Formation and size control of titanium particles by cathode discharge electrolysis of molten chloride

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Abstract

Cathode discharge electrolysis of $LiCl$–KCl–K_2TiF_6 has been conducted under 1 atm of Ar. Near spherical particles consisting of metallic or partially oxidized titanium in the core and TiO_2 in the surface layer were obtained. The Ti particles are originally formed in the melt by reduction of Ti ions, and a surface TiO_2 layer is formed when the Ti particles are exposed to air or water. The particle sizes were in the range 10–400 nm, and were strongly dependent on electrolytic conditions, such as quantity of electricity, K_2TiF_6 concentration, bath temperature and current per melt volume. The particle growth mechanism was also investigated, and it was confirmed that reduction of ions at particle surfaces is involved in particle growth.

1. Introduction

TiO_2 particles are important materials for photoelectronic devices such as dye-sensitized solar cells and photo catalysts [1, 2]. In these applications, characteristics such as energy conversion efficiencies and the decomposition rates are sensitive to the sizes of TiO_2 particles [3, 4]. On the other hand, metallic Ti particles are also expected to be useful for photoelectronic applications. For example, a porous electrode, which is formed from well-defined Ti particles and is oxidized its surface, might be useful for dye-sensitized solar cells. This electrode should have a higher conductivity than that simply formed from TiO_2 particles, because there is a porous Ti structure under the TiO_2 layer. Therefore, it is important to establish a process that accurately controls the sizes of Ti particles.

The authors previously reported cathode discharge electrolysis as a new method to form metal particles [5, 6]. In this method, the tip of the cathode was positioned above the bath surface and the anode was immersed in the melt, as shown in Figure 1. Then, by applying a high d.c. voltage between the anode and the cathode, a discharge was generated between the melt and the cathode. This discharge was dominantly maintained by electron emission from the cathode to the melt. When a metal ion source was added to the melt, metal particles were formed by reduction of metal ions. Furthermore, the particle sizes were controllable by electrolytic conditions, such as concentration of metal ion, current,

quantity of electricity and bath temperature. These phenomena were previously ascertained in the cases of Ag and Ni particles [5, 6]. From these experimental achievements, it is expected that Ti particles are also producible and the sizes of the Ti particles are accurately controllable by this method.

In this study, cathode discharge electrolysis of $LiCl$–KCl–K_2TiF_6 under 1 atm of Ar was conducted to form Ti particles and the possibility of controlling particle size was examined. Furthermore, the particle growth mechanism was also investigated.

2. Experimental procedure

The apparatus is shown in Figure 1. A mixture of LiCl and KCl (LiCl:KCl = 58.5:41.5 mol %; 99.9% and 99.5% purity, respectively, Wako Pure Chemical Co.) was dried at 450 K under vacuum for over four days and pure Ar gas bubbling was conducted for over 20 h after melting at 723 K. K_2TiF_6 (95% purity, Wako Pure Chemical Co.) was used as the titanium ion source. The cathode was a 3 mm diameter tungsten rod (99.95% purity, Nilaco Co.) which had a cone-shaped tip. The anode was a glassy carbon rod (Tokai Carbon Co.) and the surface area was smaller than 0.5 cm^2. As shown in Figure 1, the tip of the cathode was positioned above the bath surface and the anode was immersed in the melt. The crucible was made of Pyrex glass. For stabilizing a discharge, a resistor was placed between
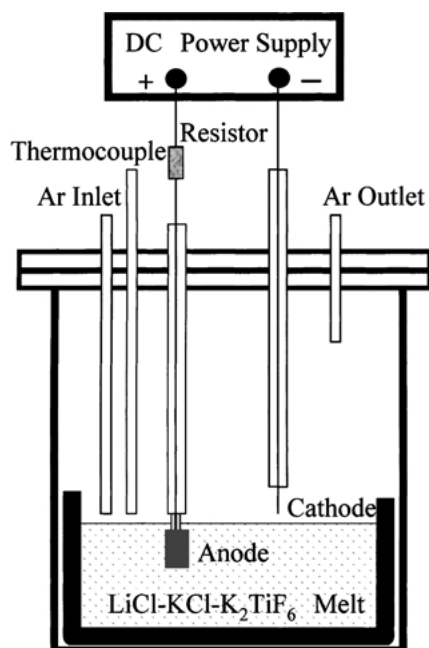
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Fig. 1. Experimental apparatus for cathode discharge electrolysis.

