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ARTICLE

Preparation of Spherical Scandium Oxide Powders by Ammonium Bicarbonate Precipitation

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Abstract: The preparation of spherical scandium oxide powders by ammonium bicarbonate precipitation was investigated. The carbonate containing scandium was prepared in the solution with $ScCl_3 \cdot XH_2O$ as precursor. The effect of reaction temperature, amount of precipitant and stirring speed on the recovery of scandium was discussed. The effect of pH on the crystalline structure and particle size of carbonate containing scandium was characterized by the powder X-ray diffraction and laser particle sizer. Results demonstrate that the structure of carbonate containing scandium changes from non-crystalline structure to crystalline structure with increasing the reaction pH value. It indicates that when the initial change pH value is about 6, the crystalline structure of scandium oxide is cubic structure. Meanwhile, scandium sediment particles with 3.756–103.8 μm in size can be obtained in a certain condition, depending on the pH value,. When the feasible pH value is 7, the D_{50} of scandium sediment can be 6.634 μm. The carbonate containing scandium is used as a precursor for the preparation of scandium oxide. The TG-DTA result indicates that the decomposition temperature of the carbonate tends to about 600 °C. Based on the XRD and IR analysis, it can be concluded that the appropriate calcination temperature for obtained relatively pure scandium oxide is 1000 °C. Meanwhile, the obtained scandium oxide powders were characterized by the laser particle size analyzer, BET and SEM-EDS. The crystallite size of spherical scandium oxide powders is less than 10 μm with a surface area of about 373.952 m^2/g. The microstructure is very homogeneous with spherical structure.

Key words: Sc_2O_3 power; precipitation; spherical structure

With the rapid development of science and technology, the application of the rare earth elements is increasing due to their unique properties. The scandium as an important rare metal has been widely used in emerging industries, such as electronics, airplane construction, rail transportation[1–4]. Scandium (Sc_2O_3) is a cubic structure material (space group, Ia3) that has particular characteristics, such as higher volume refractive index (nH=2.0 at λ=300 nm), band-gap (5.7 eV, corresponding to an ultraviolet (UV) cut-off of 215 nm), melting point (about 2430 °C) and thermal conductivity (17 W/mK) [5–6]. The particular property with excellent thermal conductivity and optics makes scandium base material attractive for applications such as damage-resistant and high-reflection material in light-emitting diodes and high-power pulsed UV lasers, etc[7–8].

Scandium has a special strengthening effect on a variety of materials, such as Sc-strengthened alloys and Sc_2O_3-stabilised ZrO_2 materials. The scandium can result in excellent mechanical properties for the Al or Mg alloy, which is mainly attributed to the grain refinement of scandium element[9–10]. For example, the scandium element improves the strength, thermal resistance, durability and weight property of the alloy, which expands the application of aluminum alloy. When scandium is added into the magnesium alloy for aircraft engines, it can reduce the consumption of electricity and energy[11]. Meanwhile, in recent years, solid oxide fuel cell (SOFC) as the third generation fuel cell, is a new type of all-solid power generation device that converts chemical energy stored in fuel and oxidizer directly and efficiently into energy. With the increasing energy and environmental problem, the

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research of SOFC has become one of the hot spots in the field of energy and materials. The electrolyte is the core component of the whole SOFC, which can effectively enhance the conductivity. Therefore, research on the electrolyte materials is the key to the commercial development of SOFC. Scandium oxide stabilized zirconia is electrolyte material with the highest ionic conductivity in zirconium based solid electrolyte[12–13]. Meanwhile, the thermal barrier coating containing scandium has the best performance and application prospects and is one of the effective surface protective coatings. It has been approved that the thermal barrier coating with scandium has better performance than the pure Y_2O_3-ZrO_2 coating, such as the phase stability at 1400 °C, 5−10 times better resistance, and lower thermal conductivity[14–17].

