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Processing and properties of high-purity micro-lamellate $(NH_4)_2RuCl_6$ particles

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Abstract: $(NH_4)_2RuCl_6$ is an important precursor in the synthesis of Ru powder with high-purity requirement. In this study, high-purity (>99.999 wt%) micro-sized $(NH_4)_2RuCl_6$ pieces were synthesized by distillation and precipitation from crude Ru powder. Then, the thermal decomposition behavior of the $(NH_4)_2RuCl_6$ pieces was investigated. The decomposition process included two stages. First, $(NH_4)_2RuCl_6$ was decomposed from 255.0°C to 314.0°C, with the endothermic peak located at 309.4°C. At this stage, HCl and NH_3 were released, while the dense micro-pieces were transformed to loosened micro-pieces due to the thermal decomposition. Then, the solid phase $[(NH_3)_4Ru_3Cl_{12}]$ kept decomposing from 314.0°C to 352.7°C, HCl and N_2 were released, and agglomerated Ru particles were achieved. Thermogravimetric analysis-differential thermal analysis-mass spectrum coupling (TG-DTA-MS) was used to monitor the thermal decomposition process and identify the released gaseous phases, respectively. The solid phases in different stages were characterized by high-temperature X-ray diffraction (HTXRD). A good understanding of the processing and thermal decomposition of $(NH_4)_2RuCl_6$ is crucial in the creation of Ru products.

Keywords: $(NH_4)_2RuCl_6$; HTXRD; ruthenium; TG-DTA-MS; thermal decomposition.

1 Introduction

The applications of high-purity ruthenium as magnetic recording material (hard digital disk, HDD) and electrode material are rapidly expanding [1–10]. The $(NH_4)_2RuCl_6$ compound is one of the most important precursors in the synthesis of Ru powder with high-purity requirement, because it is easily prepared at room temperature and can be totally decomposed at 600°C [11–14]. Rhys [15] reviewed the fabrication and properties of ruthenium, and demonstrated that high-purity Ru powder can be achieved by ignited high-purity $(NH_4)_2RuCl_6$ powder. In our previous study, well-dispersed high-purity (>99.995 wt%) micro-spherical ruthenium particles were synthesized from raw Ru powders (<99.9 wt%) by chemical refining method, and in that work, $(NH_4)_2RuCl_6$ served as the precursor of as-synthesized Ru particles [16]. However, few details on the properties of the $(NH_4)_2RuCl_6$ compound have been published based on experimental results. Even the X-ray diffraction information of $(NH_4)_2RuCl_6$ compound is not listed in the International Centre for Diffraction Data (formerly known as the Joint Committee on Powder Diffraction Standards JCPDS 7–240 database) [17]. More importantly, the purity of $(NH_4)_2RuCl_6$ should be improved due to the development of the recording materials. Hence, studying the detailed processing and properties of $(NH_4)_2RuCl_6$ compound is desirable for the development of the ruthenium industry.

The current study shows the processing and properties of high-purity micro-lamellate particles from crude ruthenium sponge by using the method of chemical separation combined with chemical precipitation. The processing technologies in this study are environmental-friendly, because it does not generate any waste products. The purpose of this investigation is to acquire more detailed information on the processing and thermal decomposition behavior of $(NH_4)_2RuCl_6$, so that the thermal decomposed processing can be controlled by adjusting the decomposition conditions. A good understanding of the thermal decomposition of $(NH_4)_2RuCl_6$ is not only crucial to the reliability of Ru powder and further creation of Ru products, it is also significant to the further development of the platinum group metals (PGM) industry.

2 Materials and methods

2.1 Materials

All reagents and solvents were used as received without further purification. Crude ruthenium powder (≤99.9 wt%) was purchased from Sino Platinum Metals (Yimen) Co., Ltd. (Yimen, Yunnan, P.R. China),

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and the high purity chlorine (Cl_2) came 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 came from Sigma (St. Louis, MO, USA). The self-made distilled water was used as the solvent.

2.2 Synthesis of $(NH_4)_2RuCl_6$ powder

To avoid the interferences of contaminations, high-purity $(NH_4)_2RuCl_6$ powder was synthesized from crude Ru powder by chemical refining method (oxidation distillation + chemical precipitation). The starting 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). The product was then collected in a solution of hydrochloric acid (6 mol/l), from which H_2RuCl_6 can be obtained. Then, the saturated NH_4Cl solution was slowly added into the H_2RuCl_6 solution with high-speed magnetic stirring. The high-purity micro-lamellate $(NH_4)_2RuCl_6$ particles were achieved.

