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Suppressing spinodal decomposition by incorporation of reduced graphene oxide into \((\text{Sn}_{0.5}\text{Ti}_{0.5})\text{O}_2\) solid solution

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Abstract

Here, it is found that the incorporation of rGO into \((\text{Sn}_{0.5}\text{Ti}_{0.5})\text{O}_2\) solid solution suppresses spinodal decomposition via two characteristic routes. First, the addition of rGO to the solid solution leads to the compositional change from \((\text{Sn}_{0.5}\text{Ti}_{0.5})\text{O}_2\) to \((\text{Sn}_{0.1}\text{Ti}_{0.9})\text{O}_2\) moving out of the miscibility gap at \(\text{SnO}_2-\text{TiO}_2\) phase diagram, which suppresses spinodal decomposition. The results indicate that addition of rGO promotes reduction and evaporation of \(\text{SnO}_2\) during heat treatment. Secondly, the incorporation of rGO is found to produce the solid solution with lower Sn and Ti valences and more oxygen vacancies, which can also suppress spinodal decomposition.

1. Introduction

Spinodal decomposition is one of the methods of phase separation leading to the unique microstructure by a nearly sinusoidal composition modulation at the nanometer level, which is a general phenomenon observed in various systems such as metallic alloys, polymers, glasses, and metal oxides [1–5]. Although the spinodal decomposition in ceramic materials is relatively rare, it has been known to happen particularly in several metal oxide/non-oxide systems: e.g., \(\text{SnO}_2-\text{TiO}_2\), \(\text{TiO}_2-\text{VO}_2\), \(\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3\), \(\text{CoFe}_2\text{O}_4-\text{CrO}_3\), and \(\text{SiC}-\text{AlN}\) [2, 5]. Among them, \(\text{SnO}_2-\text{TiO}_2\) solid solution is the representative system found from the early study of spinodal decomposition in ceramic materials, where it has a tetragonal rutile-type structure and the well-defined miscibility gap which is a phase-separation region by spinodal decomposition at its phase diagram [2–4, 6, 7]. In this tetragonal system, phase separation occurs by the modulation of the composition in the [001] direction which minimizes the elastic strain energy while maintaining coherency [7].

Both solid-solution and spinodally-decomposed phases in the \(\text{SnO}_2-\text{TiO}_2\) system have been used in various functional applications related to gas sensors, photocatalysts, and varistors [8–13]. For such practical applications, phase separation can be regarded occasionally as an adverse phenomenon to be avoided and suppressed. In this regard, diverse studies on controlling the kinetics of spinodal decomposition have been performed in this material system. For example, the anisotropic elastic long-range interactions between composition fields can determine the appearance of lamella structure and its coarsening via spinodal decomposition [14]. As the most effective and feasible method, the aliovalent cationic dopants have been used for controlling the kinetics of spinodal decomposition in bulk materials [15–18]. In particular, it was reported that divalent and trivalent cation dopants accelerate while pentavalent dopants suppress the kinetics of phase separation through modulation of cation diffusion coefficients in the diffusion-controlled \(\text{SnO}_2-\text{TiO}_2\) system [18]. Moreover, such aliovalent dopants can affect particle size and surface morphology for the change in microstructure via phase separation [19]. For thin-film materials, it is known that the rate of spinodal decomposition in \((\text{Sn}_{0.5}\text{Ti}_{0.5})\text{O}_2\) thin films, grown on single-crystalline sapphire substrates, is dependent on the type of substrate and the preferred orientation of film [2]. Similarly, different modes of spinodal decomposition and film microstructure can be achieved depending on the type of sapphire substrate in \(\text{TiO}_2-\text{VO}_2\) thin films [20]. However, no doping effect of carbon species is still known throughout the material system.

Here, we expect that carbon species can modulate the kinetics of spinodal decomposition with its strong reduction effect in the oxide system, of which the working mechanism would be different from that of the
conventional aliovalent cationic dopants. However, if carbon species is incorporated into the oxide system in the form of normal carbon black, amorphous/glassy carbon, or graphite particles, the effect would not appear because of their low reactivity. Instead, those carbon forms can be alloyed with other materials, which can decompose spinodally into carbon-rich and carbon-depleted phases [21, 22]. Therefore, we consider that activated carbon and nanostructured carbon species such as graphene, graphene oxide, and carbon nanotube (CNT) can effectively modulate the kinetics of spinodal decomposition based on their high reactivity due to high specific surface area. But notice, given that the high-temperature heat treatments in air are needed to induce the phase separation by spinodal decomposition in this work, ‘graphene oxide’ particles are particularly chosen as the appropriate dopant to prevent oxidation as a side effect.