Therefore, the scandium is very effective in improving the performance of the material. Hence, research on the extraction and preparation of scandium has very important significance for the development of materials and the improvement of their properties. In order to study the extraction of scandium and the preparation of scandium oxide powder materials, the following work was implemented in this study: the recovery of scandium, the physical properties of scandium such as specific surface area, grain size, and crystalline structure, and the microscopic structure of the scandium oxide powder materials. We hope this research can expand the application range of scandium oxide and promote the development of scandium series materials.

1 Experiment

The raw material in this research was scandium chloride, which was prepared by the scandium oxide dissolved with hydrochloric acid. It was prepared into a solution with a certain concentration from 9 g/L to 12 g/L to spare. Meanwhile, 20% solution of ammonium bicarbonate as the precipitant was prepared. At the beginning of the experiment, 200 mL scandium chloride solution was measured and placed into a three holes flask. When the temperature of the reaction system reaches to a certain level, a certain amount of precipitant was added for precipitation reaction under a certain condition of reaction stirring. The aging reaction was carried out for a certain time after adding precipitant. Then, the scandium sediment was obtained by the filtration, washing and drying treatments for the scandium sediment solution system.

The concentration of Sc^{3+} in the scandium-containing sediment was tested by the inductively coupled plasma emission spectroscopy (ICP-OES; Optima 8000, PerkinElmer, USA) to calculate the scandium precipitation recovery. The mass and energy changes with increasing temperature were detected using TG-DTA (TG-DTA; STA449, Netzsch, Germany). Then, the formed phase of the sample during heating process was analyzed by X-ray diffraction (XRD; X`Pert, Philips, Netherlands). Meanwhile, the characterization of the scandium-containing sediment and scandium was conducted by Fourier transform infrared spectroscopy (FTIR; T27, Bruker, Germany). The microstructure of the scandium was analyzed by scanning electron microscopy (SEM-EDS; JSM-6700F, JEOL, Japan). The specific area and pore size distribution of scandium were demonstrated by Brunner-Emmet-Teller (BET; NOVA3200e and iQ, Quantachrome, USA).

2 Results and Discussion

2.1 Scandium extraction results

The reaction temperature has an influence on the scandium precipitation recovery. Fig. 1 demonstrates that in the temperature range of 15−40 °C, with the increase in reaction temperature, the recovery rate of scandium increases first and then decreases. It can be up to about 94% at 30°C and then begins to reduce above 30 °C, which may be because the precipitation reaction speed is relatively low, and the particle size of scandium sediment is relatively small when the reaction temperature is relatively low. It leads to an increase in the solubility of scandium sediment and a decrease in the recovery rate of scandium precipitation. However, the solubility of scandium sediment increases as the continuous reaction temperature increases, which results in the decrease in scandium precipitation recovery. Therefore, the appropriate reaction temperature is 30 °C.

Meanwhile, in the precipitation reaction, the amount of precipitant has an important effect on the precipitation rate. Fig.2 indicates the change of scandium recovery with different

