Influence of ammonia gas exposure on microstructure of nanocrystalline titanium nitride powder synthesized from titanium dioxide

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In this study, we investigated the preparation conditions of titanium nitride (TiN) through nitridation of nano-sized titanium dioxide (TiO2) without particle agglomeration. Synthesis of nanocrystalline TiN powder was attempted via ammonia (NH3) nitridation of nanocrystalline TiO2 powder. The nitridation behavior was investigated using thermogravimetry (TG) in an NH3 atmosphere. Non-isothermal TG experiments showed that nitridation of the nanocrystalline TiO2 powder began at ~750°C. Two types of experiments were performed using isothermal TG. In the first experiment, an argon atmosphere was used while heating at 5 °C/min. On reaching the holding temperature (900 or 1,000°C), the atmosphere was changed to NH3/Ar (50/50 kPa). This atmosphere was used throughout the second experiment. The first experiment produced a nitride powder with severely agglomerated particles. In the second experiment, nano-sized powder particles with inhibited agglomeration were obtained, and long holding time of 6 h at 900 or 1,000°C was effective in obtaining the small nitrided particles.

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1. Introduction

Among transition metal nitrides, titanium nitride (TiN) has received the most attention because of its excellent corrosion and wear resistance, extreme hardness (2,160 kg/mm²), high melting temperature (2,950°C), high chemical stability, and high electrical conductivity.1–7 These properties make TiN a useful material for coatings for cutting tools,8–10 additives in composites,9,11,12 diffusion barriers in microelectronics,11,13 optical coatings,11,14 solar energy absorbers,11,15 IR reflectors,11 thin film resistors,16,17 and bio-replacements.8,17 Compared with conventional bulk materials, nanoscale TiN has a high surface area, which makes it an attractive candidate for conferring enhanced conductivity,9,12 extremely high hardness, excellent toughness, and good sinterability at low temperatures9,12,18 on supercapacitors9,19 catalysts9,20 and nanocomposites. Furthermore, nanocrystalline TiN may find promising applications in tribological and high-performance ceramics.1,21 TiN nanocrystalline powder prepared using a plasma- gas -phase reaction possesses a high specific surface area (250 m²/g) with an average particle size of 10 nm, resulting in good sintering ability. However, the high oxygen levels in the powder (reaching 15 or 20%) hinder densification when conventional sintering techniques are used.22 Furthermore, nanocrystalline TiN has been synthesized using rapid solid-state metathesis of titanium tetrachloride (TiCl4) or trichloride22 with various solid nitrogen sources, such as Li3N,9 NaN3, sodium amide (NaNH2), Ca3N2, and NH4Cl/Na.9 In a two-step synthesis, nano sized TiN crystallites were obtained by heat treating a precursor obtained by reacting liquid TiCl4 with NH3 in an anhydrous organic liquid.9,23 Nanocrystalline TiN was also prepared by a one-pot solvothermal synthesis at 350–380°C using TiCl4 and...
sodium azide as source materials, but amorphous carbon was also inevitably produced from the carbonization of benzene.\(^\textsuperscript{1,9,24}\) In 2001, Li et al.\(^\textsuperscript{2}\) reported direct nitridation of nanocrystalline TiN powder using nanocrystalline titanium dioxide (TiO\(_2\)) powder as a starting material in an NH\(_3\) gas flow. Aghababazadeh et al.\(^\textsuperscript{3,5}\) also reported that nano-sized TiO\(_2\) powder was synthesized from nano-sized TiO\(_2\) powder using direct NH\(_3\) nitridation at temperatures reaching 1,000°C. They showed that a low heating rate was effective in forming of nano sized TiN powder, but the mechanism was not shown. Thermogravimetric analysis (TGA) and/or differential thermal analysis (DTA) in an NH\(_3\) atmosphere are powerful methods to determine the reaction temperature and elucidate the reaction mechanism of the formation of nitrides. However, NH\(_3\) is severely corrosive and toxic, and the majority of commercially available equipment cannot be operated in an NH\(_3\) atmosphere. In our laboratory, we built a thermogravimetry (TG) system to be operated in an NH\(_3\) atmosphere, and it was used to investigate the synthesis of TiN from TiO\(_2\).\(^\textsuperscript{11}\) TGA and DTA in an NH\(_3\) atmosphere have also been conducted by other groups to investigate the reaction mechanism of TiO\(_2\) and NH\(_3\) reaction.\(^\textsuperscript{25}\)

In this study, we investigated the preparation conditions of TiN through nitridation of nano-sized TiO\(_2\), inhibiting particle agglomeration. To determine the influence of atmosphere on the microstructure of TiN powder, experiments were conducted using argon during ramp periods, with ammonia gas introduced at a specified temperature and from the beginning of the reaction. During the experiments, to observe the reaction sequence from TiO\(_2\) to TiN directly, thermogravimetric experiments were performed in NH\(_3\) atmosphere.