2.3 Analysis and characterization

The ruthenium content and purity of as-synthesized powder was measured by inductively coupled plasma-atomic emission spectrometry (ICP-ASE, Optima 5300 DV, PerkinElmer, USA). The oxygen-nitrogen analyzer (G8 GALILEO ON/H, Bruker, USA) was employed to measure the nitrogen content in the as-synthesized compound. The solid phases in different stages were characterized by high temperature X-ray diffraction (HTXRD, 9-KW SmartLab®, Rigaku, Japan). The thermal decomposition behavior and released gas of $(NH_4)_2RuCl_6$ powder during the heat treatment was measured by the thermogravimetric analysis-mass spectrum coupling (TG-MS, QMS 403D Aëolos®, Netzsch, Germany) in He atmosphere and at 5°C/min heating rate. The microstructure of $(NH_4)_2RuCl_6$ particles and thermal decomposed products were observed by scanning electron microscopy (SEM, S-3400N, Hitachi, Japan).

3 Results and discussion

3.1 Elemental analysis

The element analysis results of starting Ru sponge and as-synthesized $(NH_4)_2RuCl_6$ powder are shown in Table 1, where Ru, N, and several impurity elements are listed. The impurities in the starting Ru sponge exceeded 500 ppm, thus indicating that the purity of starting Ru sponge was lower than 99.95 wt%. The ruthenium and nitrogen contents in the compound were 28.89 and 8.00 wt%, respectively, which coincided with the theoretical stoichiometric ratio of the $(NH_4)_2RuCl_6$ compound. After the chemical refining processes described in this study, all the element contents of the impurities effectively decreased. In the as-synthesized $(NH_4)_2RuCl_6$ powder, the Na, Ca, and Si contents were 1.3, 1.2, and 2.9 ppm, respectively. The purity of refined $(NH_4)_2RuCl_6$ powder was higher than 99.999%. Thus, the impurities in the raw Ru sponge could be effectively reduced through the chemical refining process.

Table 1: Element analysis of the as-synthesized $(NH_4)_2RuCl_6$ powder.

Elements	Ru sponge	As-synthesized $(NH_4)_2RuCl_6$ powder
Main (wt%)	–	28.89
Ru	–	8.00
N	–	
Impurity (ppm)		
Na	80.3	1.3
K	40.7	<1
Ca	38.2	1.2
Al	110.1	<1
Si	33.0	2.9
Fe	148.8	<1
Cr	21.2	<1
Cu	43.9	<1
Mg	21.6	<1

3.2 Thermal analysis

The thermal decomposition behavior and released gases of the $(NH_4)_2RuCl_6$ powder during the heat treatment was measured by TG-DTA-MS in He atmosphere at 5°C/min heating rate. The thermograms recorded for $(NH_4)_2RuCl_6$ are shown in Figure 1. As can be seen, a slight weight loss (2.191 wt%) occurred between room temperature and 255°C. The $(NH_4)_2RuCl_6$ compound is hygroscopic, which means it can readily absorb moisture in air. Thus, when the $(NH_4)_2RuCl_6$ powder was heated, the moisture evaporated. The thermal decomposition of

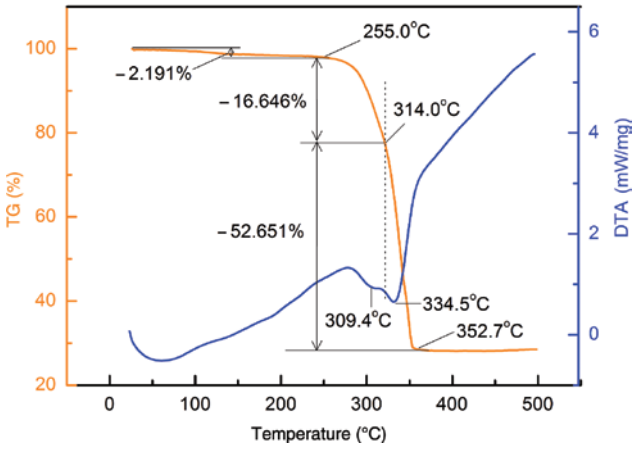

Figure 1: TG-DTA analysis of the as-synthesized $(NH_4)_2RuCl_6$ powder.