Fig. 2. X-ray diffraction pattern of the powder formed by cathode discharge electrolysis of LiCl–KCl–K_2TiF_6 (0.1 mol %) at 723 K. Current 180 mA; quantity of electricity 300 C and volume of the melt 0.06 dm^3. Key: (○) TiO_2 (rutile); (△) TiO_2 (anatase).

3. Results and discussion

3.1. *Analyses of the product*

After cathode discharge electrolysis, the powder product was obtained from the melt. SEM observations revealed that the product consisted of near spherical particles whose sizes were 10–400 nm. By the EPMA, only Ti was detected from all obtained particles. This suggests that the product was Ti or a titanium compound. A typical XRD pattern of the particles obtained is shown in Figure 2, which suggests that the product contained TiO_2. All the obtained particles showed similar patterns. Typical spectra of XPS for Ti $2p_{1/2}$ Ti $2p_{3/2}$ and O 1s are shown in Figure 3. Ar ion sputtering provides further information on the inner parts of the particles. The binding energy of Ti $2p_{1/2}$ and Ti $2p_{3/2}$, are 4.5–5.0 eV higher than that of metallic Ti, which suggests the

the anode and a negative terminal of a power supply (Takasago Co., GP0500-1) [5]. Then, a discharge was generated by applying a voltage of d.c. 300 V between the anode and the cathode. After cathode discharge electrolysis, the formed powder was sampled together with the melt using a syringe and was dipped into distilled water to remove the solidified salt. After drying, the particles were characterized by scanning electron microscopy (FE-SEM; Hitachi Co., S-900), electron probe microanalysis (EPMA; Horiba Co., EMAX ENERGY), X-ray diffraction (XRD; Rigaku Corp., Multi Flex) at a scanning rate of 2.0 deg/min, and X-ray photoelectron spectroscopy (XPS; Shimadzu Corp., ESCA 3200).
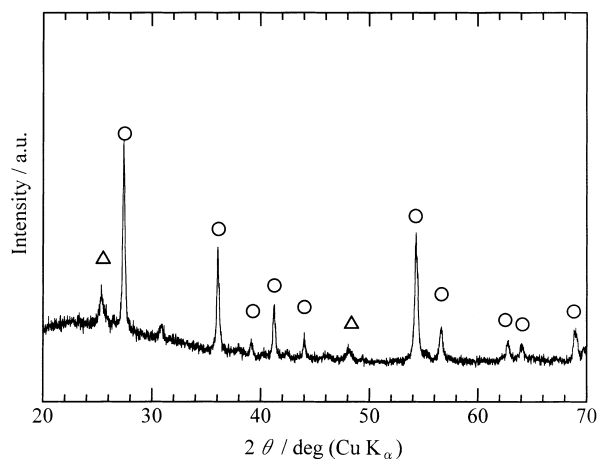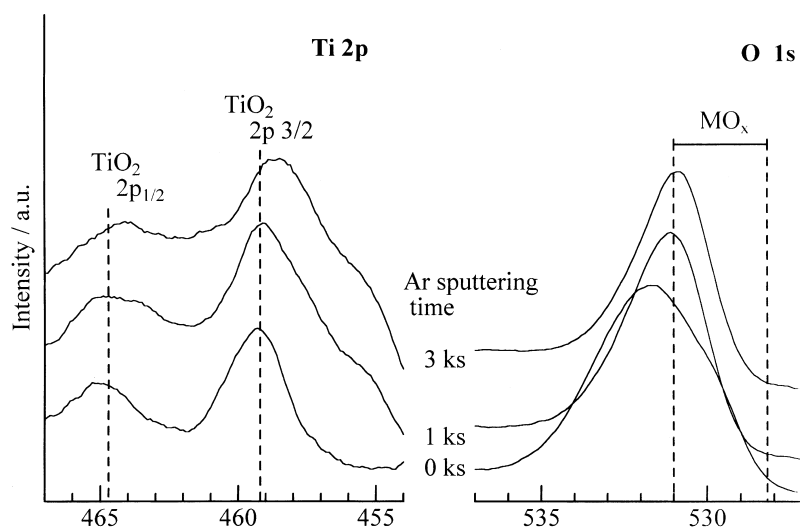

