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Formation of needle-like titanium oxynitride particles through nitridation of hydrated titanates

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Abstract

The process of nitridation of hydrated titanate wires was examined by thermal gravimetric (TG) analysis in an NH_3/Ar (50/50 vol.%) gas mixture, X-ray diffraction (XRD) measurement, field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM) observations and X-ray photoelectron spectroscopic (XPS) analysis. The nitridation of the hydrated titanate nanowires was accompanied by a two-stage weight loss. In the first stage, occurring in the temperature range of 50–400 °C, the hydrated titanate wires changed to anatase-type TiO_2 nanoparticles with the releasing of H_2O molecules. In the second stage, occurring in the temperature range of 700–1000 °C, the TiO_2 nanoparticles were converted to rock-salt-type titanium oxynitride (TiN_xO_y) nanoparticles. Subsequently, the TiN_xO_y nanoparticles were sintered each other at around 1000 °C. Under a gas flow of 100% NH_3, the hydrated titanate wires were completely changed to TiN_xO_y particles at a temperature greater than 950 °C, which was maintained for 2 h. It is possible to fabricate needle-like TiN_xO_y particles by selecting thick hydrated titanate wires as the starting materials.

Keywords: Nitridation; Needle-like particles; Titanium oxynitride; Hydrated titanate

1. Introduction

Titanium nitride (TiN) is used as a coating material because of its low friction coefficient, high hardness, abrasion resistance, golden color, high melting point, low electrical resistivity. Additionally, titanium oxynitride (TiN_xO_y), which can be synthesized as a solid solution between TiN and titanium oxide (TiO), depending on the synthesis conditions, has a potential as high as that of TiN [1–4]. Recently, nanocrystalline particles of TiN and TiN_xO_y, which can be used as fillers or additives in order to improve the mechanical or electrical properties of composites, have been also attracted considerable attention [5–9]. As a result, a number of synthesis methods of those powders have been reported. These methods can be classified into three types. The most commonly employed method involves a heating of powdered titanium compounds in an NH_3 gas at elevated temperatures [10–17]. It has been reported that the extent of nitridation condition strongly depended on the composition, particle size, and crystalline phase of the titanium compound powders used. The second method makes use of a carbothermal reduction method; titanium compound powders are heated with carbonaceous powders in a N_2 gas [18]. With the availability of various compounds containing nitrogen atoms such as cyanamide, urea [19] and carbon nitride [20,21], it is not always necessary to make use of the nitrogen atoms in the atmosphere, present in the form of, i.e., N_2 for the reaction The third method involves a chemical reaction at low temperatures between a titanium compound and a nitrogen-containing compound such as sodium azide [22,23], ammonium chloride [24,25], ammonia [26] and liquid nitrogen [27].

For improving the properties of the composites, it is important to control the morphology of TiN or TiN_xO_y powders. There are the fibrous powders with high aspect ratio can be used as efficient and effective fillers for improving the mechanical or electrical properties of composites. However, there are only a few report on the method for controlling morphology of either TiN or TiN_xO_y powders. Zukalova et al. reported that

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nanocrystalline fibrous TiO_2, prepared by electrostatic spinning from an alkoxide solution, was converted to TiN or TiN_xO_y powders while maintaining its fibrous form [10], and Joshi et al. described that the preparation of titanium nitride nanorods having different aspect ratios by solid state metathesis between titanium chloride and sodium azide [22].

In the present study, TiN_xO_y powders were synthesized by heating of titanate nanowires under NH_3 gas flow, and the effect of the synthesis conditions on the structure and composition of TiN_xO_y powders was investigated. Because the hydrated titanate used was fabricated by hydrothermal treatment of titania particles in a highly concentrated KOH aqueous solution and its dimensions can be controlled by selecting a suitable form of starting titania particles as staring material, reported previously [28], the conditions for the fabrication of needle-like TiN_xO_y powders by using the titanate nanowires are also discussed.

