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Reaction synthesis of several titanium oxides through electrical wire explosion in air and in water

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Abstract

An experimental method to synthesize titanium oxide (Ti–O) through electrical wire explosion was performed. In this study, one experiment was conducted in air atmosphere, and the other with the wire fully dipped in distilled water. In air atmosphere, TiO_2 in anatase and rutile phases with ultrafine spherical particles was recovered. In distilled water, conversely, nanosized Ti–O material was recovered from an unknown phase, possibly a special phase of TiO_2 or a different type of titanium oxide such as Ti_nO or Ti_nO_{2n-1}. Recovered powders were analyzed using Scanning Electron Microscopy (SEM), High-resolution Transition Electron Microscopy (HR-TEM) and X-ray Diffraction (XRD) techniques.

Keywords: A. Powders; B. Microstructure-final; D. TiO_2; Gas phase reaction; Wire explosion

1. Introduction

Synthesis of various intermetallics and alloys using intensive energetic conditions—those which can induce high temperatures and pressures by impulsive loading—has been widely investigated [1–11]. Several energy sources have been used to induce chemical reaction including powder gun [1,2], explosive [3,4], high energy laser ablation [5,6] and electrical wire explosion [7–11]. Some authors of this study previously synthesized anatase phase titanium dioxide (TiO_2) in distilled water using high-energy Nd:YAG laser ablation [12] as well as titanium nitride (TiN) and titanium aluminum nitride (TiAlN) in liquid nitrogen using an electrical wire explosion [13] or explosive [14].

The electrical wire explosion technique has been applied to spray coating [15–17], a common industrial application for surface coating of pipes. This technique, as it allows larger mass production of powder per pulse compared with other methods, has also been studied for the generation of nanosized pure metal powders [7,8] and synthesis of powders of various chemical compounds [9–11]. TiO_2 in oxygen gas [9], aluminum oxide (Al_2O_3) and TiO_2 in a surrounding oxidizer (argon–oxygen mixture) [10] as well as TiN in nitrogen gas atmosphere [11] have been investigated. This electrical wire explosion technique employing a high-energy capacitor bank (about 10 kJ) has achieved synthesis in liquid nitrogen of TiN with well-crystallized spherical fine particles in the order of 50 nm [13]. Since the released instant energy is sufficiently high to vaporize the metal wire to an excited state, induction of chemical reaction with surrounding media such as liquid or gas is possible. Application of wire explosion underwater allows generation of underwater shockwaves and pulsed bubbles; these bubbles generate highly-energetic conditions upon their collapse and thus are able to induce high pressure and high temperature conditions repetitively [12].

Similarly, TiN and AlN have been synthesized using sparks from a metal electrode in liquid nitrogen [18]. Other researchers have synthesized X-ray amorphous and crystalline anatase phase TiO_2, Ti_nO and Ti_nO_{2n-1} through arc plasma discharge in distilled water [19]. In the later case, metastable phase and non-stoichiometric oxides were synthesized due to the phase quenching effect by rapid cooling through the low intensity of

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a single pulse. Likewise, the reaction of titanium and oxygen produces titanium oxides and substances created from other specific phases such as high pressure phase [20–22]: α-PbO_2, srilankite and baddeleyite. The present investigation aims to synthesize titanium oxide (T–O) through electrical wire explosion both in air atmosphere and in distilled water, whose existing oxygen is expected to react with the excited titanium. Since underwater discharge can induce extremely rapid vaporization and since the cooling effect of water is higher than that of air, chemical reactions resulting from each condition are expected to differ.

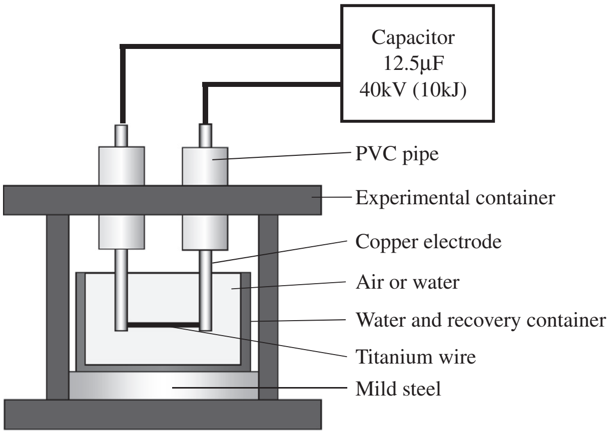

Fig. 1. Schematic illustration of the experimental set-up of wire explosion.