Fig. 3. X-ray photoelectron spectra of the powder formed by cathode discharge electrolysis of LiCl–KCl–K_2TiF_6 (0.1 mol %) at 723 K. Current was 180 mA, quantity of electricity was 300 C and volume of the melt was 0.12 dm^3.

existence of TiO_2 at the surface of the obtained particle [7]. However, as sputtering progresses, another shoulder appears near the binding energy of metallic Ti. This suggests that low valence Ti ions or metallic Ti exists under the surface TiO_2 layer. Oxygen mainly exists as a metal oxide and a part of O exists as a metal hydroxide on the surface.

From the results mentioned above, the obtained particle consists of TiO_2 in the surface layer and metallic or partially oxidized titanium in the core. Therefore, the original product of this method is Ti particles formed by reduction of Ti(IV);

$$Ti(IV) + 4e^- \rightarrow Ti \qquad (1)$$
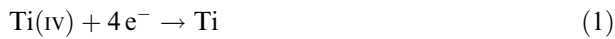
TiO_2 is formed when Ti particles were exposed to air or water after electrolysis. In general, the thickness of oxide films formed naturally at Ti surfaces is several dozens to hundreds of nanometers, which is close to the sizes of the presently obtained particles. Therefore, the small ones might be fully oxidized and metallic Ti cores might exist only in the large ones.

3.2. Size variation of the particles obtained

First, the influence of quantity of electricity on the sizes of obtained particles was examined by means of SEM. SEM images of the obtained particles, when quantity of electricity varied from 100 to 1000 C, are shown in Figure 4. To clarify the variation of the particle sizes, the particles were classified into some groups by their diameter and counted from the SEM images magnified 30 000-fold. Here, the size distributions based on volume are introduced, which shows the relative frequencies based on volume of each size classes. The relative frequencies are defined by Equation 2:

$$q_i = \frac{n_i d_i^3}{\sum n_i d_i^3} \qquad (2)$$

where q_i denotes the relative frequency of class i, n_i the number of particles classified into class i, and d_i the intermediate diameter of class i. Figure 5 shows the size distributions of the particles estimated from Figure 4 with Equation 2. These Figures show that the average particle size is larger as the quantity of electricity increases. In previous studies [5, 6], the authors proposed that collision and coalescence processes are involved in particle growth during cathode discharge electrolysis. In the cases of the LiCl–KCl–AgCl and LiCl–KCl–NiCl$_2$ systems, the size distributions of the Ag and Ni particles obtained may be explained by the numerical solutions of the Brownian collision–coalescence, assuming that a certain size of particles initiated the growth and that afterwards particles grew together only by collision and coalescence [5, 6]. The present results are also explained by this growth process, that is, a large quantity of electricity causes an increase in the quantity of Ti and the frequency of collision, which consequently leads to a progression of particle growth.