In this work, it is shown, for the first time, that the incorporation of reduced graphene oxide (rGO) into (Sn0.5Ti0.5)O2 solid solution suppresses its spinodal decomposition via structural characterization. The mechanism is demonstrated in terms of changes in composition and oxidation state.

2. Experimental methodology

For the preparation of (Sn0.5Ti0.5)O2 solid solutions, rutile SnO2 (1 μm in diameter, 99.9% purity, High Purity Chemicals, Japan) and rutile TiO2 (2 μm in diameter, 99.9% purity, High Purity Chemicals, Japan) powders were equivalently mixed and softly ground. The X-ray diffraction (XRD) pattern for SnO2–TiO2 as-mixed starting powder is shown in figure 1(a). To obtain (Sn1–xTx)xO2 solid solutions without and with 1, 3, or 5 mol% of rGO, the equivalent amount of rGO particles was independently mixed with the 1:1 mixture of SnO2 and TiO2. In fact, it is usually hard to know the molecular weight and chemical structure of GO or rGO, obtained by chemical exfoliation of graphite. Thus, in this work, the additional amounts of rGO were determined by assuming that the composition of rGO is simply CO and thus its molecular weight is about 28 g/mol.

Subsequently, the powder (8 g) was uniaxially pressed at 3 MPa into the pellet of 12 mm diameter and then cold isostatically pressed for 10 min at 200 MPa to be made into a green pellet. Prior to the cold isostatic press, the pellet was vacuum-sealed with a latex-based package. Sintering was carried out in an air-filled box furnace at 1673 K for 24 h, followed by being rapidly quenched to room temperature. For the rapid quenching, the sintered pellet was quickly removed to room ambient conditions and air-cooled, opening the furnace door. The spinodal decomposition in solid solution was induced by the additional aging at 1373 K, the temperature within the miscibility gap at SnO2–TiO2 phase diagram [2], for 1 or 24 h, followed by being rapidly quenched to room temperature.

The rGO was prepared by adding a mixture of graphite flake (Sigma-Aldrich) and KMnO4 (Sigma-Aldrich) to a 9:1 mixture of sulfuric acid/phosphoric acid, as reported previously [23, 24]. The as-synthesized GO was dispersed in a solution of dimethylformamide (450 ml) and deionized water (50 ml). The dispersed solution was ultrasonicated (100 W, 40 kHz) for 30 min to exfoliate the GO. Finally, GO was reduced by hydrazine at 353 K for 12 h. After separating by centrifuge, the mixture was dried in an oven at 353 K for 12 h. The as-synthesized GO is stacked in layers, and the sheets are partially separated, as observed by field-emission scanning electron microscopy (FE-SEM) [23]. The dimensions of rGO are several hundred nanometers with wrinkled surfaces.

The structural characterization was performed with the help of X-ray diffraction (XRD), D8-Advance, Bruker) using Cu Kα radiation (λ = 1.5406 Å) and field-emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL). The elemental composition of samples was examined by energy-dispersive X-ray spectroscopy (EDS) coupled to the FE-SEM system. The chemical composition was further investigated by X-ray photoelectron spectroscopy (XPS, AXIS-His, Kratos) with microfocused Mg Kα radiation (1253.6 eV).

3. Results and discussion

The solid solutions and spinodally-decomposed phases of (Sn0.5Ti0.5)O2 have been successfully prepared using the conventional solid-state reaction and aging process. Figure 1(b) shows their XRD patterns, where (hk0) reflections remain sharp whereas (hkl) reflections with l ≠ 0, especially (101), (111), (211), and (301) peaks, are flanked gradually by sidebands with aging time. The split peaks with sidebands reflect the periodic lamellar structure with Sn-rich and Ti-rich phases in (Sn0.5Ti0.5)O2. Specifically, such characteristic XRD reflections indicate the invariant lattice parameter α and the formation of a composition-modulated structure in the c direction (along the [001] direction) by coherent spinodal decomposition in (Sn0.5Ti0.5)O2 as shown schematically in figure 1(c), which is consistent with prior work [2–4]. The longer aging for 24 h in (Sn0.5Ti0.5)O2 revealed binodal phase separation through a nucleation and growth mechanism, which is deduced by completely split XRD (hkl) reflections [2, 5].

