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Original Research Paper

Synthesis of high-purity micro-spherical ruthenium particles by chemical refining method

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ABSTRACT

Ruthenium is widely used as magnetic recording and electrode materials. In this study, high-purity micro-spherical Ru particles were synthesized from crude ruthenium sequential by distilling, precipitation, dry spraying and ignition. Impurities in the starting Ru powders were eliminated by distilled and precipitated treatments. The morphology and size of as-synthesized Ru particles were controlled by dry spraying and ignition processes. The influences of heating rate in ignited treatment on the morphology and size of Ru particles were investigated. The purity of as-synthesized Ru particles was higher than 99.995 wt%, and the average size was about 12 μm. It should be noted that the powder technology in this study could be applied to synthesize other metals particles with high-purity requirement.

1. Introduction

The applications of ruthenium as magnetic recording material (hard digital disk, HDD) and electrode material are rapidly expanding [1–4]. Those kinds of HDD or electrode are generally fabricated by sputtering Ru target. In order to guarantee the operational performance as a reliable electronic device, it is important to minimize impurities in the Ru target that are deleterious to the device. The impurities that must be removed to minimum contents include alkali metals, transition metals and radioactive elements. Alkali-metal elements such as Na and K easily migrate in the gate insulator and cause the MOS-LSI interfacial quality to deteriorate. Transition metal elements such as Fe, Ni, Co, Cr and Cu cause trouble at the interface bonding. Radioactive elements such as U and Th cause a soft error of element due to alpha emitted from such elements [5].

Normally, foregoing Ru targets were manufactured using powder metallurgical techniques such as hot pressing (HP), hot isostatic pressing (HIP) and spark plasma sintering (SPS) [6–8]. Impurities included in the Ru powder neither be increased nor decreased after the sintering process. Therefore, synthesis of high-purity Ru powder is the crucial process of Ru target fabrication. Shindo and Hisano [9] synthesized a high purity ($\geqslant$99.995 wt%) Ru powder by electrolytic refining from the crude Ru powder ($\leqslant$99.9 wt%). The Ru powder wherein the content of the respective alkali metal elements such as Na and K were 10 ppm or less, and the content of Al was the range of 1 to 50 ppm. But the morphology and particle size of the refining Ru powder were uncontrollable. Lu et al. [10] synthesized the chain-like Ru nanoparticle array by liquid chemical reduction process. The obtained chain-like Ru nanoparticle arrays showed high activity in hydrogenation of phenol with broad concentration. However, the purity of Ru powder was not enough due to the limitation of the liquid chemical processing. To development high purity, controllable size and morphology Ru powder is desirable.

In this study, we present a chemical refining process, with which high-purity micro-spherical ruthenium particles are synthesized. To best of our knowledge, there is no report on the kind of Ru powder. A good understanding of the processing conditions is crucial to the reliability of Ru powder and further Ru target, and is also significant for the further development of refining technique for high-purity materials.

2. Materials and methods

All reagents and solvents were used as received without further purification. Crude ruthenium powder ($\leqslant$99.95 wt%) was purchased from Sino Platinum Metals (Yimen) Co. LtD. (Yimen, Yunnan, P.R. China), high purity chlorine (Cl_2) and hydrogen (H_2) from Pengyida Co. LtD. (Kunming, Yunnan, P. R. China), guarantee grade sodium hydroxide (NaOH), ammonium chloride (NH_4Cl), hydrochloric acid (37.5 wt%, HCl) and ethanol from Sigma (St. Louis, MO). The self-made distilled water was used as the solvent.