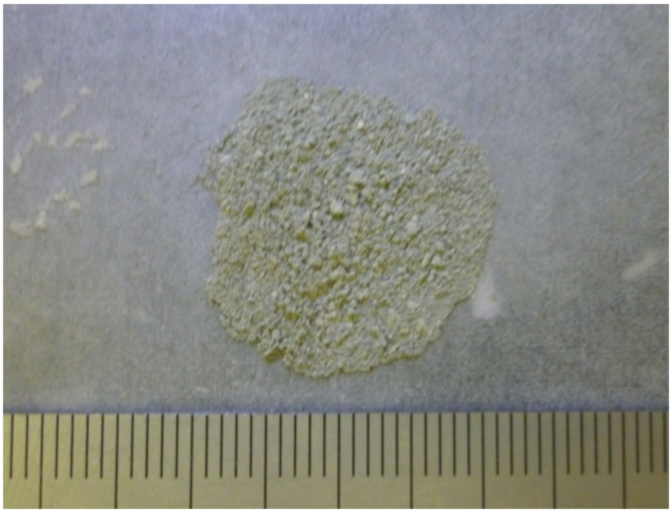

Fig. 2. Appearance of recovered powder in experiment in air atmosphere.

2. Experimental procedure

The assembly used for the wire explosion is illustrated in Fig. 1, with its details reported elsewhere [14]. Titanium wire (99.5 mass% Ti) 0.5 mm in diameter and 300 mm in length was connected to the copper electrodes. A high capacity condenser, operated at its maximum capacity of 10 kJ (12.5 μF, 40 kV, Nichicon Corporation) was employed for the experiment. For recovery of reacted powders, a powder container with a volume of 1.5×10^{-3} m^3 was used.

After fixing the wire to electrodes, a high voltage was loaded to the wire. This study conducted two experiments by changing the wire surroundings: one in air atmosphere, and the other with the wire fully submerged in distilled water. The instantaneously released energy is sufficiently high to vaporize the titanium wire to plasma state, and its chemical reaction is induced by its surroundings. The reaction of oxygen existent in the air atmosphere or distilled water with titanium leads to the formation of nanosized titanium oxide during the condensation process. The powder and particle sizes were observed using scanning electron microscopes (SEM), and the morphology of recovered particles was examined by high-resolution transmission electron microscopy (HR-TEM). The phase structure of these particles was analyzed using X-ray diffraction technique.

3. Results and discussion

Figs. 2 and 3 show the appearance and SEM images of recovered powders, respectively, from wire explosion in air atmosphere. As seen in Fig. 2, the color of the recovered powders appears white. Fig. 3(a) shows the powder size to be in the order of several 10 μm, and the enlarged SEM image shown in Fig. 3(b) indicates that each particle seems to be composed of agglomerated ultrafine spherical particles. The spherical particles are believed to have originated from liquid droplets, characteristic of the wire explosion technique [7–10]. Fig. 4 presents a bright field TEM image and selected area

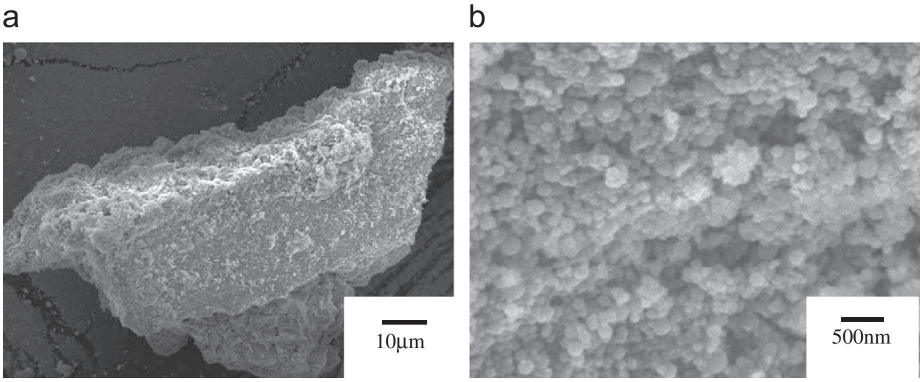

Fig. 3. SEM image of recovered powders using experiment in air atmosphere (a) and its enlarged image (b).

