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Influence of strain on latent heat of VO_2 ceramics

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ABSTRACT

Vanadium dioxide (VO_2), which undergoes a metal–insulator transition (MIT) at 67 °C, is an attractive material for caloric applications, possessing a latent heat comparable to that of ice-water. Here, we have investigated the variation in latent heat due to residual strain induced by spark plasma sintering (SPS). SPS pressure linearly increased the degree of inhomogeneous strain, thereby reducing the latent heat and broadening the MIT temperature range. Optical observation of MIT revealed a slow transition in highly strained samples. Moderate annealing of highly strained VO_2 can eliminate this strain, and thereby recover the high latent heat. The present study indicates the importance of strain tuning for the utilization of intrinsic latent heat in VO_2 ceramics.

1. Introduction

Much thermal energy can be stored in materials through their phase transitions (PTs), offering energy savings by releasing the stored thermal energy and maintenance of a desired temperature. Current heat-storage materials use solid–liquid PTs, as seen in ice, paraffin ($C_{18}H_{38}$), and sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) [1,2]. However, their low thermal conductivities, typically <1 W/m·K, prevent effective heat exchange. Encapsulation against liquid leakage is another obstacle. Solid–solid PT materials [3] can overcome these issues.

Vanadium dioxide (VO_2) undergoes a metal–insulator transition (MIT) at 67 °C [4]. The latent heat per unit volume is comparable with that of ice-water PT. The thermal conductivity is ~6 W/m·K [5]. Furthermore, the PT temperature is tunable by chemical doping [6–8]. These characteristics suggest potential applicability as a future heat storage material [9].

During the MIT, the crystal structure changes from monoclinic to tetragonal. The origin of the MIT is attributed to both Peierls transitions, due to the structural changes, and Mott transitions originating in electronic correlation [10,11]. In other words, the state of spin, charge, and lattice drastically changes through the MIT. This leads to the large latent heat of VO_2 [12].

In this study, we investigated the influence of strain on the latent heat of VO_2 ceramics. So far, the impact of strain on the MIT has been extensively researched in nanobeam VO_2 [13–15] as well as in an epitaxial thin film constrained by a substrate [16], which showed a shift of the transition towards higher temperature under compressive strain. However, the change in the latent heat by the strain has remained uncertain, most probably because of limitations relating to sample size in these studies. Here, we applied spark plasma sintering (SPS) as a sintering procedure. Meanwhile, high pressure reaching the order of gigapascals was applied, which enabled control of the strain in the ceramics. The results elucidate the importance of strain release in utilizing the intrinsic latent heat of VO_2.

2. Experimental procedures

2.1. SPS sintering

Commercially available VO_2 powder (3 N, powder under 180 μm mesh, Kojundo Chemical Laboratory) was used as a raw material. The powder was pulverized to sub-micrometer particles using planetary ball milling. Without pulverization, the ceramics could not exceed 90% of the theoretical density. A powder sample of 0.5 g was loaded in a mold of cemented tungsten carbide, heated to 500 °C with a heating rate of 50 °C/min, and held at 500 °C for

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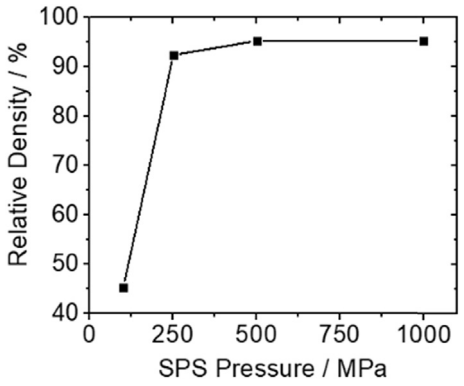

Fig. 1. Relative densities of VO_2 ceramics with varied sintering pressures. Samples were heated at 500 °C for 5 min.

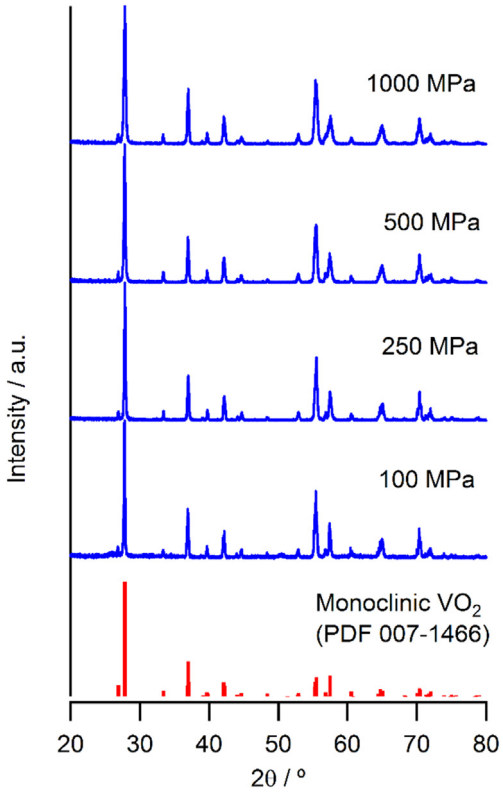

Fig. 2. XRD patterns of VO_2 ceramics.