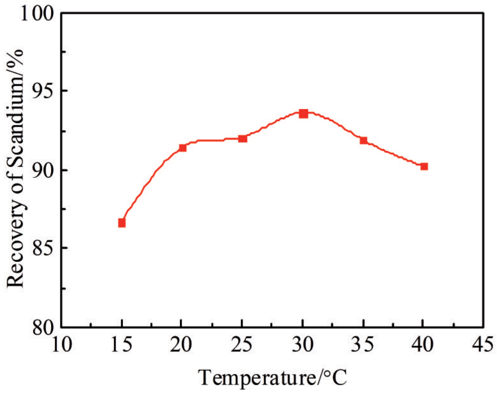

Fig.1 Change of scandium recovery with temperature

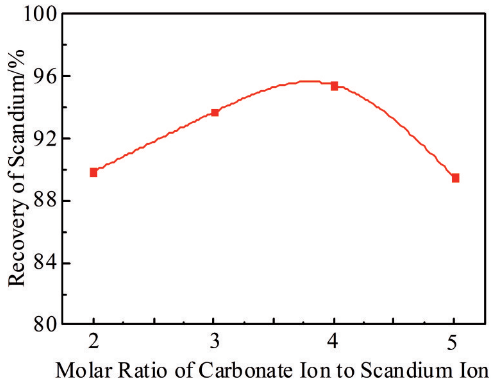

Fig.2 Change of scandium recovery with different amount of precipitant

amounts of precipitant, and the range of molar ratio of carbonate ion to scandium ion is 2–5. It demonstrates that the recovery rate of scandium increases as the molar ratio increases from 2 to 4 and then decreases when the molar ratio is greater than 4.

The intensity of agitation in precipitation reaction directly determines the results of complexation and precipitation reaction. Fig. 3 shows the change of scandium recovery with stirring rate from 100 r/min to 400 r/min. It indicates that the recovery rate of scandium increases as the stirring rate increases from 100 r/min to 200 r/min and then decreases when the stirring rate is greater than 200 r/min. Therefore, the appropriate stirring rate is 200 r/min.

2.2 Influence of pH on scandium sediment and scandium oxide

Fig. 4 shows XRD patterns of scandium sediment obtained at different pH values (pH=4, 5, 6, 7). The reaction pH has an important influence on the crystal structure of scandium sediment. As the reaction pH value increases, the crystal of scandium sediment changes from amorphous structure to crystal structure. The crystal of scandium is amorphous structure when the pH value is less than 6. When the pH value is 6, the crystal structure begins to form in the scandium sediment and the crystal structure gradually improves. The scandium sediment has good crystal structure when the pH is 7. Therefore, in order to obtain scandium sediment with good crystalline structure, the optimum reaction pH value is 7.

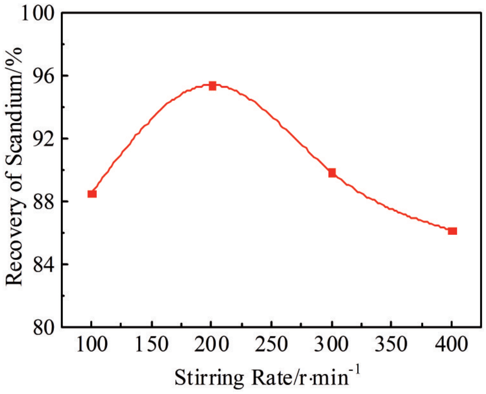

Fig.3 Change of scandium recovery with different stirring rates

Table 1 shows the laser particle size analysis results for scandium sediment obtained at different pH values (pH=4, 5, 6, 7). It demonstrates that D_{50} and D_{90} of the particle obtained at pH=4 is less than 29.72 and 103.8 μm, respectively. When the reaction pH value is 5, D_{50} and D_{90} of the particle change into 11.85 and 36.97 μm, respectively. Meanwhile, when the reaction pH value changes to 7, the D_{50} and D_{90} of the particle change to 6.634 and 10.74 μm, respectively. It indicates that the pH value has an important effect on the particle size of the scandium sediment. The particle size decreases with the increase in pH value. Therefore, suitable pH value should be selected to obtain suitable size of scandium oxide powder to conform the specific requirements.

Fig. 5 shows XRD patterns of scandium oxide obtained at different pH values (pH=4, 5, 6, 7) with the same roasting process conditions at 1000 °C. The material has better crystal structure when the diffraction peak is stronger and sharper. As the reaction pH value increases, the intensity of the diffraction peak increases gradually. The scandium oxide has better crystal structure with increasing the reaction pH value. It demonstrates that the reaction pH has an important influence on the crystal structure of scandium oxide. Therefore, in order to obtain scandium oxide powder with good crystalline

