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IDENTIFICATION OF MICRO-MECHANICAL CHARACTERISTICS OF MONOCLINIC TUNGSTEN TRIOXIDE MICROPARTICLES BY NANOINDENTATION TECHNIQUE

A.B.D. Nandiyanto[1*], F. Triawan[2], R. Firly[3], A.G. Abdullah[4], Y. Aono[3], K. Inaba[5], K. Kishimoto[5]

[1]Departemen Kimia, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudi no 229, Bandung 40154, Indonesia

[2]Faculty of Engineering and Technology, Sampoerna University, Jl. Raya Pasar Minggu, Kav. 16, Pancoran, Jakarta, Indonesia

[3]Department of Mechanical Engineering, School of Engineering, Tokyo Institute of Technology, 2-12-1 Okayama, Meguro, Tokyo 152-8552, Japan

[4]Departemen Teknik Elektro, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudi no 229, Bandung 40154, Indonesia

[5]Department of Transdiciplinary Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552 Japan

*e-mail: nandiyanto@upi.edu

Abstract. Tungsten trioxide (WO_3) has excellent mechanical properties, making them to be applied in various applications. However, researches on the mechanical properties of WO_3 in the micrometer scale are limited. Here, the purpose of this study was to demonstrate nanoindentation technique in an attempt to study the micro-mechanical characteristics of monoclinic WO_3 microparticles that were previously synthesized using a direct heat treatment of ammonium tungstate pentahydrate powder at a temperature of 800°C. The experiment comprises a measurement by load controlled nanoindentation test on the particle sample to obtain force and displacement relationship. The results exhibited variability on the force-displacement curves for similar applied load. This could be due to the micro-mechanical effects generated by the existence of inclusions, precipitates, and oxides inside the micron WO_3 particles. The present study demonstrates the importance of understanding the micro-mechanical characteristics of WO_3 for clarifying the inhomogeneity effects on its macro-mechanical properties.

Keywords: tungsten trioxide, micro-mechanical characteristics, nanoindentation, porous material

1. Introduction

Recently, tungsten trioxide (WO_3) has been grown for being used in a variety of engineering applications due to its excellent performance (i.e., high mechanical strength, relatively harmlessness, active under visible light with good photostability, chemical and thermal stable, as well as chemical and biological inertness) [1,2]. Therefore, no question argues that WO_3 is still attractive to date, and numerous of the applications rely on its behaviors[3].

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Despite the quality improvement of WO_3 over the years, this challenging material still suffers from the understanding information regarding mechanical properties of WO_3 particles. Although several reports regarding the mechanical properties of WO_3 have been published [4-7], they are limited to the specific size, specifically in the bulk or nanometer size. Further, there is almost no report on the analysis of mechanical properties of WO_3 in the micrometer scale.

Reports on the mechanical properties of WO_3 in the micron scale are still interesting since mostly WO_3 are applied in this size range. In fact, this micron-scaled mechanical properties data is vital, in which this dimension may reach larger impacts when the material is restructured into bulk or even smaller scale[8]. Further, micron scale WO_3 is typically disregarded, while it has been largely used since it has possessed excellent properties in applications that are different from bulk and nanometer sizes[1,2]. Thus, understanding the mechanical properties of WO_3 in the micron scale is inevitable.

Based on our previous studies regarding the synthesis of WO_3 particles [1,2,9-15] and analysis of mechanical strength of various structures [16-19], the purpose of this study was to demonstrate a nanoindentation technique in an attempt to study the micro-mechanical characteristics of WO_3 particles. The experiment comprises a systematic measurement of load controlled nanoindentation technique to obtain force and displacement relationship. Nanoindentation, or ultra-low load indentation, is used as one of the standard techniques over the last decade. This technique has been utilized for probing the mechanical properties of materials even at very small scales [20]. One of the great benefits of the technique is the ability in determining mechanical properties only by analyzing the indentation load-displacement data alone.

2. Materials and Methods

Specimen. This study used WO_3 microparticles as a specimen, which were produced using the similar method reported in literature [1,2,13]. In short, the particles were prepared by heating 2 grams of ammonium tungstate pentahydrate (ATP; >99%; Kanto Chemical Co., Inc., Japan). The heating process was done using a commercial electrical furnace under a fixed condition (a heating rate of 50 °C/min and a holding time at 800°C for 30 min) in the atmospheric condition. To gain WO_3 with a monoclinic phase, the heating process was subsequently followed by a cooling process to room temperature (a cooling rate of 50°C/min).

