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Fabrication of VO_2 nanopowder via direct reaction of vanadium metal and hydrogen peroxide

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A vanadium-oxide-based precursor fine powder was prepared by the reaction of vanadium metal and H_2O_2. A VO_2 powder with particles tens of nanometers in size was obtained by treatment of the precursor powder at 650°C in an H_2/Ar atmosphere. The particle size of the resulting VO_2 powder was 40 nm, and the transition temperature of the obtained VO_2 powder was 68.5°C.

Key-words : Vanadium dioxide, Nanopowder, Thermochromic

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1. Introduction

VO_2 exhibits a metal–insulator transition at about 68°C, accompanied by a crystallographic transition from a low-temperature monoclinic phase to a high-temperature tetragonal rutile structure.[1),2)] This phase transition causes abrupt changes in the electrical and optical properties, hence VO_2 has potential applications in thermochromic smart windows.[3)–8)] There have been several studies focused on applications of VO_2 fine particles, such as composites of VO_2 powders in polymeric matrices,[9)] and coating nanosized VO_2 powders on glass substrates.[10)]

In previous studies, VO_2 fine particles were fabricated by reduction of VO_2 (B) nanopowders,[10)] reduction of $V_2O_5 \cdot x\text{pyridine} \cdot yH_2O$ particles,[11)] and reduction of vanadium oxide precursor particles from a vanadium oxyisopropoxide solution.[12)] We have found that a vanadium oxide nanopowder (two-dimensional V_2O_5-like,[13)] 2D-V_2O_5) can be obtained by direct reaction of vanadium metal and H_2O_2, without cooling. The 2D-V_2O_5 powder[13)] can be dissolved in water, however, the vanadium oxide nanopowder obtained in this investigation cannot be dissolved in water. Since the powder in this investigation does not deliquesce with water vapor in air, it is easy to handle in experiments. In this investigation, VO_2 powders of nanometer size were fabricated by reduction of precursor nanopowders, and the thermal properties and microstructures of the resulting VO_2 powders were evaluated.

2. Experimental procedure

Metallic vanadium powder (Wako, Osaka, Japan) was used as the starting material. Vanadium powder (0.3 g) was mixed with 30% H_2O_2 solution (30 mL) at room temperature, without cooling. The mixture reacted vigorously, and a dark-brown powder was obtained. The resulting powder was dried at 100°C to remove residual water, and the dried powder was heat-treated at 500–700°C for 2 h in an H_2/Ar (4% H_2) atmosphere.

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The crystal structure of the VO_x powder was determined by X-ray diffraction (XRD) using a Miniflex II diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation. Differential scanning calorimetry (DSC) was performed on the resulting powder using a DTG-60 calorimeter (Shimadzu, Kyoto, Japan), with the temperature increasing at a rate of 10°C/min. The microstructures of the precursor and the heat-treated powders were observed by transmission electron microscopy (TEM; EM-002B, Topcon Corp., Tokyo, Japan); the powders were supported on copper grids during the observations.

3. Results and discussion

The precursor powder was obtained by direct reaction of vanadium metal and H_2O_2, and the precursor powder was obtained by heat-treatment at 500–700°C in an H_2/Ar atmosphere. **Figure 1** shows the XRD patterns of the precursor powder and the heat-treated powders. The precursor powder was assigned the 2D-V_2O_5 structure. The structures of the powders heat-treated at 500 and 550°C were the V_3O_7 phase. The powder heat-treated at 600°C consisted of V_3O_7 as the main phase and V_6O_{13} as a secondary phase. Above 650°C, the heat-treated powder was a VO_2 single phase of high crystallinity. The sample heat-treated at 700°C was also a VO_2 single phase, but of low crystallinity, and the resulting powder melted slightly. When the sample was heat-treated above 700°C, the sample melted completely. The precursor powder was very similar to V_2O_5, and the melting point of the precursor was close to 690°C (the V_2O_5 melting point). The crystallinity of the sample heat-treated at 700°C therefore decreased. These results show that the optimal heat-treatment temperature for obtaining VO_2 powder was 650°C.

The crystallite size of the VO_2 powder heat-treated at 650°C was calculated from the full-width at half-maximum (FWHM) of the XRD peaks, using Scherrer's equation:[14)]

$$D = K\lambda/(B\cos\theta),$$

where D is the particle diameter, λ is the X-ray wavelength used, B is the FWHM of a diffraction peak, θ is the diffraction angle,

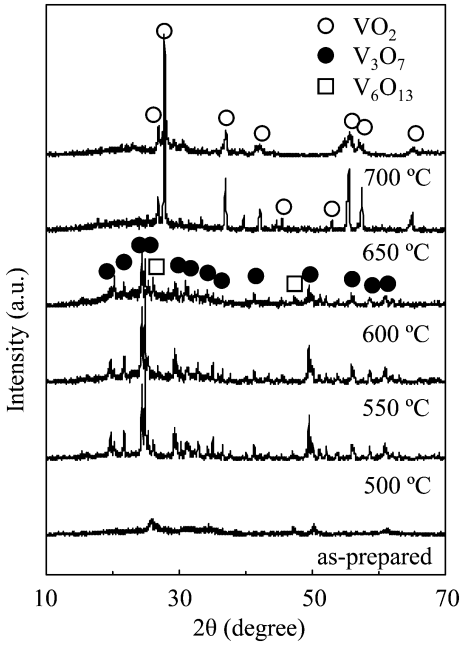

Fig. 1. XRD patterns of as-prepared powder and VO_2 powders heat-treated at various temperatures.