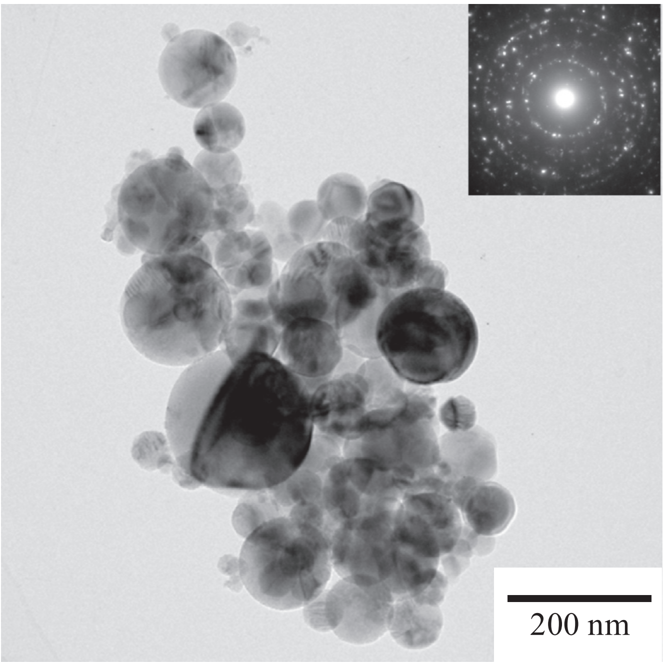

Fig. 4. TEM image of recovered powder in air atmosphere.

diffraction pattern (SADP) of powders recovered from air atmosphere. The size distribution of the particles seems to be in the range of 10–200 nm. The results of SADP reveal a set of polycrystalline diffraction rings corresponding to anatase and rutile phases, which were detected from the enlarged image in TEM. Fig. 5(a) and (b) shows an enlarged TEM image with diffraction patterns of anatase- and rutile-phase TiO_2, respectively. The structure of the anatase phase was single crystal, while the rutile phase consisted of both single- and twin-crystal structures.

Park et al. [23] reported the existence of defects in particles formed by the electrical wire explosion process in liquid and further stated that the non-equilibrium process conditions lead to the formation of imperfect particles containing defects such as twins and dislocations. Our study clearly detected only the twin structure, likely caused by the extremely high energy loading. The formation of a twin was detected by an intense loading using powder gun [24] and explosive [25].

The X-ray diffraction pattern of powders recovered from air atmosphere shown in Fig. 6 shows clear peaks of anatase- and rutile-phase TiO_2 indicating that the recovered powders were well-crystallized. The diffraction intensities of maximum peaks