5 min, followed by cooling to room temperature with a cooling rate of 50 °C/min in vacuum. A carbon sheet was placed between the punch and the powder in order to ensure an electric conduction path. During SPS, the pressure of 100, 250, 500, or 1000 MPa was applied to a pellet of 10 mm in diameter. After SPS, the specimens were annealed in air at 200 °C for 1 h using a muffle furnace. The specimen surfaces were mechanically ground by 200 μm in thickness to remove the impurity surface layers. The sample sintered at the pressure of 1000 MPa was annealed further in an evacuated quartz ampoule for 12 h at 400 °C. This released residual strain, as noted in Section 3.

2.2. Characterization of specimens

The relative densities of the VO_2 ceramics were measured by the Archimedes method. X-ray diffraction (XRD) patterns were obtained with a parallel beam optics using Cu Kα radiation (Rigaku, RINT2000). Inhomogeneous strain was evaluated using the Williamson–Hall plot [17], in which peaks without overlap were selected. Differential scanning calorimetry (DSC, Bruker; DSC3300SA) measurements were performed under ambient air. The DSC measurement temperature ranged from 40 to 80 °C with the heating and cooling rate of 1 °C/min. The MIT behavior of each grain was observed by optical microscopy (Keyence, VHX-900) mounted with a Peltier stage.

3. Results and discussion

The pressure in SPS effectively promoted densification, as shown in Fig. 1, although the sintering temperature was only at 500 °C. Applying pressures >250 MPa during SPS yielded high relative densities exceeding 90% of the theoretical density. The constitutive phase of the ceramics was confirmed by XRD. Only the monoclinic phase of VO_2 was observed in the XRD patterns for all samples, as shown in Fig. 2. Magnified peaks as shown in Fig. 3 indicate broadening in the full width at half maximum (FWHM) and a shift in the peak position with increase in pressure. Their trend is summarized in Fig. 4. The cell volume expands with increases in pressure, as shown in Fig. 4 (c). Oxygen vacancies are likely to form during SPS sintering because of the reduced atmosphere [12], leading to expansion of the cell volume [18]. The inhomogeneous strain can be quantitatively evaluated by a Williamson–Hall plot, as shown in Fig. 5, which indicates a linear increase in the strain with increasing pressures.

Fig. 6 shows the result of DSC measurements. The latent heat, FWHM of the PT peak, and transition temperature (peak top and onset) are summarized in Fig. 7. High pressure clearly reduces the latent heat and broadens the PT. As with the PT temperature (onset), the endothermic peak (during heating) is shifted lower, while the exothermic peak (during cooling) is shifted higher. These results suggest that the residual strain has a strong impact on the thermophysical properties of VO_2 ceramics. In addition, we confirmed that the ball milling process also reduced the latent heat to 35 J/g, which also supports the negative effect of strain on the latent heat.

In order to further investigate the strain effect, ceramic samples sintered at 1000 MPa were annealed at 400 °C. This process fully released the strain evaluated based on the inhomogeneous strain: a reduction from 0.082% to 0.001% occurred. With this release in strain, the latent heat is significantly increased to 43 J/g, and both endo- and exothermic peaks are remarkably sharpened. However, this recovered latent heat remains lower than the reported value of 51 J/g [19]. We believe that oxygen vacancies remaining in the specimen cause this difference [12].

The influence of the residual strain on the PT was microscopically observed by optical imaging, originating in the reflection of the near-infrared spectrum in the metal state [20]. The images of low- and high-strain samples are shown in Fig. 8(a) and (b), respectively. Here, the color change from white to blue represents the PT from insulator to metal. Both samples comprise large grains on the order of 10 μm in diameter as well as sub-micrometer grains; their microstructural aspects are very similar in both strain states. However, the PT progresses differently. In the low-strain sample, MIT in one grain occurs rapidly, while a slow PT is observed in