2. Experimental procedure

Two types of hydrated titanate wires with different dimensions were used as the staring materials. The hydrated titanate nanowires were fabricated as follows; we used either titania nano powders with a mixed phase of anatase and rutile-type structures (P 25 Degussa Co., Ltd.), or submicron titania powders with a rutile-type structure (CR-EL Ishihara Sangyo Co., Ltd.) were used as the starting materials. Titania powders of 2.5 g was mixed with 12.5 g of KOH and 11.2 g of H_2O in a 100 cm^3 polytetrafluoroethylene (PTFE) vessel. The vessel was capped with PTFE lid and sealed in a stainless steel autoclave. The autoclave was then heated at 150 °C for 20 h in the case of P 25 and 150 h in the case of CR-EL, respectively. Titanate nanowires were isolated by filtering and rinsing the reactant powders with a 0.1 mol dm^{-3} HCl solution and purified water so as to remove the residual KOH and then were dried at 110 °C. Titanate nanowires made from P 25 and CR-EL are named as Titanate-P and Titanate-C, respectively. Titanate-P consists of fibrils that are with a diameter of approximately 3 nm and a length of several micrometers whereas Titanate-C consists of fibrils that are a diameter of around 50 nm and a length of several to 10 μm.

The gravimetric change during the nitridation process of Titanate-P was investigated in a mixed gas of NH_3 and Ar (50/50 vol.%) and having the flow rate of 50 cm^3 min^{-1}. The heating rate was 5 K min^{-1}. We did not use 100% NH_3 gas to avoid corrosion of TG apparatus.

The nitridation of titanate nanowires was carried out by using a tube electric furnace in an NH_3 gas of 100%. Titanate nanowires were heated up to 600 °C and maintained at that temperature for 1 h and then successively heated up to 800, 850, 900, 950 or 1000 °C and maintained at those temperatures for 0, 1 or 2 h. The flow rate was 50 cm^3 min^{-1}, and the heating rate was 10 K min^{-1}.

The crystalline phase of the sample was characterized by XRD powder pattern that was recorded by using Ni-filtered Cu Kα radiation. The morphology of the sample was observed by employing FE-SEM and TEM. The binding energy of N 1s, O 1s, and Ti 2p electrons and the atomic ratio of N/Ti in the sample were investigated by XPS using monochromated Al Kα radiation.

3. Results and discussion

The TG curve of Titanate-P in a mixed gas of NH_3 and Ar (50/50 vol.%) is shown in Fig. 1. The weight loss in the sample take places in two stages. The weight loss in the first stage, which occurs in the temperature range of 50–400 °C, is approximately 15%, and the weight loss in the second stage, which occurs in the temperature range of 700–1100 °C, is approximately 17%. Because the weight loss in the first stage occurs as a result of a release of H_2O molecules from the hydrated titanate, the composition of Titanate-P can be represented as TiO_2–0.78 H_2O. The weight loss of 17% in the second stage can be attributed to the formation of TiN from TiO_2, but the value of the weigh loss is smaller than the theoretical weight loss of 19%. The theoretical weight loss, which was determined as the difference in chemical formula weight of TiO_2 and that of TiN, which was expressed as a percent of the chemical formula weight of TiO_2–0.78 H_2O, implying the incomplete nitridation or formation of TiN_xO_y. This result indicate that nitridation of the titanate powders starts at temperature greater than 700 °C and that proportion of oxygen atoms in the structure of the sample is significant.

The XRD patterns of Titanate-P nitrided at 800, 850, 900, and 950 °C for 1 h and at 950 °C for 2 h are shown in Fig. 2. Titanate-P treated at 800 °C for 1 h exhibits an anatase-type structure. A partial phase transformation from anatase- to rutile-type structure is observed in the case of Titanate-P treated at 900 °C for 1 h. 200 diffraction lines at a 2θ value of approximately 43°, of which indicates the presence of the rock-salt-type TiN structure, is observed in the Titanate-P treated at 950 °C for 1 h. The complete transformation to the rock-salt-type TiN structure was accomplished by heating the Titanate-P at 950 °C for 2 h. The rock-salt-type structure formed in the

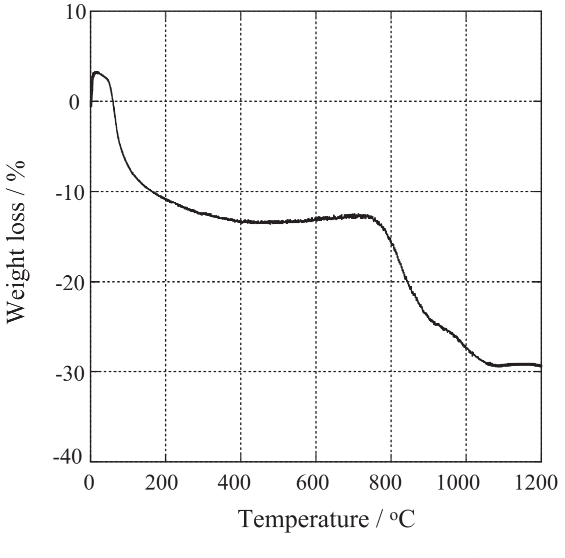

Fig. 1. TG curve of Titanate-P under a mixed gas of NH_3/Ar flow. The volume ratio of NH_3/Ar is 50/50.