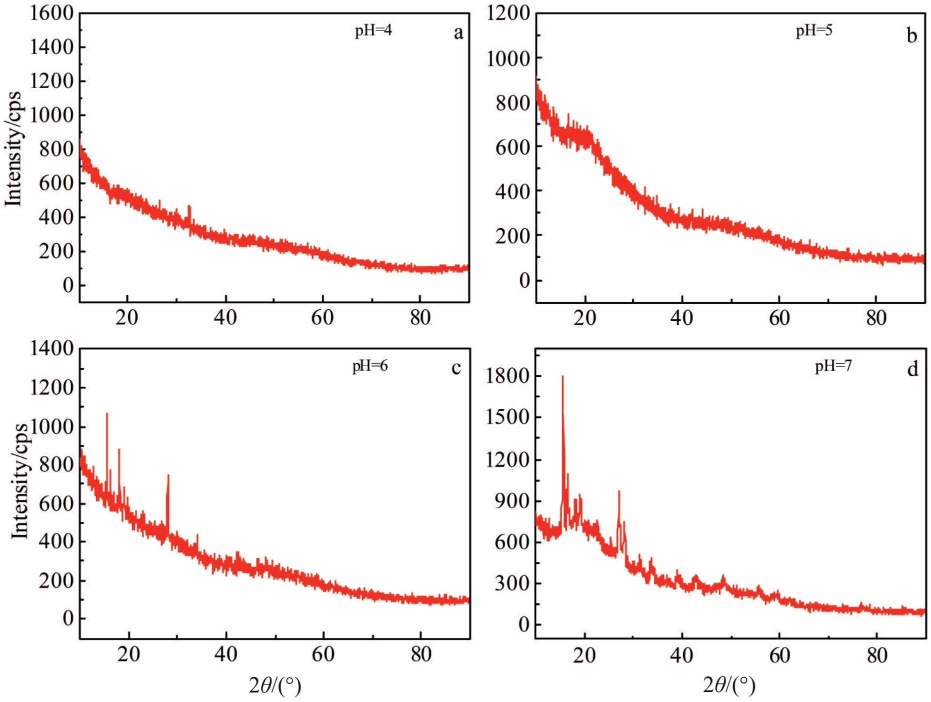

Fig.4 XRD patterns of scandium sediment at different pH values: (a) pH=4, (b) pH=5, (c) pH=6, and (d) pH=7

Table 1 Laser particle size of scandium sediment (μm)

Cumulative distribution	D_{10}	D_{25}	D_{50}	D_{75}	D_{90}
pH=4	4.691	9.191	29.72	67.78	103.8
pH=5	4.246	6.424	11.85	23.26	36.97
pH=6	3.760	5.637	11.44	28.09	45.83
pH=7	3.756	4.785	6.634	8.667	10.74

structure, the optimum reaction pH value is 7.

2.3 Properties of scandium oxide powder materials

TG-DTA test was conducted with the heating rate of 5 °C/min from 20 °C to 1200 °C. Fig. 6 shows the TG-DTA result of scandium sediment. It shows that there is a serious exothermic peak at about 200 °C for DTA curve, which demonstrates the dehydration reaction of scandium sediment. TG curve indicates that the weightlessness of the scandium sediment is mainly divided into three stages. The first stage is from 140 °C to 200 °C with a weightlessness rate of 40.31%; the second stage is from 200 °C to 600 °C with a weightlessness rate of 27.89%; the third stage is from 600 °C to 650 °C with a weightlessness rate of 6.85%. In the first stage, dehydration and dehydroxy reactions occur to produce pure scandium carbonate, which leads to big weightlessness. In the second and third stages, the weightlessness is mainly due to the combustion reaction of carbonate ions, which generate scandium oxide. Therefore, the appropriate roasting temperature should be higher than 650 °C to obtain the pure scandium oxide.