In addition, in order to obtain the properties of the specimen, physical observation was performed using a Scanning Electron Microscope (SEM; SEM, JSM-6360LA; JEOL Ltd., Japan) and a Transmission Electron Microscope (TEM, JEOL JEM-1400, JEOL Ltd., Japan). Then, the resulted images were applied into Feret analysis to obtain the particle outer diameter and morphology. In order to analyze the chemical composition and the crystal structure of the specimen, a Fourier Transform Infrared Spectroscopy (FTIR; FTIR-4600, Jasco Corp., Japan) and a powder X-ray diffraction (XRD; XRD; PANalytical X'Pert PRO; Philips Corp., The Netherland) were utilized, respectively.

Nanoindentation Technique. In order to evaluate the elastic modulus and micro-hardness, the WO_3 specimen was tested by a nanoindentation test technique (TriboScope®, Hysitron, US) based on Oliver and Pharr Method[21]. The nanoindentation test equipment was completed with portable add-on equipment to scanning probe microscope (SPM, SPM-9500J3, Shimadzu Corp., Japan). It uses a capacitive force/displacement transducer that generates the loading force and measures both force and displacement data.

Before mounting the specimen to the SPM plate, the specimens were diluted into the methanol and spread out into the specimen holder. Force penetrations were located on several arbitrary particle surfaces in order to get technically statistical data. Prior to every test, calibration is conducted using an air indent method.

In order to obtain the force and displacement relationship, the indenter was first loaded to the peak load by certain time both set up by the user and then unloaded according to the defined profile. Loading rate for all testing was kept constant at 2 μN/s. Force control-type input was employed. The max load for each specimen was determined based on the preliminary tests which show the most suitable force and displacement curve. Each maximum load measurement was done at least 6 times at different locations. In addition, as a standard analysis, aluminum bulk plate was used. Using the same procedure, we also examined the mechanical properties of ATP particles.

3. Results and Discussion

Figure 1 shows the physicochemical properties of WO_3 used as the specimen in this study. The physical appearance of the specimen is a yellowish green powder (Fig. 1(a)), which is different from its originated ATP (white powder) [13]. The SEM image in Fig. 1(b) confirmed that the prepared particles were in the micrometer range with mean sizes of about 60 μm. The high-magnified SEM image (Fig. 1(c)) confirmed the rough surface, indicating the aggregated of crystal structure inside the particles. To verify the aggregate structure, Fig. 1(d) presents the TEM image of the particles. The TEM image identified that the particles are relatively dense (no porous structure).

The FTIR analysis in Fig. 1(e) showed that the particles were tungsten-related materials, in which this was detected by the appearance of peaks at wavenumber of less than 1000 cm^{-1} [13]. The XRD analysis in Fig. 1(f) also verified the structure of monoclinic-type WO_3 material, based on the joint committee for the powder diffraction system (JCPDS) no. 72–1465[2].