2. Experimental procedure

2.1 Heating of nano sized TiO\(_2\) powder in NH\(_3\) atmosphere

Nano sized TiO\(_2\) powder was heated in an ammonia atmosphere. Commercial nanocrystalline TiO\(_2\) powder (99.5%, 19.7–101 nm, Kanto Chemical) was used without treatment. TGA was performed in NH\(_3\)/Ar atmosphere to determine the nitridation conditions required to transform the TiO\(_2\) nanopowder into TiN. A laboratory-made thermogravimetric system with a vertical tube furnace was used for this non-isothermal TGA. An electronic weighing unit (Cahn D200) was used in the system. Approximately 8–15 mg of the TiO\(_2\) nanopowder was heated to 1,200°C at 5°C/min in NH\(_3\)/Ar (50/50 kPa). To determine the crystalline phases during heating, the TiO\(_2\) nanopowder was also heated in a horizontal tube furnace to various temperatures with no holding time in the same NH\(_3\)/Ar gas flow.

Isothermal TGA was also performed at 900 and 1,000°C for 6 h under the same conditions. Two types of experiments were conducted using isothermal TGA. In the first experiment, the atmosphere was Ar at the beginning and was changed to NH\(_3\)/Ar (50/50 kPa) when the holding temperature was reached. In the second experiment, only an NH\(_3\)/Ar (50/50 kPa) atmosphere was used. In both experiments, the heating rate was set at 10°C/min to minimize the effects of the heating periods.

2.2 Characterization

The resulting powder phase composition of each sample was characterized by X-ray diffraction (XRD; RIGAKU RINT, TTR-200) and X-ray photoelectron spectrometry (XPS, JEOL ESCA5600). The average size and morphology of the TiN nanoparticles were observed using scanning electron microscopy (SEM; JEOL JSM-7400F) and transmission electron microscopy (TEM; JEOL JEM-2010FX).

3. Results and discussion

Figure 1 depicts a typical non-isothermal TGA plot in an NH\(_3\)/Ar atmosphere for temperatures reaching 1,200°C. At a lower temperature, a small weight loss was observed up to 400°C, possibly due to evaporation of adsorbed water. Similar weight losses were observed after the TG experiments. The weight decreased sharply from approximately 750 to 950°C. Thereafter, the slope decreased, and the weight continued to decrease until the end of the experiment (i.e., up to 1,200°C). The total weight loss from 750 to 1,200°C during the experiment was approximately 19%, corresponding to 84.4% mass conversion, which was comparable to the theoretical value (22.5%) based on Eq. (1).

\[
2\text{TiO}_2 + 2\text{NH}_3 \rightarrow 2\text{TiN} + 3\text{H}_2\text{O} + 1/2\text{O}_2. \quad (1)
\]

Figure 2 shows XRD patterns of samples heated in the horizontal tube furnace to 750, 900, and 1,000°C under the same conditions as those used in the TG experiments shown in Fig. 1, as well as XRD pattern of the starting material. In the patterns, data from the International Centre for Diffraction Data (ICDD) for cubic TiO (ICDD 77-2170) and TiN (ICDD 87-0632) are also included, and the lattice parameters are 4.185 and 4.225 Å (1 Å = 0.1 nm), respectively. In addition to peaks of the anatase phase, peaks close to those of c–TiO were observed at 900°C [Fig. 2(c)]. At 1,000°C [Fig. 2(d)], the peaks of the anatase phase are absent. At 1,200°C [Fig. 2(e)], the pattern is almost the same as that at 1,000°C, but the positions of the...
peaks are close to those of TiN. The lattice parameters obtained from the positions of the peaks due to the cubic phase were 4.176 Å (900°C), 4.186 Å (1000°C), and 4.217 Å (1200°C). The observed lattice parameter of the cubic phase at 900°C was close to the reported value of c-TiO. TiO crystalized well below 990°C, has vacancies ordered in a rock salt structure, and exhibits extra peaks because of ordered vacancy.26) Our sample did not show such extra peaks, thereby suggesting that the TiO in our sample has random vacancies probably because of nitrogen doping. In addition, the change of the lattice parameters suggests that the cubic phase was transformed from TiO to TiN via nitrogen doped TiO (TiO\textsubscript{x}N\textsubscript{y}) with increasing temperature.

Figures 3 and 4 show N 1s XPS spectra and Ti 2p XPS spectra, respectively, for samples heated to 900, 1000, and 1200°C under the same conditions as those used in the TG experiments shown in Fig. 1. Additionally, they show N 1s XPS spectra and Ti 2p XPS spectra for a sample heated in an NH\textsubscript{3} atmosphere to 900°C and held for 6 h, as described in the following section. The N 1s spectra (Fig. 3) of the samples heated to 900°C and above are similar and have a single peak at about 396.5 eV. This peak corresponds to metal nitrides and oxynitrides,9),27) showing that the sample contains a TiN or TiO\textsubscript{x}N\textsubscript{y} phase. The Ti 2p spectrum of the samples has two broad peaks at around 464 and 458.6 eV. Increasing the reaction temperature to 1,200°C increased the relative intensity of the shoulder at about 455.4 eV. It was reported that peaks at 455.4 and 460.9 eV indicated the formation of TiN,9),27) a peak at 456.7 eV indicates TiO or TiO\textsubscript{x}N\textsubscript{y}, while one at 458.6 eV indicates TiO\textsubscript{2}.27) The spectral change shows that the chemical species corresponding to TiN increase with temperature, while those corresponding to TiO\textsubscript{2} decrease but do not disappear. The mass conversion of 84.4% obtained by heating to 1,200°C in the TG experiments (Fig. 1) also supports this result. In this respect, the phase-to-detection limits of XRD measurements are a few weight percent, and small quantities of crystalline TiO\textsubscript{2} are not detected by XRD.