The effects of K$_2$TiF$_6$ concentration and bath temperature on the particle sizes are also explained by the
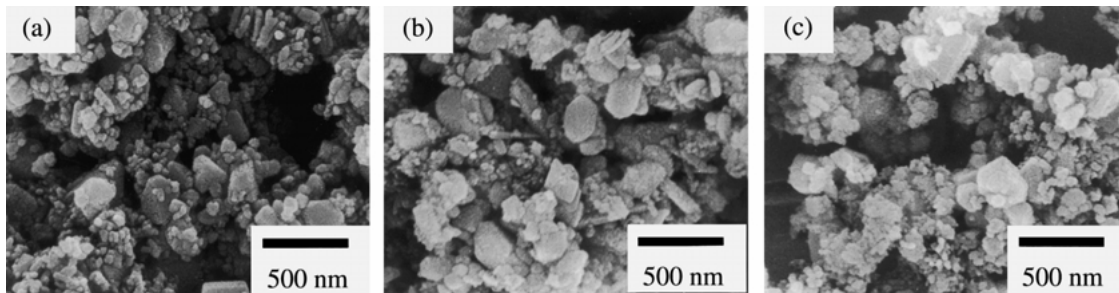
Fig. 4. SEM images of the particles formed by cathode discharge electrolysis of LiCl–KCl–K$_2$TiF$_6$ (0.1 mol %) at 723 K. Quantity of electricity: (a) 100, (b) 300 and (c) 1000 C, respectively; current 180 mA and volume of the melt 0.12 dm^3.
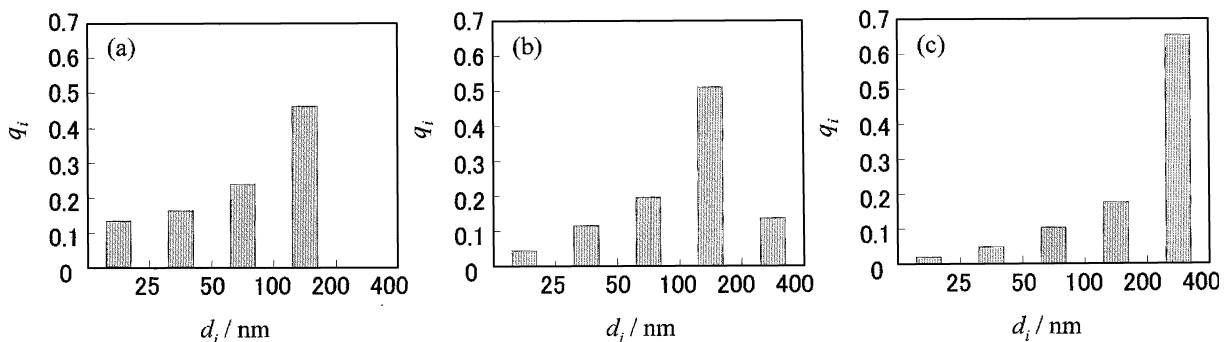
Fig. 5. Volume base size distributions of the particles formed by cathode discharge electrolysis of LiCl–KCl–K$_2$TiF$_6$ (0.1 mol %) at 723 K. Quantity of electricity (a) 100, (b) 300 and (c) 1000 C, respectively; current l80 mA and volume of the melt 0.12 dm^3.

collision and coalescence process. Under conditions of high K_2TiF_6 concentrations, the average particle size became larger. On the one hand, high K_2TiF_6 concentration causes a shorter distance between particles, which consequently leads to a high frequency of collision. This explains the present result. On the other hand, it was suggested that a high K_2TiF_6 concentration should prevent growth in view Reaction 3;

$$Ti(IV) + Ti \rightleftharpoons 2\,Ti(II) \qquad (3)$$

However, such an effect was not observed in the present results. At high bath temperatures, the particles were large in size and had low uniformity. This results from a high frequency of particle collision at high bath temperature.