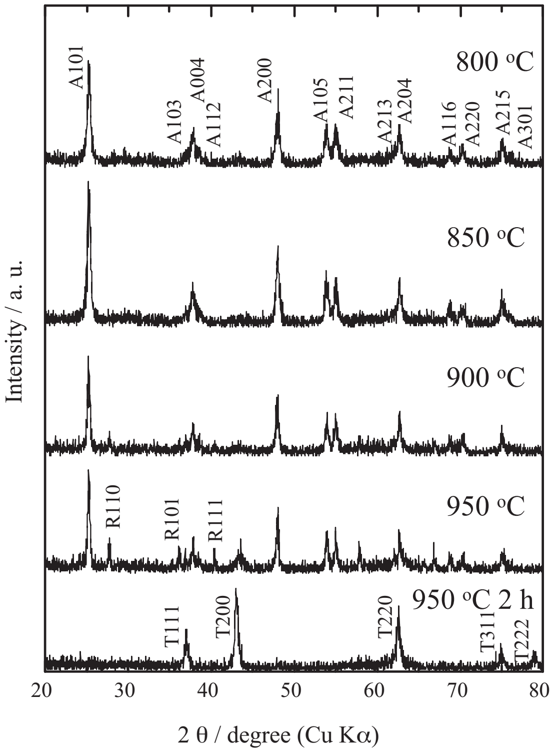

Fig. 2. XRD patterns of Titanate-P nitrided at 800, 850, 900, and 950 for 1 h and 950 °C for 2 h under 100% NH_3 gas flow. A: anatase-type TiO_2, R: rutile-type TiO_2, T: rock-salt-type TiN.

sample has a smaller lattice constant a_c of 0.420 nm, which is smaller than the literature value of 0.425 nm. The smaller lattice constant is considered to be due to a result of the formation of solid solution between TiN and TiO, which has a lattice constant a_c of 0.417 nm [10].

FE-SEM images of Titanate-P treated at 800 °C for 1 h and 950 °C for 2 h are shown in Fig. 3 along with an FE-SEM image of Titanate-P. The Titanate-P treated at 800 °C has granular structure, unlike the fibril structure of the starting material Titanate-P. This morphological change is attributed to the phase transformation from the hydrated titanate to the anatase-type titania accompanied with the release of H_2O molecules. The Titanate-P treated at 950 °C shows also granular particles. The size of the particles is larger than those in the Titanate-P treated at 800 °C. Because a Titanate-P is supposed to undergo volume shrinkage as a result of nitridation, it can be concluded that the titanium oxynitride particles are sintered each other simultaneously during the process of nitridation at 950 °C.

XPS spectra of the N 1s, O 1s, and Ti 2p region of Titanate-P samples having undergone nitridation at different temperatures and those of commercially available titanium nitride (TiN) are shown in Fig. 4. Commercial TiN shows N 1s peak at 395 eV with a shoulder at approximately 396 eV, two small O 1s peaks at 529 and 532 eV, and three Ti $2p_{3/2}$ peaks between 454 and 459 eV and three Ti $2p_{1/2}$ peaks between 460 and 464 eV. The N 1s peak of 396 eV and the N 1s shoulder of 395 eV are attributed to a TiN or TiN_xO_y phase [10–12,14]. The O 1s peak of 532 eV corresponds to a TiN_xO_y phase and that of 529 eV corresponds to TiO_2 [10–12,14]. The Ti $2p_{3/2}$ peaks at 458, 456, and 454.5 eV are because of the presence of the TiO_2, TiN_xO_y, and TiN phases, respectively [10–12,14]. These XPS data indicate that the surface of commercial TiN is oxidized in air to form TiO_2 and TiN_xO_y phases. For Titanate-P nitrated at different temperatures, with the increase in the heating temperature, the intensity of the N 1s peak at 395 eV increases, the intensity of the O 1s peak at 528.6 eV decreases accompanied by a slight sift to the larger energy side, the intensity of the tail observed at higher-energy side of the O 1s peak at 528 eV increases, and the intensity of the Ti $2p_{1/2}$ and $2p_{3/2}$ peaks for TiO_2 at 464 and 457 eV decreases. Ti $2p_{1/2}$ and $2p_{3/2}$ peaks for TiN_xO_y observed at approximately 462 and 455.5 eV were detected only in the sample heated at 950 °C for 2 h. The atomic ratio of N/Ti was calculated form XPS spectra was found to be 0.03, 0.03, 0.07, 0.21, 0.64, and 0.96 for nitrided Titanate-P labeled as 800, 850, 900, 950 °C, 950 °C 2 h, and TiN, respectively. Titanate-P treated at 950 °C for 2 h has a rock-salt-type structure with a smaller lattice constant a_c of 0.420 nm, which is smaller value than the value from the literature of 0.425 nm (Fig. 2), and it has a N/Ti ratio of 0.63. This also indicates that the Titanate-P treated at 950 °C for 2 h has a certain number of oxygen atoms in its structure.