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The crude Ru powder was heated (85 °C) and dissolved in NaOH solution, and a stream of Cl_2 passed through it causing the ruthenium to distill as the tetroxide (RuO_4) which was collected in a solution of hydrochloric acid (6 mol/l), from which H_2RuCl_6 can be obtained [11]. The high-purity $(NH_4)_2RuCl_6$ powder was precipitated from the H_2RuCl_6 solution by addition of NH_4Cl. The $(NH_4)_2RuCl_6$ powder was, then, spraying dried to micro-spherical particles. After that, high-purity micro-spherical $(NH_4)_2RuCl_6$ particles were ignited in N_2/H_2 (Vol 9:1) at 500 °C for 4 h followed by cooling under N_2/H_2. High-purity micro-spherical Ru particles were synthesized.

A commercial dry spraying machine (B290, Buchi, Switzerland) was used to prepare high-purity micro-spherical particles. The thermal decomposition behavior of spraying dried powder was analyzed by Thermogravimetric Analysis-Differential Scanning Calorimetry (TG-DSC, SPA409PC, NETZSCH, Germany) in N_2 atmosphere, 10 °C/min heating rate. The impurities of as-synthesized Ru particles were measured by Glow Discharge-Mass Spectrometry (GD–MS, GD PLUS GD, ELEMENT™, Thermo scientific, U.S.). X-ray diffraction (XRD, Empyrean, PANalytical, the Netherlands, Cu Kα radiation at 40 kV) was performed to analyze the phases of solid materials. The microstructure of $(NH_4)_2RuCl_6$ and Ru particles were observed by Scanning Electron Microscopy (SEM, S-3400 N, Hightech, Japan).

3. Results and discussion

The TG-DSC analysis of $(NH_4)_2RuCl_6$ powder is shown in Fig. 1, where two main thermal decomposed stages located at around 350 °C are observed. Because $(NH_4)_2RuCl_6$ powder was precipitated from H_2RuCl_6 aqueous solution, some NH_4Cl residual would be mixed with $(NH_4)_2RuCl_6$ powder. In the TG-DSC analysis, NH_4Cl completely decomposed when the temperature increased to 255.0 °C, and the as-precipitated powder lost 2.784 wt%. The 1st decomposition temperature range of $(NH_4)_2RuCl_6$ was from 255.0 °C to 353.5 °C, with the peaking temperature at 334.5 °C. At this stage, the weight declined by 30.962 wt%. With the temperature elevating, the 1st stage solid residual kept decomposing. The 2nd decomposition temperature range was from 353.5 °C to 418.8 °C, with peaking temperature at 367.0 °C. At this stage, the weight continuously decreased by 29.244 wt%. The final solid residual was 31.99 wt% of the precursor powder. According to the stoichiometric ratio of Ru in $(NH_4)_2RuCl_6$ compound, the as-ignited powder should be Ru. This is consistent with the $(NH_4)_2RuCl_6$ thermal decomposition [12]. The chemical transforming process of $(NH_4)_2RuCl_6$ thermal decomposition would be described as follows:

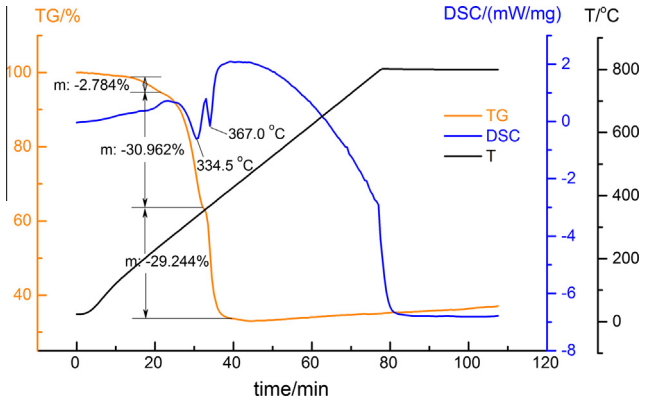

Fig. 1. TG-DSC analysis of as-precipitated $(NH_4)_2RuCl_6$ powder.