However, with respect to the influences of current and volume of the melt, the collision and coalescence process is not sufficient to interpret the obtained results. When current and melt volume were varied, the uniformity of the particle size increased as current increased and volume of the melt decreased, respectively. These results reveal that current per melt volume has a significant effect on the uniformity of the particle size. Figure 6 shows the SEM images of particles obtained under various current per melt volumes. For further considerations, the size distributions were estimated and the standard deviations of the particle sizes were also calculated, as shown in Figure 7 and Table 1, respectively. The uniformity of the particle size was higher as

Table 1. Mean diameters and standard deviations of particle sizes

Current per melt volume/A dm^{-3}	Mean diameter/nm	Standard deviation/nm
1.5	29	38.3
3.0	129	26.9
4.5	86	17.3

Table 2. Influence of electrolytic conditions on the sizes of particles

Electrolytic condition	Mean diameter	Uniformity
Large quantity of electricity	large	*
High concentration of K_2TiF_6	large	*
High bath temperature	large	decrease
Large current per melt volume	*	increase

* Obvious effects are not confirmed.

current per melt volume became larger. It was noticeable that the ratio of particles smaller than 50 nm decreased significantly in large current per melt volumes. If particle growth is controlled only by the collision and coalescence process, these small particles should exist at any time during cathode discharge electrolysis.

The above results show that the sizes of particles obtained by cathode discharge electrolysis is significantly dependent on electrolytic conditions, and these effects are summarized in Table 2. Based on these results, uniform particles are producible in appropriate conditions, as shown in Figure 8.
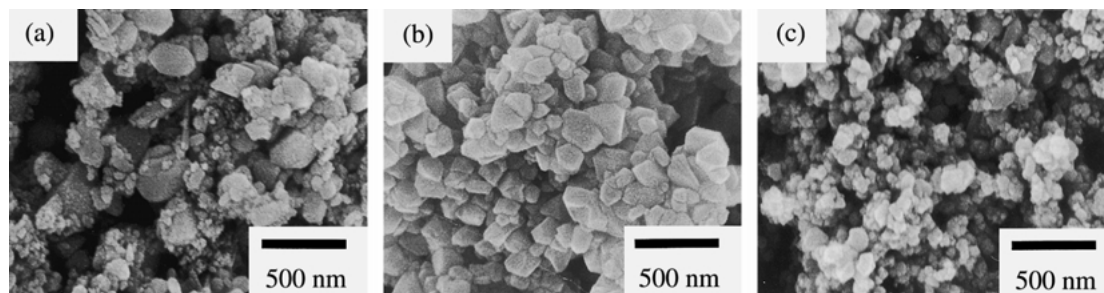

Fig. 6. SEM images of the particles formed by cathode discharge electrolysis of LiCl–KCl–K_2TiF_6 (0.1 mol %) at 723 K. Current per melt volume: (a) 1.5, (b) 3.0 and (c) 4.5 A dm^{-3} respectively; quantity of electricity was 300 C.
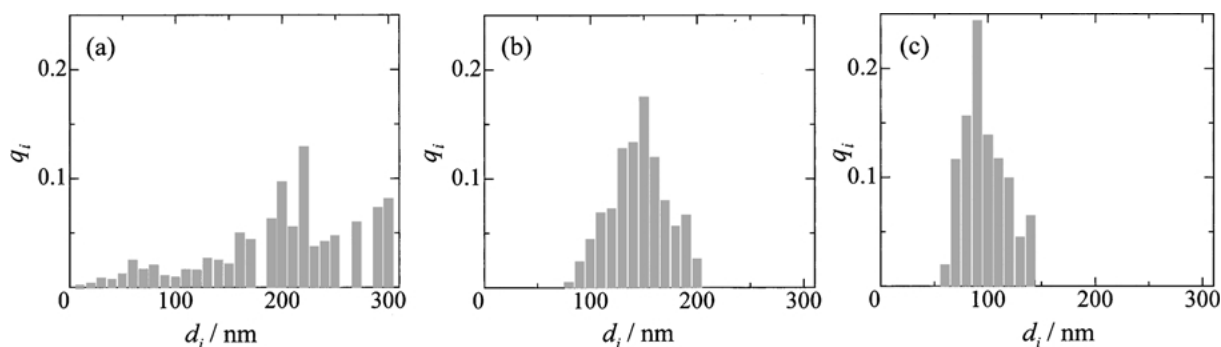

