential of enhanced densification and suppressed grain growth due to a fast heating rate and apparent low firing temperature. Therefore, the actual hardness measured in the fabricated FGMs is on the slightly higher side. The hardness inside the fabricated

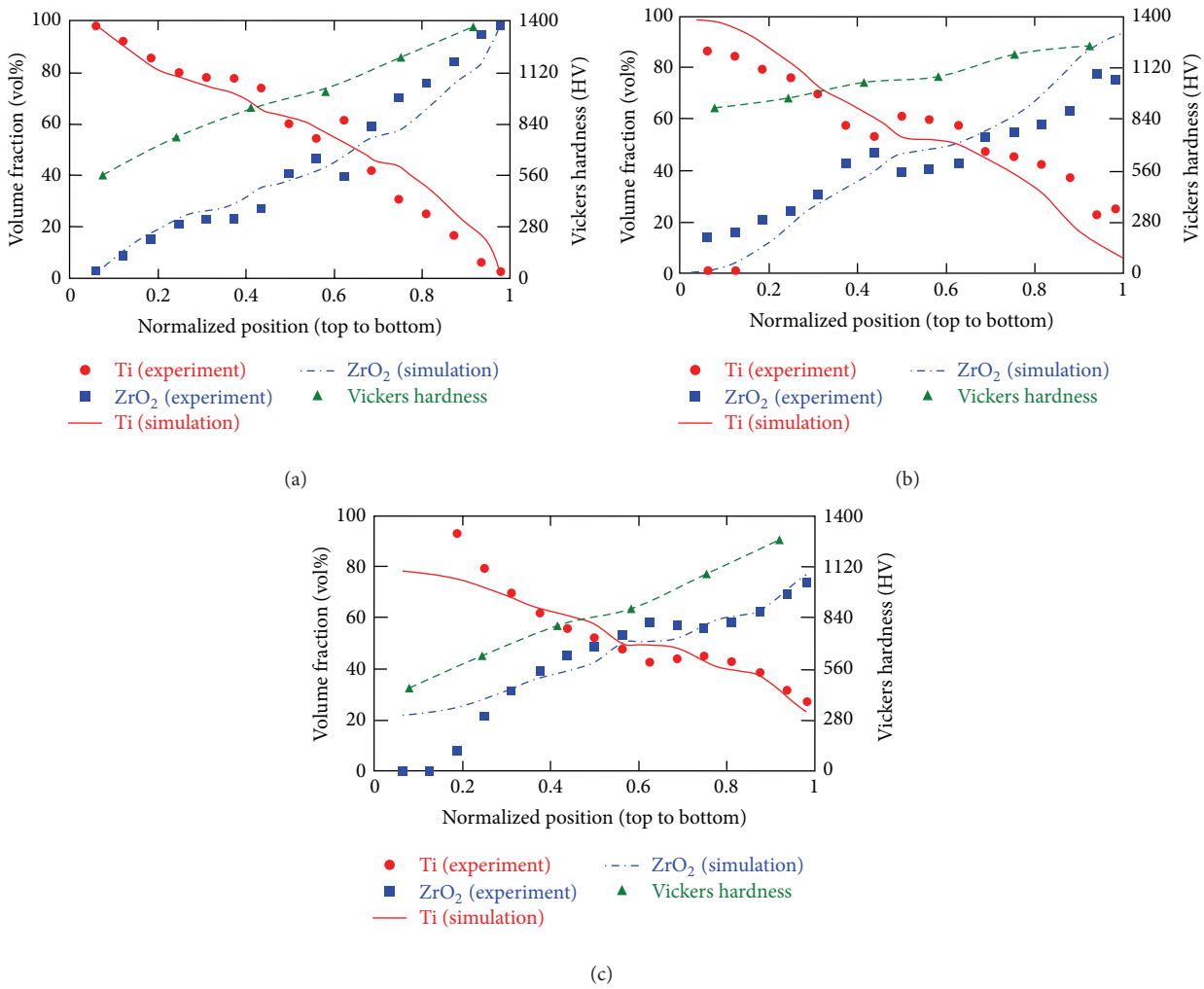

Figure 8: Comparison of experimental volume fraction results with simulation results and effects of hardness number in Ti-ZrO_2 FGMs (a) sample A (b) sample B, and (c) sample #C.

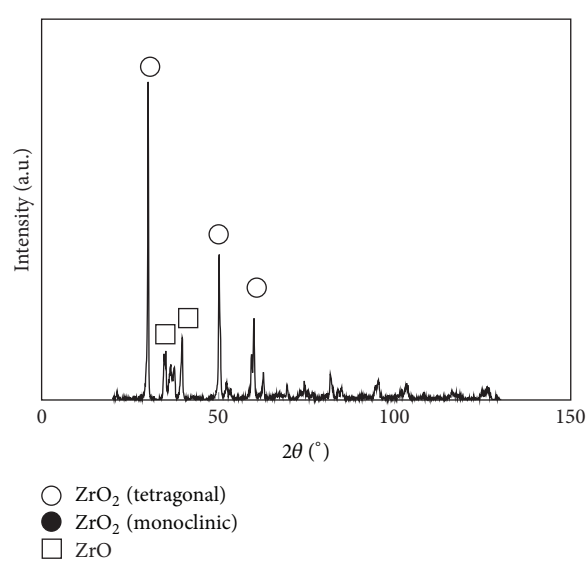

Figure 9: XRD pattern from the ZrO_2 surface in sample A.

FGMs increases with the increase in normalized position 0 to 1, thereby, confirming the increasing ZrO_2 content across the normalized position.

5. Conclusions

In this study, FGMs were fabricated using a mixed-powder pouring method followed by SPS. The desired continuous compositional gradient with 100% Ti at one side and 100% ZrO_2 at another side in the Ti-ZrO_2 FGMs was obtained. Numerical simulation considerably represented experimental results, which can be used to select suitable sizes of powders and experimental conditions to obtain predesigned compositional gradients in the FGMs.

Acknowledgments

This work is supported by Regional Innovation Cluster Program (Gifu Technical Innovation Program, Japan) of the Ministry of Education, Culture, Sports, Science and Technology of Japan. H. Sato and Y. Watanabe gratefully acknowledge the financial support from The Light Metal Educational Foundation Inc. of Japan. The authors are also grateful to Ms. Motoko Yamada for her helpful work in carrying out the experiments.

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