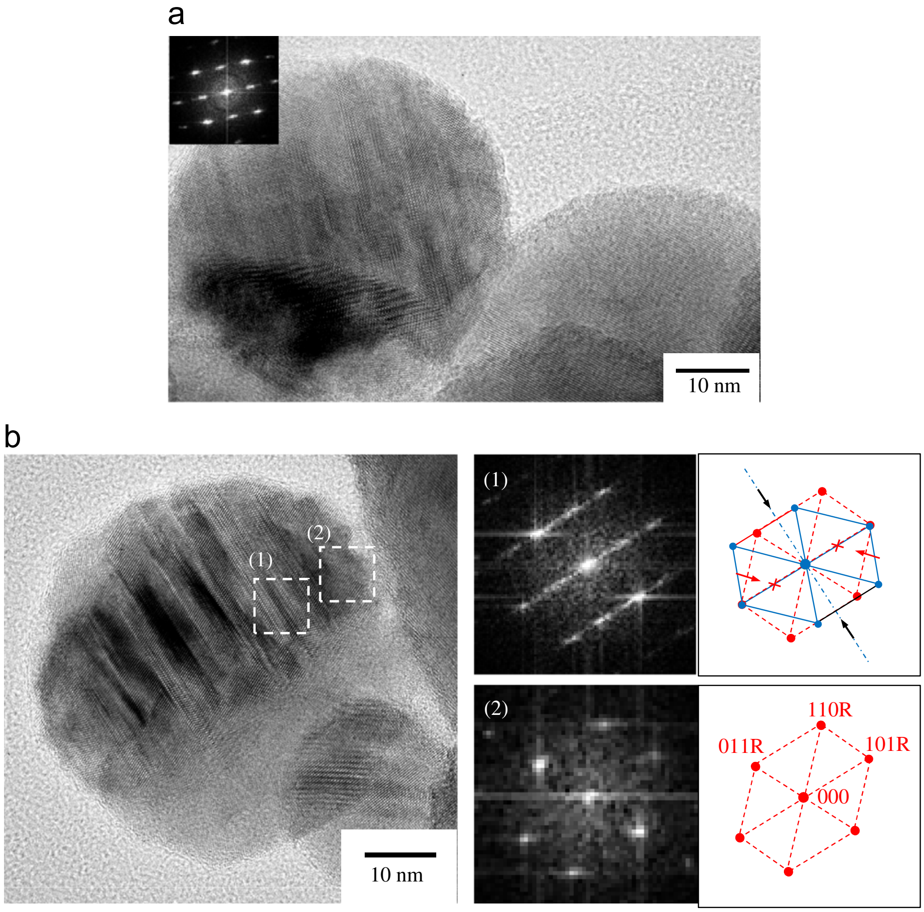

Fig. 5. Enlarged TEM image of recovered powder with FFT image of anatase-phase (a) and rutile-phase (b) in air atmosphere (Red and blue shapes mean rutile and its twin structure respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

indicate a high proportion of anatase-phase TiO_2 compared with the rutile phase in the recovered powders. The content of anatase phase in TiO_2 powder can be calculated from the following equation [26]:

$$W_A = \frac{I_A}{I_A + 1.265 I_R} \times 100 \tag{1}$$

where W_A is the content of anatase phase TiO_2 and I_A and I_R are the peak intensities of anatase and rutile, respectively, as obtained from XRD patterns. From this relationship, W_A was calculated as approximately 60%. Other research using wire explosion loading at low energy [27] or the thermal plasma oxidation method [28,29] showed recovery of anatase- and rutile-phase TiO_2 similar to our investigation. The crystallite size of the powders recovered was calculated from the peak broadening results by the Scherrer equation [30] shown below:

$$t = \frac{0.9\lambda}{(B\cos\theta)} \tag{2}$$

where t is the crystallite size, λ is the wavelength of the X-ray used, $\lambda = 1.54$ nm for Cu-K_α radiation, B is the full-width at half maximum (FWHM) intensity, and θ is the Bragg angle. Using this equation, the crystallite sizes of anatase t_A and rutile t_R were calculated as $t_A = 10.3$ nm and $t_R = 14.6$ nm, respectively. Crystallite size is discussed in more detail below.

The material recovered from the water media was, in contrast, quite different from that recovered from the air atmosphere. Figs. 7 and 8 show the appearance and SEM images of the powders recovered by wire explosion in water. In this experiment, the powder color appears to be dark blue. The size distribution of the particles as shown in Fig. 8(a) was quite broad compared with that recovered from the air atmosphere. Several particles reaching almost 5 μm in size along with a relatively large number of agglomerations of much smaller size can be seen. From Fig. 8(a) and (b), the powders recovered seem to be composed of three types of particles:

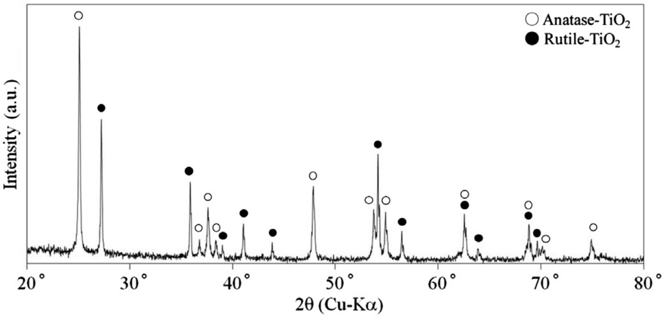

Fig. 6. X-ray diffraction pattern (Cu-K_α) for recovered powder in air atmosphere.