Fig. 7. Volume base size distributions of the particles formed by cathode discharge electrolysis of LiCl–KCl–K_2TiF_6 (0.1 mol %) at 723 K. Current per melt volume: (a) 1.5, (b) 3.0 and (c) 4.5 A dm^{-3} respectively; and quantity of electricity was 300 C.
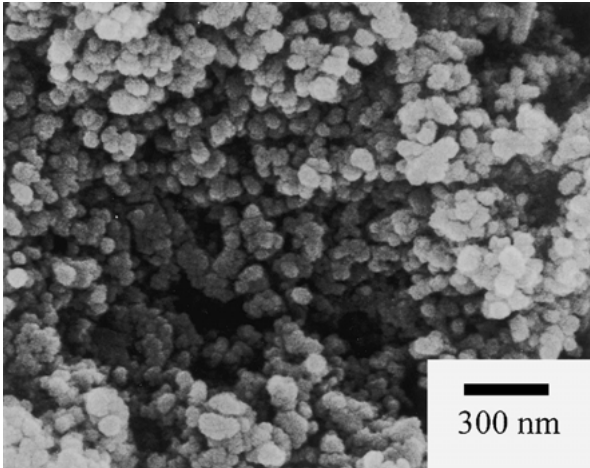
Fig. 8. SEM image of the particles formed by cathode discharge electrolysis of LiCl–KCl–K$_2$TiF$_6$ (0.0l mol %) at 723 K. Current 500 mA, quantity of electricity 100 C and volume of the melt 0.06 dm^3.

3.3. *Growth mechanism of particle*

As mentioned in Section 3.2, the particle size variations with quantity of electricity, K$_2$TiF$_6$ concentration and bath temperature can be explained by the collision and coalescence process. However, this process cannot be used to interpret the influence of current per melt volume on the particle size distributions. Therefore, another process should be involved in the particle growth. To reveal the mechanism of the particle growth, a further process is now introduced. For convenience of discussion, the bath was divided into two regions as shown in Figure 9. Region A is the bulk melt. Region B is the area immediately under the plasma, which is spontaneously generated by the discharge.

In region A, the influence of the plasma on particle growth is negligibly small and, during electrolysis, particle growth progresses through collision and coalescence. In addition, this particle growth also progresses
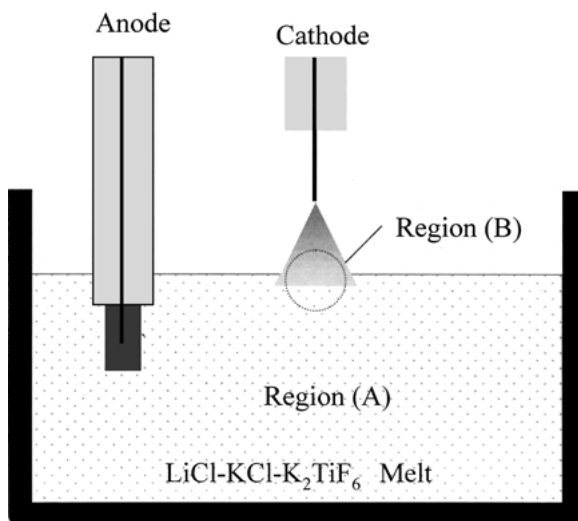