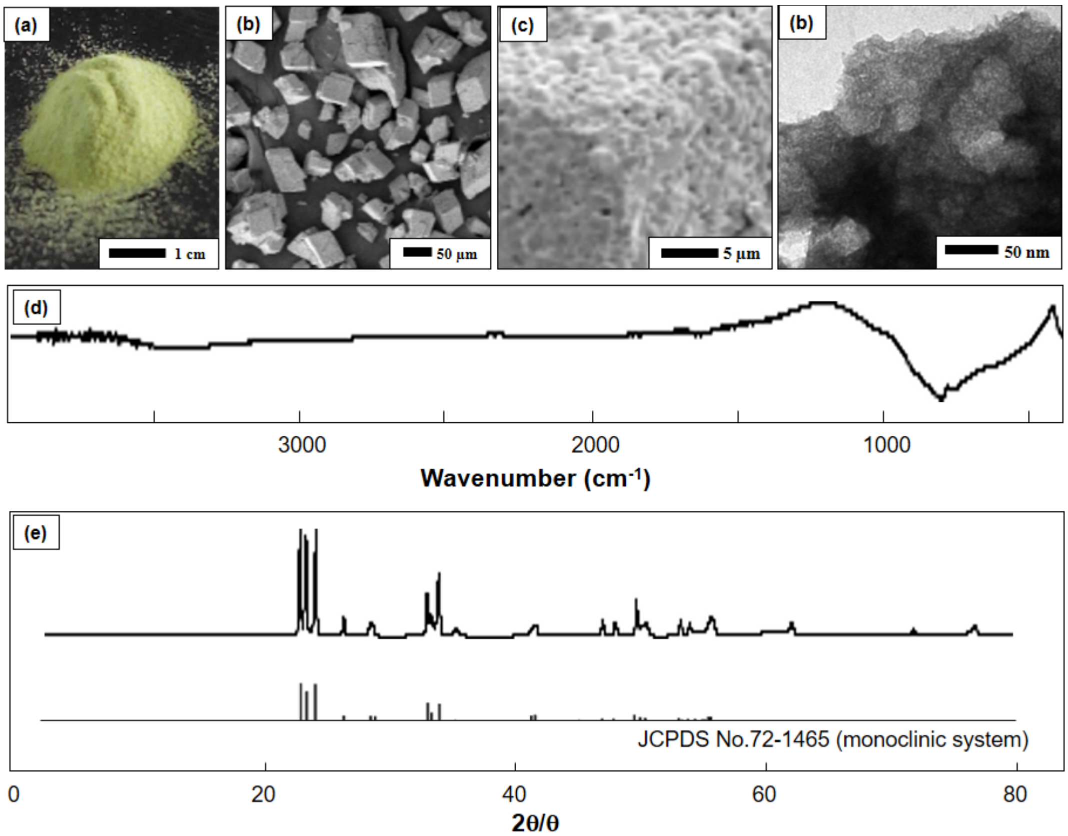

Fig. 1. (a) the photograph image, (b) the low-magnified SEM image, (c) the high-magnified SEM image, (d) the TEM image, (e) FTIR analysis, and (f) XRD results of WO_3 specimen

The typical nanoindentation test results of the WO_3 microparticles are shown in Fig. 2. As a comparison, we also analyzed the initial ATP particles. The results showed force-displacement curve for nanoindentation of WO_3 particles on 6 different locations with constant controlled maximum load (i.e., 200 µN) and loading rate. The final displacement after unloading for one and other data varies as far as more than 2000 nm. This is still less than 10% of the average particle diameter. Moreover, the loading slope of one and other curves has some discrepancies. This result implies that WO_3 particles have the inhomogeneity characteristics. This could be due to inclusions, precipitates, or oxides that present on the specimen at micro-scale (see Fig. 1(c)). However, in overall, all force-displacement curves showed similar tendency.

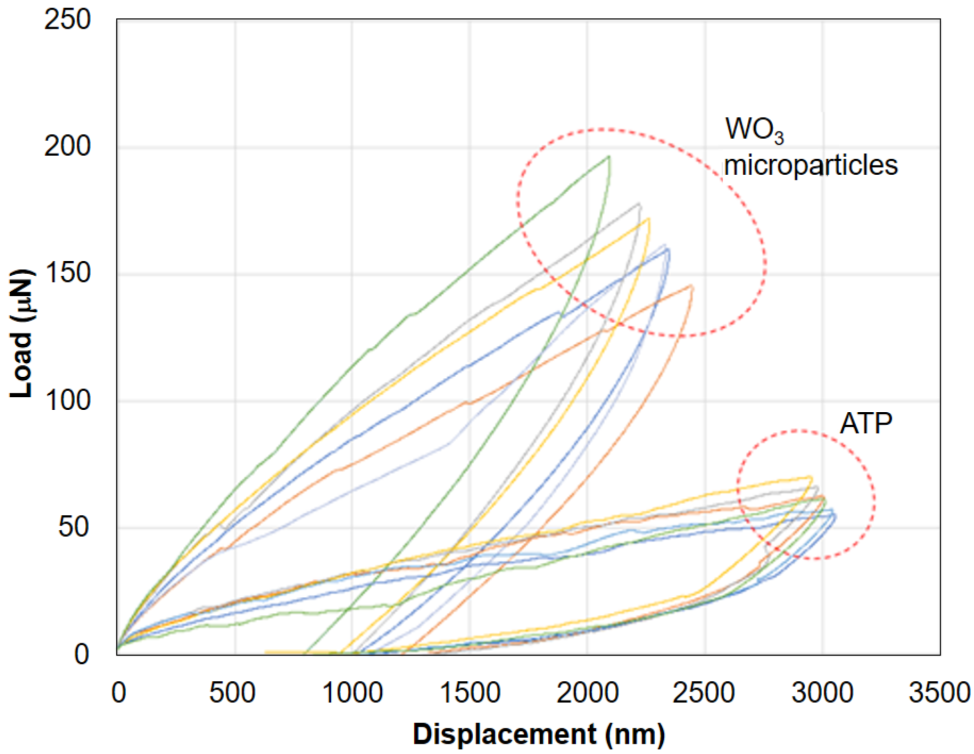

Fig. 2. Typical force-displacement curves of ATP and WO_3 microparticles obtained from nanoindentation tests

By Oliver and Pharr method[21], analysis on the elastic modulus and micro-hardness of ATP and WO_3 particles were conducted. Figure 3 shows the measurement results. Here, the measured elastic modulus is the effective value which still contains some effects from the substrate as well as the indenter (Berkovich indenter). Because in this study the same substrate and indenter were used for every test, therefore, the measured value can be compared to evaluate the mechanical properties' tendency. However, if the true value is required, we need to extract the effect of substrate and indenter from the measured value.