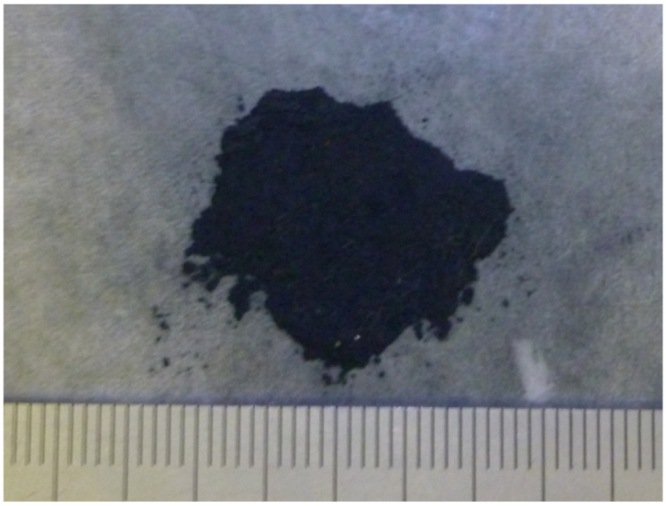

Fig. 7. Appearance of recovered powder in experiment in water. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

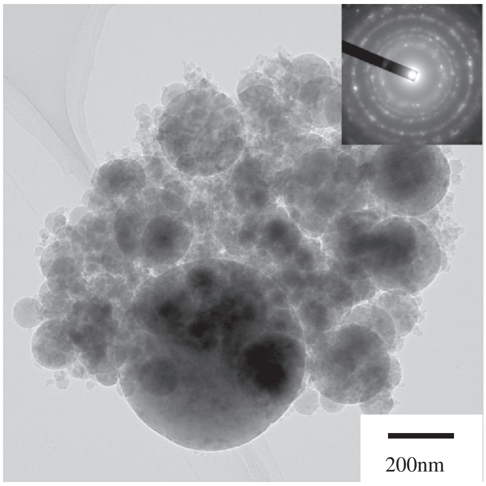

Fig. 9. TEM image of recovered powder in water.

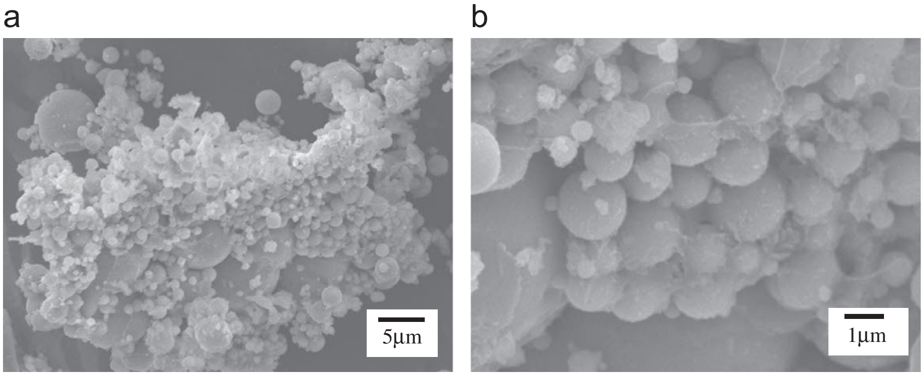

Fig. 8. SEM image of recovered powders using experiment in water (a) and its enlarged image (b).

large particles with a size of around 5 μm, small particles with a size of around 1 μm, and fine particles in the order of nanometer. Fig. 9 shows a TEM image of powders recovered from water which focuses on fine particles, whose size distribution was from 10 nm to 300 nm, with a large amount of ultrafine particles under 50 nm also confirmed. This result indicates that particle growth was low due to the rapid cooling effect of water compared with that recovered from the air atmosphere. This result was clearly observed by TEM analysis. The electron diffraction pattern shown in Fig. 9 revealed a set of polycrystalline diffraction rings corresponding to the anatase and rutile structures. In this electron diffraction pattern, an unknown structure was also confirmed. Fig. 10(a) and (b) shows the particle and an enlarged TEM image of recovered