Fig. 9. Conceptual drawing of reaction field. Region A is the bulk melt, and region B is the point immediately under the plasma.
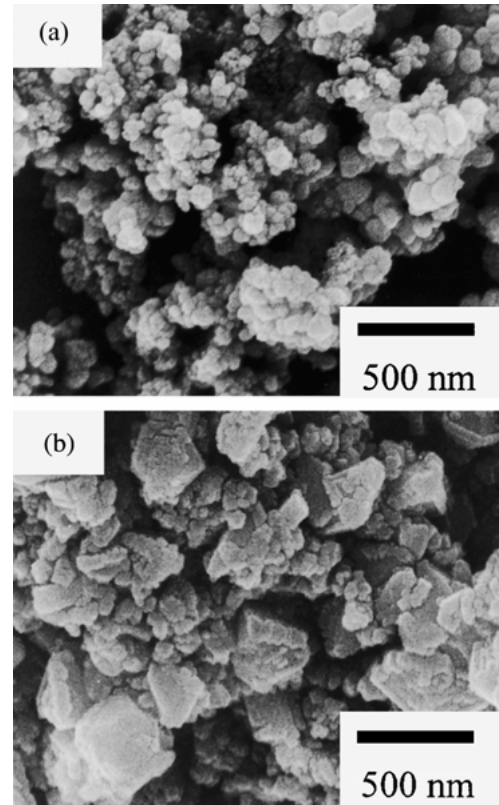

Fig. 10. SEM images of the particles formed by cathode discharge electrolysis of LiCl–KCl–K$_2$TiF$_6$ (0.1 mol %) at 723 K. Current 500 mA, quantity of electricity 1000 C, volume of the melt 0.12 dm^3 holding time: (a) 0 s and (b) 4 ks.

even after electrolysis as shown in Figure 10, a comparison of the particles obtained immediately after electrolysis and 4 ks later.

The features of region B are considered as follows: (a) temperature is very high because of thermal transfer from the plasma; (b) reduction of metal ions occurs. Since stationary emission of white smoke was observed during cathode discharge electrolysis, the temperature is suggested to be over the boiling point of LiCl (1600 $\sim$ 1620 K). In this region, it is considered that Ti, Li or K atoms are initially formed by reduction of Ti, Li and K ions. These Li or K atoms should donate their electrons to Ti ions and form Ti atoms. Then, Ti atoms should form Ti particles by coalescence. After considerable quantities of Ti particles have been formed, the collision–coalescence process also progresses particle growth in region B, as well as in region A. In addition to this process, reduction of Ti ions at the formed Ti particle surfaces may occur.

To confirm the latter process, reduction of ions at particle surfaces, cathode discharge electrolysis of LiCl–KCl–NiCl$_2$ containing Ti particles was conducted. If this particle growth in region B progresses, reduction of Ni ions should occur at the Ti particle surfaces, which leads to the formation of Ni or Ni–Ti alloys on the Ti particles, as shown in Figure 11(a). If not, Ni particles should be formed independently of Ti particles as shown in Figure 11(b). On the other hand, Ti particles coated
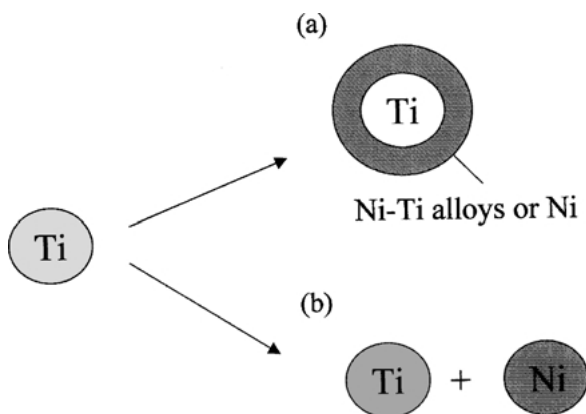
Fig. 11. Conceptual drawing of particles which will be obtained by cathode discharge electrolysis of LiCl–KCl–NiCl$_2$ containing metallic titanium particles. (a) Metallic titanium particle coated by Ni or Ni–Ti and (b) metallic nickel particle and metallic titanium particle, existing independently.

with Ni or Ni–Ti alloys might be also formed by the collision and coalescence between Ni and Ti particles, therefore, this possibility was also examined, as in the following Section.