Based on the measurement results, it is obvious that WO_3 particles (produced after heating ATP at 800°C) shows a significant increase in the values of elastic modulus and micro-hardness by 10 and 40 times, respectively. This indicates the measurement was able to show the different mechanical properties from each specimen. As a validation, the same test was also done on Aluminum bulk specimen with maximum load of 1000 µN. The result demonstrated good accuracy for analyzing the values of elastic modulus and micro-hardness of WO_3 materials as also reported in the literatures [6].

The above mechanical properties data revealed that the micrometer-sized WO_3 particles have excellent mechanical properties. The mechanical properties in elastic modulus and micro hardness increased compared to the initial ATP raw material. We believe that this data can inform that the use of micrometer-sized WO_3 particles is potentially used for various processes involving extreme conditions such as high pressure reaction.

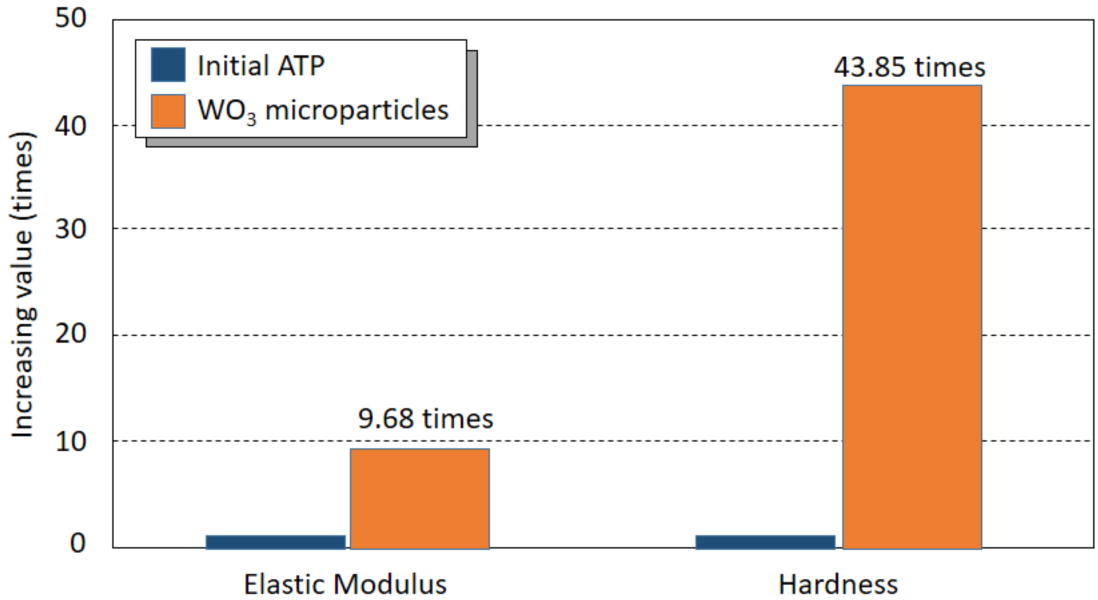

Fig. 3. Increases in Elastic Modulus and Hardness values of ATP and WO_3 microparticles

4. Conclusion

Micromechanical characteristics of WO_3 micron particles have been investigated using a nanoindentation test technique from which the elastic modulus and micro-hardness values were evaluated and compared with ATP particles. Although in overall the measured force-displacement curve showed similar tendency, we found an important phenomenon that revealed the inhomogeneity characteristics of WO_3 particles as indicated by the variety of force-displacement curve. This could be caused by the micro-scale characteristics of the specimen due to the existence of inclusions, precipitates, and oxidizes generated during the synthesis of WO_3. The results also confirmed that the elastic modulus and hardness values of WO_3 are in a good agreement with literature, demonstrating that the present results gives additional information for further studies in mechanical properties of WO_3 material. Furthermore, it was also revealed that the WO_3 micron particles have significantly higher values of elastic modulus and hardness compared with that of ATP particles.

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