1st decomposed stage

$$(NH_4)_2RuCl_6 \xrightarrow{255\ ^\circ C-353\ ^\circ C} RuCl_4 + NH_3 \uparrow + 2HCl \uparrow$$

2nd decomposed stage

$$RuCl_4 \xrightarrow{353\ ^\circ C-418\ ^\circ C} Ru + 2Cl_2 \uparrow$$

The XRD pattern of as-precipitated $(NH_4)_2RuCl_6$ powder is shown in Fig. 2a. However, it should be noted that $(NH_4)_2RuCl_6$ is not listed in the International Centre for Diffraction Data (formerly Joint Committee on Powder Diffraction Standards JCPDS 7-240 database) [13]. After ignited at 500 °C in N_2/H_2 (Vol 9:1) for 4 h, $(NH_4)_2RuCl_6$ was completely decomposed and transformed into Ru powder (hexagonal phase, PDF 03-065-1863), as is shown in Fig. 2b. The result is consistent with TG-DSC measurement of $(NH_4)_2RuCl_6$ powder.

The microstructures of as-precipitated $(NH_4)_2RuCl_6$ and spray dried $(NH_4)_2RuCl_6$ particles are shown in Fig. 3. The $(NH_4)_2RuCl_6$ powder was precipitated from H_2RuCl_6 solution. To control the high-purity property of precipitation, no any other reagents was added. Thus, as-precipitated $(NH_4)_2RuCl_6$ particle shows its natural morphology (piece-like), as observed in Fig. 3a. The size distribution of as-precipitated particles is between nano to micro. After spraying dried treatment, the $(NH_4)_2RuCl_6$ pieces were agglomerated and transformed into well-dispersed micro-sized ball-like particles (Fig. 3b). The particle sizes of spray dried $(NH_4)_2RuCl_6$ are between 15 and 30 μm, and the average size is about 24 μm. The $(NH_4)_2RuCl_6$ particles are incompact with very rough surface, where several pores are observed. It should be noted that the feature is a typical morphology of spraying dried particles [14].

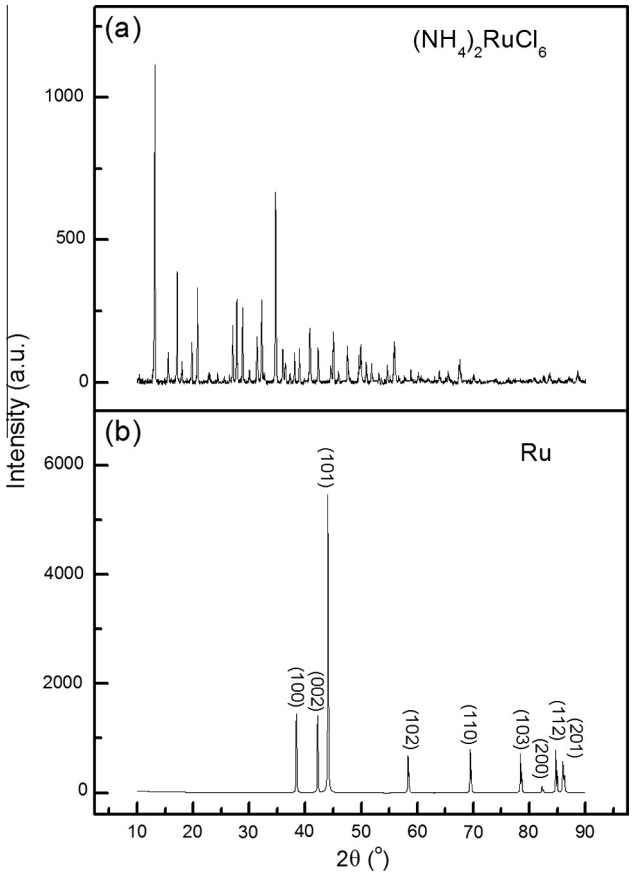

Fig. 2. X-ray diffraction patterns of as-precipitated $(NH_4)_2RuCl_6$ powder and as-synthesized Ru powder. (a) $(NH_4)_2RuCl_6$; (b) Ru.