3.4. *Confirmation of the new growth process*

First, Ti particles were formed by cathode discharge electrolysis of LiCl–KCl–K$_2$TiF$_6$. After a quantity of electricity, which is sufficient for reduction of all the Ti ions, was passed, NiCl$_2$ was added to the melt. After Ar gas bubbling, cathode discharge electrolysis was again
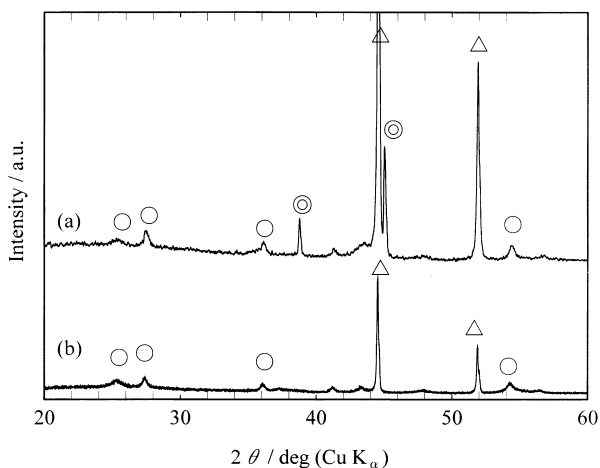

Fig. 12. X-ray diffraction pattern of the formed powders. (a) First, metallic titanium particles were formed by cathode discharge electrolysis of 800 C in LiCl–KCl–K$_2$TiF$_6$ (0.1 mol %) at 723 K. Secondly, 0.1 mol % of NiCl$_2$ was added and cathode discharge electrolysis of 400 C was conducted at 723 K. Current 180 mA and volume of the melt 0.06 dm^3. (b) First, metallic titanium particles were formed by cathode discharge electrolysis of 800 C in LiCl–KCl–K$_2$TiF$_6$ (0.1 mol %) at 723 K. Current 180 mA and volume of the melt 0.06 dm^3. Secondly, previously formed Ni particles were added and were held for 2 ks. Key: (○) TiO$_2$; (△) Ni; (◎) NiTi$_2$.

performed. As shown in Figure 12(a), the XRD result suggests the existence of NiTi$_2$ in addition to Ni and TiO$_2$. On the other hand, when Ni and Ti particles coexisted in a LiCl–KCl melt and they were held for a certain time, the peaks of NiTi$_2$ were not observed by XRD, as shown in Figure 12(b).

These results suggest that NiTi$_2$ was formed by reduction of Ni ions at the Ti particle surfaces. Consequently, it was confirmed that reduction of ions at particle surfaces is also involved in the particle growth mechanism during cathode discharge electrolysis.

4. Conclusion

Particles of sizes 10–400 nm were obtained by cathode discharge electrolysis of a LiCl–KCl–K$_2$TiF$_6$ melt. Results from EPMA, XRD and XPS suggested that the particles obtained consisted of metallic or partially oxidized titanium in the core and TiO$_2$ in the surface layer. The Ti particles were originally formed in the melt by reduction of Ti ions, and the TiO$_2$ layer was formed by exposure of the Ti particles to air or water after electrolysis. The particle sizes were strongly dependent on electrolytic conditions, such as quantity of electricity, K$_2$TiF$_6$ concentration, bath temperature and current per melt volume.

When cathode discharge electrolysis was conducted with a LiCl–KCl–NiCl$_2$ melt containing Ti particles, NiTi$_2$ was formed. Since this NiTi$_2$ is suggested to be formed by reduction of nickel ions at the Ti particle surfaces, it was confirmed that reduction of metal ions at particle surfaces is involved in the particle growth during cathode discharge electrolysis.

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