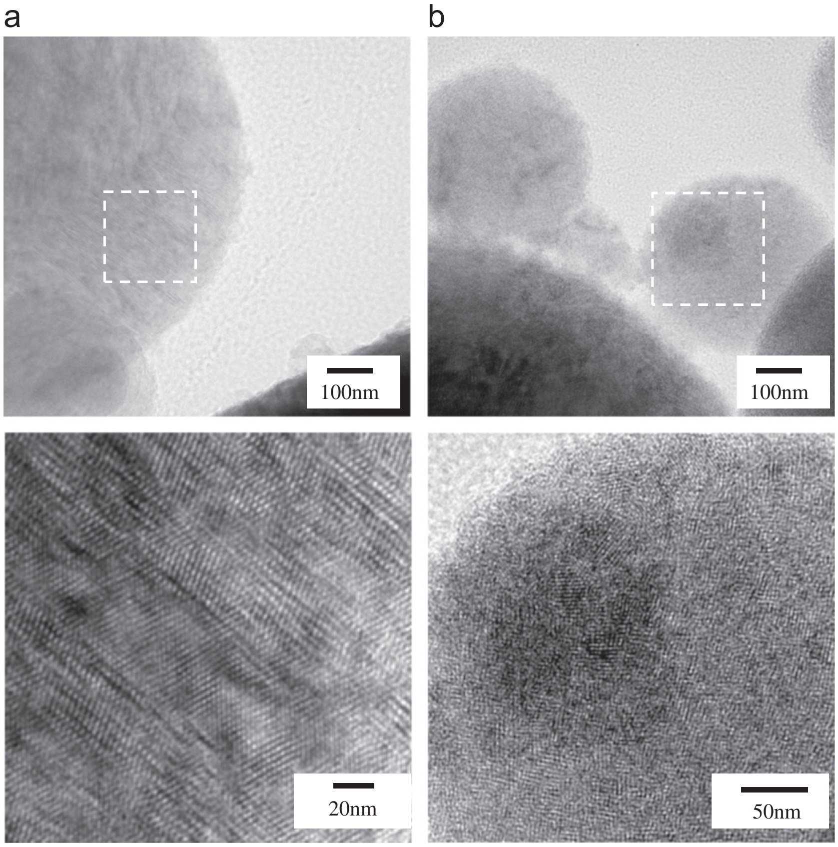

Fig. 10. TEM image of recovered powder and its enlarged image in water.

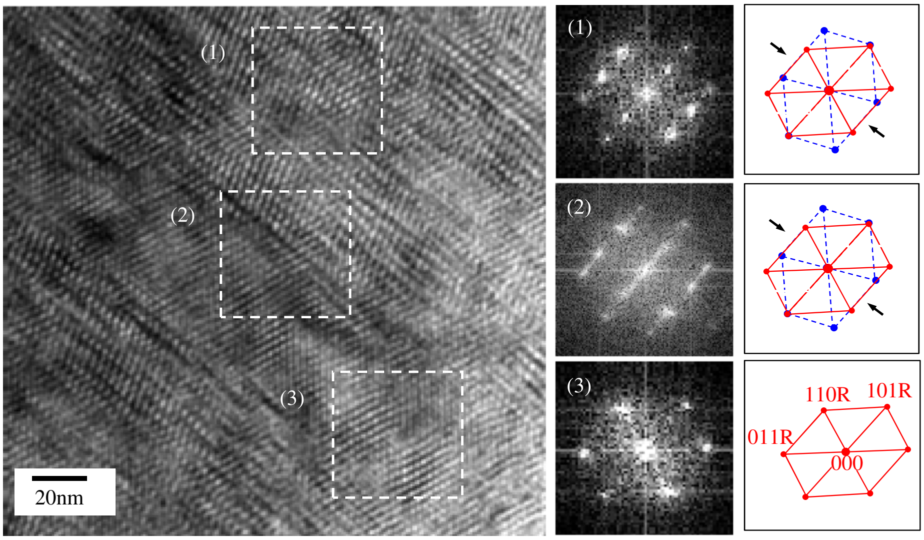

Fig. 11. Enlarged TEM image of Fig. 10 (a) and its FFT image in water (red and blue shapes mean rutile and its twin structure respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