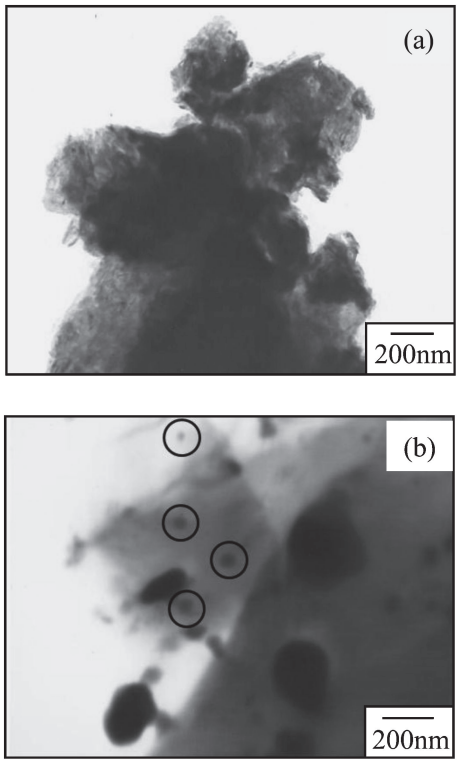

Fig. 2. TEM bright-field images of (a) the precursor powder and (b) the VO_2 powder heat-treated at 650°C in an H_2/Ar atmosphere.

and K is Scherrer's constant, which is of the order of unity for most crystals. In this investigation, the value of K used was 0.9, and the calculated size of the VO_2 powder heat-treated at 650°C was 30 nm.

To determine the particle size precisely, TEM observations were carried out on the VO_2 powder heat-treated at 650°C. **Figure 2** shows the bright-field TEM images of the precursor powder and the resulting VO_2 powder heat-treated at 650°C; the closed circles in Fig. 2(b) denote VO_2 particles. The primary particle size of the precursor powder was tens of nanometers and secondary particles were formed by aggregation of the primary particles. The primary particle size of the heat-treated powder was 40 nm, and secondary particles were also formed by aggregation of the primary particles. The secondary particle sizes before and after heat-treatment were very close to each other, therefore the secondary particle size of the VO_2 powder did not change much as a result of the heat-treatment. The estimated particle size of the heat-treated powder obtained using TEM was 40 nm, which is close to the particle size calculated from the XRD measurements. These results suggest that VO_2 powders of nanometer particle size can be obtained by heat-treatment of the precursor powder at 650°C in an H_2/Ar atmosphere.

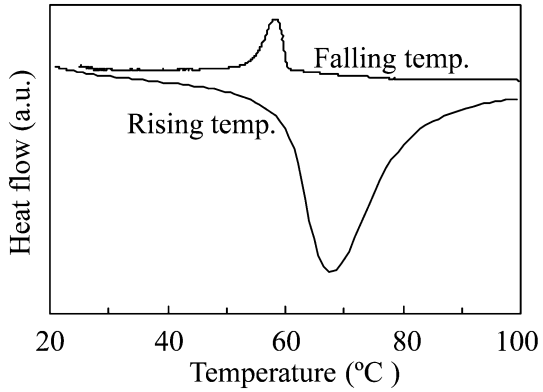

Fig. 3. DSC curve for the VO_2 powder heat-treated at 650°C in an H_2/Ar atmosphere.

To measure the transition temperature of the resulting specimens, DSC measurements were carried out on the VO_2 powder heat-treated at 650°C. **Figure 3** shows the DSC curves for the VO_2 powder. An endothermic peak was observed at 68.5°C as the temperature increased, and an exothermic peak was observed at 57.4°C as the temperature decreased. Generally, crystallographic transitions of VO_2 show thermal hysteresis, and the transition temperature of VO_2 varies depending on whether the temperature is increasing or decreasing, and is accompanied by thermal hysteresis. In this investigation, the resulting VO_2 powder also showed different transition temperature for increasing and decreasing temperatures. The transition temperature of the resulting VO_2 powder was 68.5°C as the temperature increased; this was close to the previously reported values.[1)–8)]

4. Conclusion

A vanadium-oxide-based precursor fine powder was prepared by the reaction of vanadium metal and H_2O_2, and a VO_2 powder with a particle size of tens of nanometers was obtained from the precursor powder in a reducing H_2/Ar atmosphere. In order to fabricate VO_2 powder with a particle size of tens of nanometers, the optimal heat-treatment temperature of the precursor powder was 650°C. The particle size of the resulting VO_2 powder was 40 nm. The resulting VO_2 nanopowder exhibited a phase transition, and the transition temperature was 68.5°C.

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