$(NH_4)_2RuCl_6$ took place in two consecutive stages with weight losses, for which the inflection point coincided with the temperature corresponding to the endotherms or exotherms in DTA trace in the presence of He. When the heat was applied, the weight loss was initiated, and the first intense endothermic peak was observed at 309.4°C, corresponding to the loss of the evaporation of gas from the precursor, i.e. $(NH_4)_2RuCl_6$. Further, the precursor should be changed into other Ru compound(s). This was followed by another weight loss. A quick weight loss was also observed in the temperature range of 314.0°C–352.7°C, which appeared in the TG curve due to the evolution of gases by the decomposition of the Ru compound(s). After 352.7°C, the TG trance became stable with no further weight loss; there were also no peaks to indicate the formation of Ru metal.

The theoretical MS analysis data of HCl, NH_3 and N_2 are shown in the left side of Figure 2. The released gases of $(NH_4)_2RuCl_6$ in thermal decomposition process were recorded by mass spectrum (MS), as shown in Figure 2 (right side). According to the theoretical data of MS, HCl and NH_3 were analyzed at 313.7°C (in the 1st decomposed stage), indicating that the original $(NH_4)_2RuCl_6$ powder was transformed into other Ru compounds as well as released HCl and NH_3 gases. As the temperature increased, HCl and N_2 were detected at 352.2°C, indicating that the 2nd thermal decomposed stage of $(NH_4)_2RuCl_6$ powder released HCl and N_2 gases (Figure 2B). By referring to the result of TG-DTA analysis, no gas signs were measured, (Figure 1), suggesting that the thermal decomposition process of $(NH_4)_2RuCl_6$ powder was completed.

3.3 Microstructural characterization

Based on the TG-DTA-MS analysis, HTXRD was used to characterized the solid phases [original $(NH_4)_2RuCl_6$ powder thermal decomposition process] in four different temperatures of 20°C (room temperature), 314°C, 352°C, and 500°C, respectively, as shown in Figure 3. The heating rate was 5°C/min, and the XRD characterization was initiated after dwelling at each temperature stage for 30 min. The original powder is high-purity $(NH_4)_2RuCl_6$, as shown in Figure 3A and Supplemental Table 1. When the temperature reached 314°C, $(NH_4)_2RuCl_6$ was decomposed into other Ru compounds (Figure 3B). It should be noted that the XRD pattern of the Ru compounds were not listed in the ICDD. When $(NH_4)_2RuCl_6$ was heated at 314°C, NH_3 and HCl were released, and the other solid phase became a residual. Thus, the solid phase should not be the $(NH_4)_2RuCl_6$, but must be transformed to other Ru compound(s). However, it was difficult to identify the detailed characteristics of Ru compound(s). The $(NH_3)_4Ru_3Cl_{12}$ is just the result of theoretical calculation according to the Law of the Conservation of Mass.