Figure 2(a) shows the fractured plane of (Sn0.5Ti0.5)O2 with the spinodally-decomposed microstructure, induced by aging for 1 h at 1373 K, which is observed by FE-SEM. It reveals the porous microstructure with a low
bulk density, where no density change by aging was found. Its apparent density measured by Archimedes method was 3.45 g cm$^{-3}$, 61.4% of the theoretical density (5.62 g cm$^{-3}$) for solid solution [1]. The lamellar structures formed by spinodal decomposition are clearly observed on the surface of grains (figures 2(b) and (c)). As a result, spinodal decomposition in (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ solid solution is found to lead to the modulated lamellar structure composed of Sn-rich and Ti-rich plates perpendicular to the c-axis [001] direction, which is particularly marked by the arrow on one of the grains in figure 2(b), corresponding to the XRD and the previously reported results. The low bulk density and porous structure of (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ with the spinodally-decomposed lamellar structure in grains are considered to result from low densification of SnO$_2$ particles by the predominance of a non-densifying mass transport mechanism, such as the evaporation-condensation process and surface diffusion, at high temperatures [1]. Nevertheless, the energy dispersive X-ray spectroscopy (EDS) result for the solid-solution grain with the spinodally-decomposed lamellar structure (the region demarcated by dashed lines in figure 2(c)) indicated that the mole ratio of Sn and Ti is roughly equal to 1:1, demonstrating the formation of stoichiometric (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ (figure 2(d)).

The effect of rGO on the kinetics of phase separation in (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ solid solution has been investigated by adding rGO to (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ solid solution. The fractured-plane FE-SEM images and XRD patterns acquired for the samples prepared with the incorporation of 1, 3, or 5 mol% rGO are shown in figure 3. As a result, the incorporation of 1 mol% rGO into (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ solid solution led to similar microstructure, phase, and composition (Sn/Ti ratio) to the pristine spinodally-decomposed phase prepared without rGO, as shown in figures 3(a) and (b). However, the lamellar structures formed by spinodal decomposition on the surface of grains were more rarely observed compared to the pristine one. In addition, the XRD peak split on (101), (111), (211), and (301) spectra weakened, indicating that the addition of 1 mol% rGO slightly decreases the extent of spinodal decomposition although grain size, Sn/Ti ratio, and phase remain constant. In other words, compared to the
here, the formation of SnO$_2$ nanowires observed in the region near the crucible wall provides insights into the XRD pattern of the sample prepared without rGO peak position and pattern for both samples are roughly equal, indicating the preservation of composition weakened peak split Sn-less (spinodal decomposition by adding rGO to XPS as shown in the value of 284.60 eV to compensate for surface charge effects be formed during heat treatment by equations (1) and (2))

\[
\begin{align*}
C(s) + SnO_2(s) & \rightarrow SnO(g) + CO(g) \quad (1) \\
CO(g) + SnO_2(s) & \rightarrow SnO(g) + CO_2(g) \quad (2) \\
2SnO(g) & \rightarrow Sn(l) + SnO_2 \quad (3)
\end{align*}
\]

The EDS result of the region demarcated by dashed lines in (c). It is further proved by a strengthened –OH peak (530.90 eV), implying