The theoretical weight changes during the conversions of TiO\textsubscript{2} to TiO and TiO to TiN are 20.0 and 2.5%, respectively. The TG curve slopes are 16% for the steep part and 3% for the shallow part of the curve (Fig. 1). The similarity between the theoretical and observed weight losses suggests that the steep and shallow slopes correspond to the transformations of TiO\textsubscript{2} to TiO and/or TiO\textsubscript{x}N\textsubscript{y} to TiN, respectively.

Figure 5 shows isothermal TG curves of samples heated to (a) 900°C and (b) 1,000°C with a 6 h holding time. In these experiments, the atmosphere was Ar during the temperature increase and NH\textsubscript{3}/Ar (50/50 kPa) at the holding temperatures. After the atmosphere change to NH\textsubscript{3}/Ar, a two-step weight loss was observed. A rapid weight loss
was observed in the high-temperature experiments. The weight losses at 900 and 1,000°C show similar decreases (−20 and −21%, respectively) with different slopes.

Figure 6 shows non-isothermal TG curves for samples heated to (a) 900°C and (b) 1,000°C with a holding time of 6 h. In both experiments, the weight decreases linearly, showing a slope around −17%, but the weight loss at 900°C is smaller than that at 1,000°C. After the first weight loss reaching −17%, the weight continues to slowly decrease. By the end of the holding period, the slope is nearly horizontal, but the slow weight decrease. The curves are similar to the non-isothermal curve shown in Fig. 1.

The XRD patterns of the samples obtained in the TG experiments (Fig. 6) are shown in Fig. 7. The observed peaks are consistent with those reported for TiN. Furthermore, the peaks at 1,000°C are stronger than those at 900°C. Ti 2p XPS data of the sample held at 900°C for 6 h [Fig. 4(d)] shows the presence of a TiO chemical species, which was possibly not detected by XRD due to its small amount and/or an amorphous phase. Nevertheless, based on the XRD results, it can be concluded that the nanocrystalline TiO2 powder underwent nitridation at every temperature.

Figure 8 shows the morphology of the as-received material. The particles were spherical, and most had diameters below 100 nm. The morphologies of the samples resulting from isothermal TGA at 900°C [Fig. 9(a)] and non-isothermal TGA for temperatures reaching 900°C with a 6 h holding time [Fig. 6(a)] are compared in Figs. 9 and 10. The isothermal TGA result [Fig. 9(a)] shows highly agglomerated particles with irregular shapes. Conversely, the non-isothermal TGA result [Fig. 9(b)] shows smaller particles that are almost identical to those in the starting material (Fig. 8).

A comparison was also performed using TEM. The sample particles produced by the isothermal TGA were severely agglomerated [Fig. 10(a)], but many particles of the samples from the non-isothermal experiments were less agglomerated [Fig. 10(b)].
The difference in the conditions for isothermal and non-isothermal nitridation was the atmosphere used during heating, namely, Ar and NH3/Ar, respectively. During this period, particle sintering should have been inhibited in the NH3/Ar atmosphere. In the nitridation process, the exchange between two oxygen atoms and one nitrogen atom leads to volumetric shrinkage of the particles. This phenomenon decreases the contact area between the particles and may also avoid sintering. Furthermore, nitrogen doping in TiO2 inhibits the phase transition from anatase to rutile. The phase transition involves a process of ion movement within the structure. The reason for inhibition has not been clearly explained, but nitrogen doping may suppress the movement of ions in TiO2 and the sintering of TiO2 particles. Therefore, the nitrogen doping in samples heated in an NH3/Ar atmosphere from room temperature starts at a low temperature and prevents the sintering of the particles, which would otherwise result in agglomeration.

4. Conclusions

Nanocrystalline TiN was prepared via direct ammonia nitridation of nanocrystalline TiO2 powder at 900 and 1,000°C. The weight changes caused by this nitridation were monitored by TG. The TGA results showed two-step weight losses. Based on the XRD and XPS results, the first and second weight losses were from 750 to 950°C and beyond 950°C, respectively. These corresponded to the transformations from TiO2 to TiO and/or TiO_N to TiN, respectively. During heating in NH3, oxygen was eliminated, which inhibited sintering of the TiO2 particles. This sintering inhibition resulted in the formation of nano-sized TiN particles from nano-sized TiO2.

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