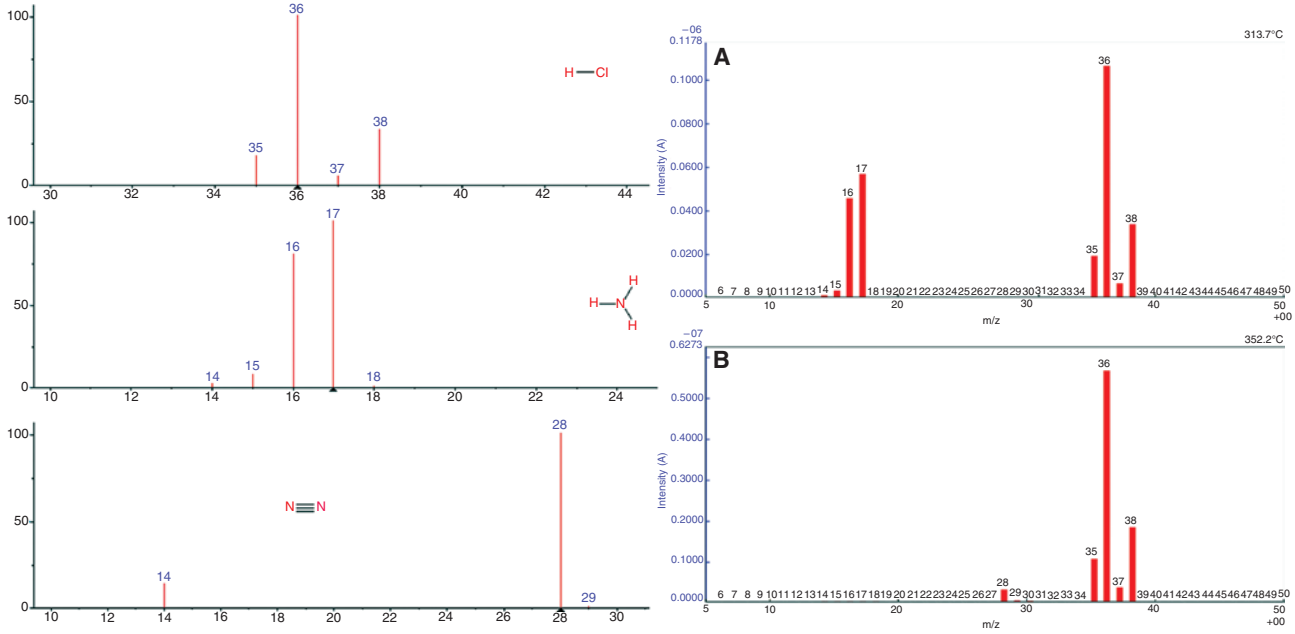

Figure 2: MS analysis of as-synthesized $(NH_4)_2RuCl_6$ powder in different heating temperatures.
(A) 313.7°C, (B) 352.2°C.

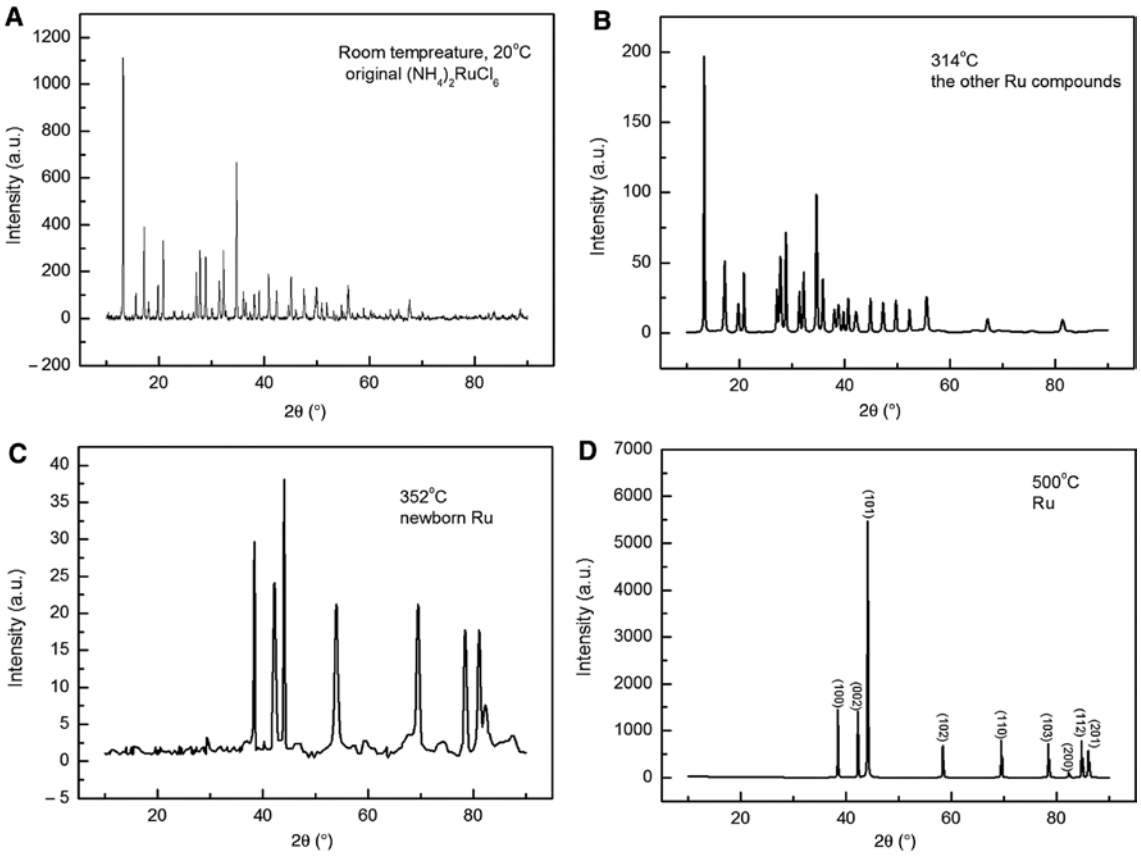

Figure 3: XRD patterns of as-synthesized $(NH_4)_2RuCl_6$ powder and their different thermal decomposition products.
(A) $(NH_4)_2RuCl_6$ powder, (B) heated at 314°C (new Ru compounds), (C) heated at 352°C (newborn Ru), (D) heated at 500°C (Ru).