Figure 2. (a) FE-SEM images of the fractured plane of (Sn$_{1-x}$Ti$_x$)$_2$O$_3$ with the spinodally-decomposed microstructure, induced by aging for 1 h at 1373 K. (b) High-magnification FE-SEM images of individual grains. In (c), composition-modulated direction along the c-axis [001] is marked by an arrow. (d) The EDS result of the region demarcated by dashed lines in (c).
a higher amount of chemisorbed hydroxyl groups which means that more surface oxygen vacancies present on the surface of the Sn-less (Sn_{0.1}Ti_{0.9})O_2 solid solution [11, 12]. Also, the binding energies of Sn 3d_{3/2} and 3d_{5/2} core-level spectra of the Sn-less (Sn_{0.1}Ti_{0.9})O_2 show the shift toward lower values compared with those of the spinodally-decomposed (Sn_{0.5}Ti_{0.5})O_2 in figure 4(c), indicating once again that Sn ions would exist with lower valence (i.e., Sn^{2+}) due to the existence of oxygen vacancies (V_O). Such a shift toward a lower value in binding energy of Sn 3d spectrum with the decreasing amount of Sn in (Sn_{x}Ti_{1-x})O_2 solid solution agrees well with the reported phenomenon [11, 27]. In particular, the shift toward lower values in binding energies of Ti 2p_{1/2} and 2p_{3/2} spectra for the Sn-less (Sn_{0.1}Ti_{0.9})O_2, compared with those of the spinodally-decomposed (Sn_{0.5}Ti_{0.5})O_2, suggests that Ti^{4+} ions would also exist with lower valence (i.e., Ti^{3+}) in figure 4(d) [28]. Thus, the incorporation of 3 or 5 mol% rGO into (Sn_{0.1}Ti_{0.9})O_2 solid solution is finally found to produce the Sn-less (Sn_{0.1}Ti_{0.9})O_2 solid solution with lower Sn and Ti valences (i.e., Sn^{2+} and Ti^{3+}) and more oxygen vacancies (V_O).

This result demonstrates that the existence of Sn^{2+} can also suppress spinodal decomposition in (Sn_{x}Ti_{1-x})O_2 solid-solution system, which corresponds with the doping effect of aliovalent cations on the kinetics of spinodal decomposition, shown in the well-documented literature. For example, Al^{3+} enhances the decomposition assuming the cation interstitial mobility to be greater than the cation vacancy mobility, while Ta^{5+} suppresses it by suppressing cation interstitial concentration within a particular concentration range in

Figure 3. (a), (c), (e) The fractured-plane FE-SEM images and (b), (d), (f) XRD patterns acquired for the (Sn_{x}Ti_{1-x})O_2 solid solutions with the incorporation of 1, 3, and 5 mol% rGO prepared by aging at 1373 K for 24 h to induce spinodal decomposition. (a), (b) for 1 mol% rGO; (c), (d) for 3 mol% rGO; and (e), (f) for 5 mol% rGO are assigned. The bottom bars are JCPDS standards.
(Sn$_{x}$Ti$_{1-x}$)O$_2$ solid-solution system [15–17]. Assuming anions to be immobile, electrostatic energy arising from the difference in cationic mobilities can retard the kinetics of spinodal decomposition in materials with high dielectric constants [17]. Therefore, the suppression of spinodal decomposition by Sn$^{2+}$ in (Sn$_{x}$Ti$_{1-x}$)O$_2$ solid-solution system might be explained by the creation of additional oxygen vacancies that reduce cation interstitial mobility although further study is needed. This study shows that the changes in composition, cationic valence, and defect state affect the kinetics of spinodal decomposition in (Sn$_{x}$Ti$_{1-x}$)O$_2$ solid-solution system. Nevertheless, further investigation should be warranted for more decisive and quantitative understanding of the spinodal decomposition mechanism in more various materials as well as in this system. Furthermore, this method for controlling microstructures through kinetics can be used as potential applications of material design for structural engineering and interface-critical devices such as gas sensors, catalysts, and varistors [8–13].

4. Conclusions

The effect of rGO incorporation on spinodal decomposition in (Sn$_{x}$Ti$_{1-x}$)O$_2$ solid solution has been investigated. Consequently, it was found that rGO suppresses spinodal decomposition via two characteristic routes. First, the addition of rGO to (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ solid solution leads to the compositional change from (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ to (Sn$_{0.1}$Ti$_{0.9}$)O$_2$ moving out of the miscibility gap at SnO$_2$-TiO$_2$ phase diagram, which suppresses spinodal decomposition. The results indicate that addition of rGO promotes reduction and evaporation of SnO$_2$ during heat treatment. Secondly, the incorporation of rGO was found to produce the Sn-less (Sn$_{0.1}$Ti$_{0.9}$)O$_2$ solid solution with lower Sn and Ti valences (i.e., Sn$^{2+}$ and Ti$^{3+}$) and more oxygen vacancies ($V_O$), which can also suppress spinodal decomposition.

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