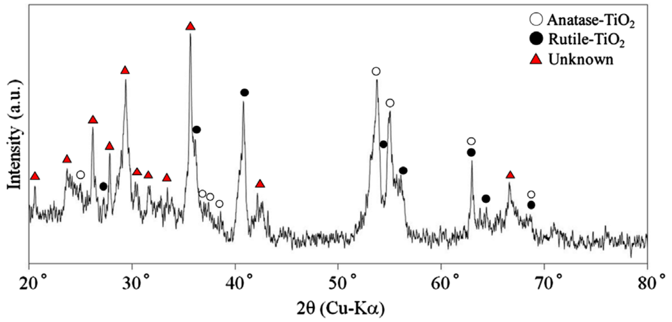

Fig. 12. X-ray diffraction pattern (Cu-K_α) for recovered powder in water.

powder, respectively, which indicates the existence of both crystallized and un-crystallized particles. This un-crystallized structure seems to be due to the rapid cooling effect of water. Fig. 11 shows an enlarged image of Fig. 10(a) and its diffraction pattern, which shows the existence of the crystallized particle rutile phase TiO_2 and its twin structure; the existence of twin-structure rutile phase TiO_2 is comparable to the results of the experiment conducted under air atmosphere.

The X-ray diffraction pattern shown in Fig. 12 shows rutile phase, a weak peak of anatase phase TiO_2, and an unknown peak of Ti–O related material. Crystallite sizes of anatase t_A and rutile t_R, which were calculated from the broadening of XRD peaks using Eq. (2), were $t_A = 5.7$ nm and $t_R = 15.4$ nm, respectively. It has been reported that anatase phase TiO_2 forms in a rapid cooling process, while rutile forms under near-equilibrium solidification condition [31,32]. Since the cooling effect of water is higher than that of air, the small-sized crystallite anatase phase TiO_2 formed in water. The unknown phase material, composed of titanium and oxygen, is likely in the phases of metastable, unstable, non-stoichiometric titanium oxides or other specific phase of TiO_2. It is well known that these kinds of titanium oxides possess photocatalytic activity under visible light [33,34]. Using impulse plasma in liquid, Mashimo et al. have clarified from XRD analysis the existence of several phases of titanium oxides Ti_nO and Ti_nO_{2n-1} [19]. Further, they have confirmed amorphous- and anatase-phase TiO_2 from XRD and TEM analysis. Their research successfully synthesized metastable oxides such as Ti_nO and Ti_nO_{2n-1}, or amorphous phase as there was minimal excitation of oxygen or ionized oxygen atoms due to the lower level of loading energy (200 V, 3 A) compared with our method (10 kJ); thus, XRD pattern results of our research clearly differ from theirs. These results indicate that the well-crystallized material, including the unknown phase Ti–O related material, was synthesized precisely because the explosion occurred underwater, an environment which can induce intensive energetic conditions, high temperatures and high pressure due to underwater shock wave or pulsed bubbles. Finally, the possibility of generation of high-pressure phase TiO_2 merits discussion here. High-pressure phase TiO_2, α-PbO_2 and srilankite are synthesized under high pressure with high loading energy using either high-energy milling [20,21] or diamond anvil cell [22]. Effects similar to those of high pressure phase were expected from this investigation, but X-ray diffraction peaks do not precisely match these materials, and TEM analysis was not confirmed due to the difficulty of analyzing unstable T–O related material. While further investigation is required to detect this unknown Ti–O related material based on analysis methods such as TEM, it is nonetheless of interest to note that the reactivity of the Ti–O clearly changes based on surrounding media and that the wire explosion technique in water has the potential to produce nanostructured crystalline unknown or metastable phases due to rapid quenching effect or high energetic condition.

4. Conclusions

Synthesis of titanium oxide using electrical wire explosion in both air atmosphere and distilled water was investigated. Energy of 10 kJ was loaded onto titanium wire of 0.5 mm diameter. It was observed that the reactivity of titanium clearly changed depending on the reaction media of Ti wire. In air atmosphere, ultrafine spherical particles of anatase- and rutile-phases of TiO_2 with well-crystallized structure were successfully recovered, while in distilled water, Ti–O material of an unknown phase, seemingly a special phase TiO_2 or oxygen-defect titanium oxide with crystallized nanostructure, was recovered.

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