$(NH_3)_4Ru_3Cl_{12}$ may comprise one Ru compound or a combination of Ru compounds. Ru metal can be characterized when the temperature increased to 352°C (Figure 3C). Given that Ru was just decomposed from Ru compound(s), the crystallization process was insufficient, and the intensity of the newly generated Ru XRD pattern was very weak. The typical Ru XRD pattern when the temperature reaches 500°C is shown in Figure 3D.

The microstructure of the $(NH_4)_2RuCl_6$ powder and its thermal decomposed products are shown in Figure 4. $(NH_4)_2RuCl_6$ pieces with dimensions of about $2\times1.5\times0.2$ μm ($L\times W\times T$) were observed, indicating that well-dispersed $(NH_4)_2RuCl_6$ particles without the addition of any other regents for the high-purity requirement could be obtained by the chemical precipitation technique (Figure 4A). When the $(NH_4)_2RuCl_6$ powder was heated to 314°C, those pieces expanded to dimensions of about 3×1.5 μm ($L\times W$), and many residual nano-pores were observed in the surface (Figure 4B). According to the MS analysis and XRD characterization results, HCl and NH_3 were released during the heat treatment, while the $(NH_4)_2RuCl_6$ was transformed to other Ru compound(s). Therefore, the volume of pieces was enlarged, while many nano-pores remained on the surface. As the heating temperature increased, the new Ru compounds kept decomposing. When the heating temperature reached 352°C, the new Ru compounds were transformed to Ru. Figure 4C shows the irregular shape and dense Ru particles. Although released gases (HCl and N_2) in the 2nd decomposed stage were observed, newly generated Ru decomposed from the Ru compounds agglomerated together due to the high surface energy and atomic diffusion. Therefore, the volume of particles shrank, thus leading to agglomerated Ru particles.

According to the TG-DTA-MS analysis, when combined with the HTXRD characterization, $(NH_4)_2RuCl_6$ powder was decomposed to HCl, NH_3, and other Ru compounds. Then, the Ru compounds continued to decompose to Ru, HCl, and N_2. Hence, the chemical equation of the chemical reaction is described by

$$3(NH_4)_2RuCl_6 \rightarrow 3Ru + 18HCl\uparrow + 2NH_3\uparrow + 2N_2\uparrow.$$

The released gases include N_2, which is different from the preceding report [18]. After the 1st thermal