Figs. 5 and 6 show the FE-SEM and TEM photos of Titanate-C and Titanate-C treated at 1000 °C for 0, and 1 h. It

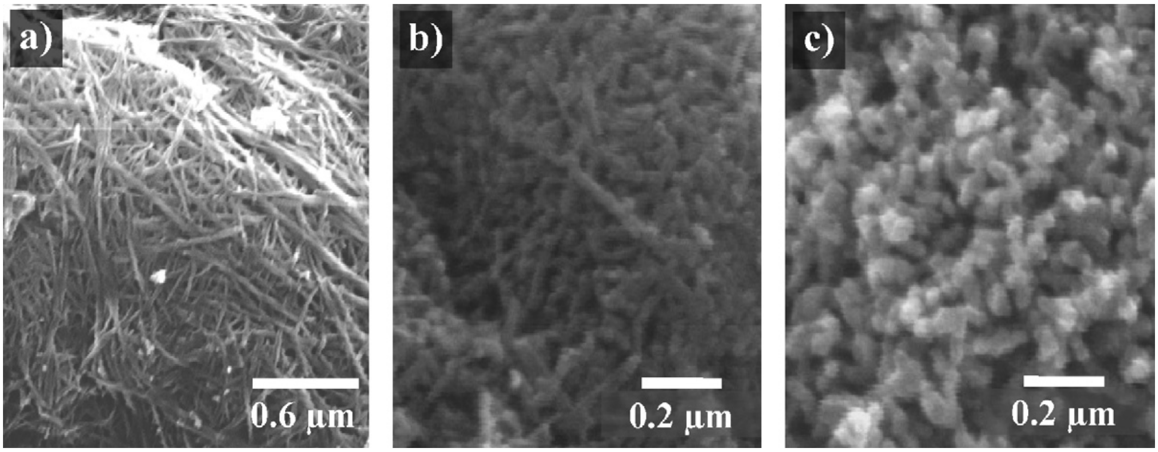

Fig. 3. SEM images of Titanate-P (a), Titanate-P nitrated at 800 °C for 1 h (b), and 950 °C for 2 h (c).

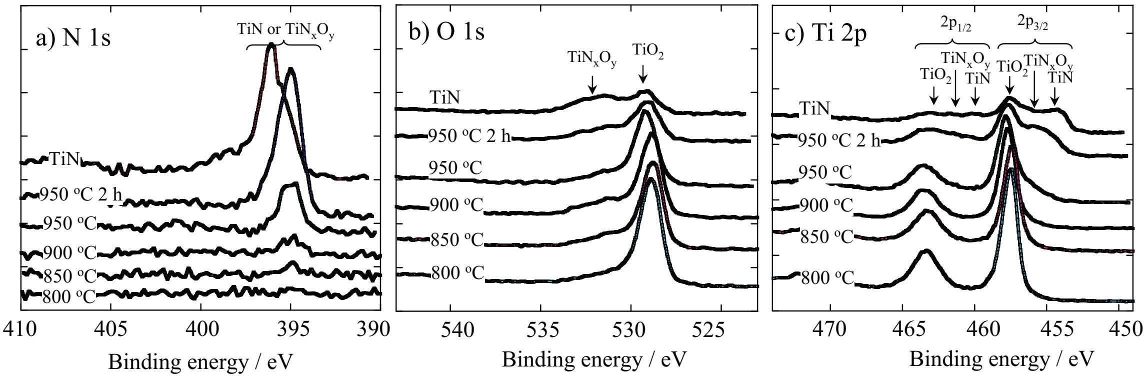

Fig. 4. XPS spectra of Titanate-P nitrided at 800, 850, 900, 950 °C for 1 h, 950 °C for 2 h and commercially available TiN. N 1s (a), O 1s (b) and Ti 2p (c).

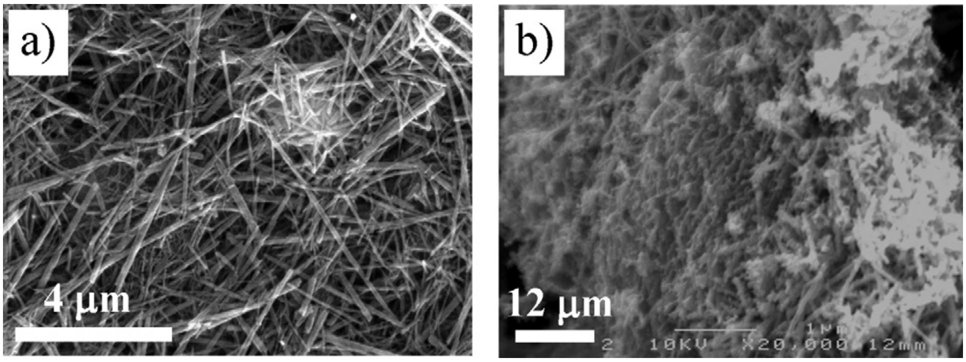

Fig. 5. SEM images of Titanate-C (a) and Titanate C nitrided at 1000 °C for 1 h (b).

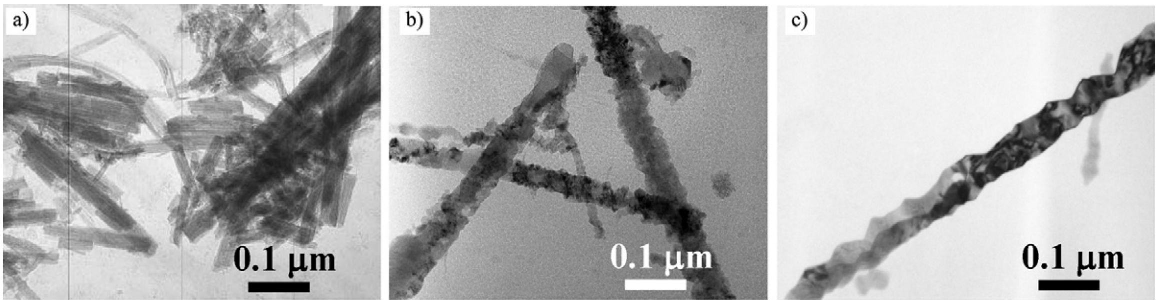

Fig. 6. TEM images of Titanate-C (a) and Titanate C nitrided at 1000 °C for 0 h (b) and Titanate C nitrided at 1000 °C for 1 h (c).

was confirmed by XRD measurements that Titanate-C treated at 1000 °C for 1 h had a rock-salt-type TiN structure with a lattice constant a_c of 0.423 nm whereas Titanate-C treated at 1000 °C for 0 h consisted of a mixed phase of an anatase-type TiO_2 structure and rock-salt-type TiN structure. The needle-like particles of Titanate-C are made to undergo nitridation process at 1000 °C, with the diameter of the needle-like particles being approximately 50 nm and the length being from several to 10 μm(Fig. 5). However, the texture of the needle-like particle is different for both the samples as shown in Fig. 6; the fibrous texture of the hydrated titanate in Titanate-C (Fig. 6a) changes to one that is granular for Titanate-C treated at 1000 °C for 0 h(Fig. 6b). This change is because of the two phase changes, the first phase change from hydrated titanate to anatase-type titanate and the second from anatase-type TiO_2 to rock-salt-type TiN accompanied by a gas release and a volume shrinkage similar to the case of Titanate-P. Further, the granular texture changes to one that has a rough-edged shape one, as observed in Titanate-C treated at 1000 °C for 1 h(Fig. 6c). This is considered to be caused by the sintering of titanium nitride particles.

4. Conclusions

Hydrated titanate nanowires were successfully nitrided under NH_3 gas flow at elevated temperature. Hydrated titanate nanowires changed to granulous particles with anatase-type TiO_2 structure in the temperature range between 50 and 400 °C and then transformed to rock-salt type TiN structure with sintering of particles. The sample nitrided at 950 °C for 2 h has significant oxygen in the structure and was reasonably represented as a titanium oxynitride, TiN_xO_y. By selecting thick hydrated titanate wires, Titanate-C powders as the starting materials, needle-like TiN_xO_y particles could be fabricated.

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