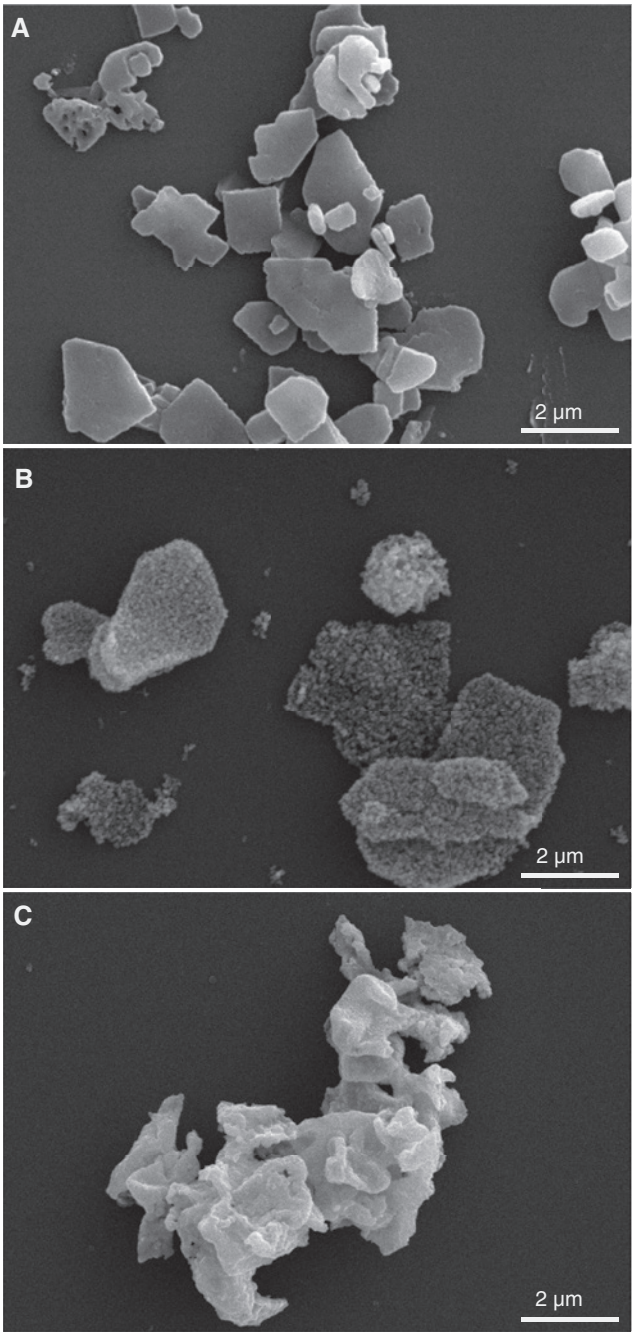

Figure 4: Microstructures of as-synthesized $(NH_4)_2RuCl_6$ powder and their different thermal decomposition products.
(A) $(NH_4)_2RuCl_6$ pieces, (B) after heating at 314°C (new Ru compound particles), (C) after heating at 352°C (Ru agglomerated particles).

decomposed stage, nitrogen element may have changed from NH_4^+ to NH_3 because of the heating environment. While some NH_3 were released from the compound, other NH_3 coordinated with Ru to transform to other Ru compounds. The released H^+ from NH_4^+ combined with Cl to become HCl. Hence, the chemical formula of the Ru compounds could be $(NH_3)_4Ru_3Cl_{12}$, and the 1st decomposed stage is given by

$$3(NH_4)_2RuCl_6 \rightarrow (NH_3)_4Ru_3Cl_{12} + 6HCl\uparrow + 2NH_3\uparrow.$$

Then, because of NH_3-coordinated bonds with Ru, NH_3 was oxidized by Ru (IV) to become N_2, and the final released gases were HCl and N_2. At this point, Cl_2 cannot be released in the $(NH_3)_4Ru_3Cl_{12}$ compound, because Cl^- is more stable than NH_3 in a senior oxidized circumstance (Ru IV). The 2nd decomposed stage is given by

$$(NH_3)_4Ru_3Cl_{12} \rightarrow 3Ru + 2N_2\uparrow + 12HCl\uparrow.$$

4 Conclusions

To summarize, high-purity (99.999 wt%) micro-lamellate $(NH_4)_2RuCl_6$ particles were achieved from crude Ru powder through the chemical separation method. The thermal decomposition behavior of $(NH_4)_2RuCl_6$ was analyzed by TG-DTA-MS combined with HTXRD and SEM techniques. TG-DTA was used to observe the thermal decomposed process. Furthermore, the MS was applied to identify the released gas during the thermal decomposition, and the solid phase transformation was characterized by HTXRD and SEM.

The thermal decomposition of $(NH_4)_2RuCl_6$ includes two stages. First, dense micro-lamellate $(NH_4)_2RuCl_6$ particles are transformed into other Ru compounds $[(NH_3)_4Ru_3Cl_{12}]$ (loosened micro-lamellate pieces) and also released HCl and NH_3 at temperatures ranging from 255.0°C to 314.0°C. Then, the solid kept decomposing to become agglomerated Ru and released HCl and N_2 at temperatures ranging from 314.0°C to 352.7°C. The chemical reaction equations of the thermal decomposition processing are given below.

– 1st decomposed stage (255.0°C–314.0°C):

$$3(NH_4)_2RuCl_6 \rightarrow (NH_3)_4Ru_3Cl_{12} + 6HCl\uparrow + 2NH_3\uparrow$$

– 2nd decomposed stage (314.0°C–352.7°C):

$$(NH_3)_4Ru_3Cl_{12} \rightarrow 3Ru + 2N_2\uparrow + 12HCl\uparrow$$

– The chemical reaction of the $(NH_4)_2RuCl_6$ thermal decomposition:

$$3(NH_4)_2RuCl_6 \rightarrow 3Ru + 18HCl\uparrow + 2NH_3\uparrow + 2N_2\uparrow$$

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Bionotes

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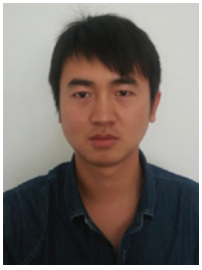

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