Scandium oxide powder is obtained from scandium carbonate precursor by roasting in tube furnace. Fig. 7 shows the XRD results of scandium oxide prepared by roasting at different temperatures and maintained for certain time (700 °C for 2 h, 900 °C for 2 h, 1000 °C for 2 h and 1000 °C for 5 h). It demonstrates that the scandium oxide powder materials can be obtained by roasting in the temperature range. It can also be seen that the diffraction peak intensity of scandium oxide powder materials increases with increasing the temperature and maintaining time, which demonstrates that the purity of scandium oxide powder materials increases. This is mainly due to the continuous oxidation and volatilization of carbon and nitrogen and other impurities in scandium sediment with the increase in roasting temperature, which increases the purity of scandium oxide power. According to the XRD results, the suitable roasting condition should be 1000 °C for 2 h.

Fig. 8 and Fig. 9 show the FTIR analysis results of scandium carbonate precursor and scandium oxide, respectively. In Fig. 8, it indicates that there is an obvious absorption width peak near 3400 cm^{-1}, which is mainly caused by the stretching vibration of free OH$^-$ in the sample[18]. Meanwhile, there is an absorption peak near 1395 cm^{-1}, which is mainly caused by the OH$^-$ absorption peak of pure water molecules. So, it can be concluded that the generated carbonate precursor contains a certain amount of pure water crystal water. The absorption peak of SO_4^{2-} is mainly distributed in the range of 1040 – 1210 cm^{-1}. However, the absorption peak of Sc-O is near 600 cm^{-1} [18]. Fig. 9 indicates that there is only one absorption peak near 630 cm^{-1}, which is the location of Sc-O. Therefore, it can be concluded that a relatively pure scandium oxide powder material is obtained by the roasting treatment of scandium carbonate precursor.

The size of powder has a certain effect on the energy state of the surface. Smaller particles produce quantum effects that the macroscopic objects do not have. Compared with

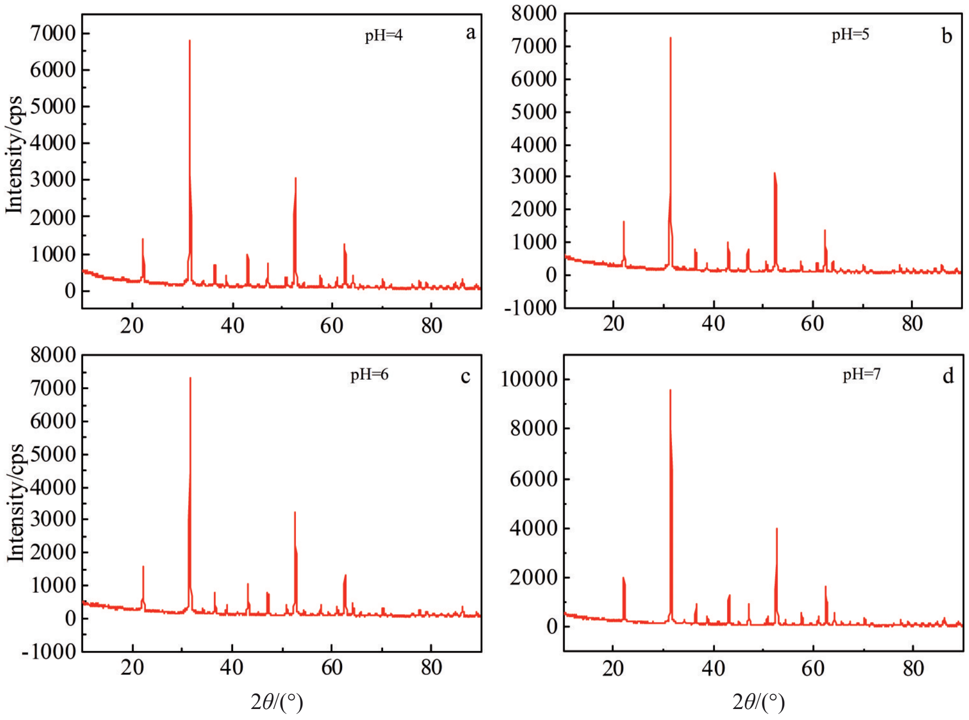

Fig.5 XRD patterns of scandium oxide at different pH values: (a) pH=4, (b) pH=5, (c) pH=6, and (d) pH=7

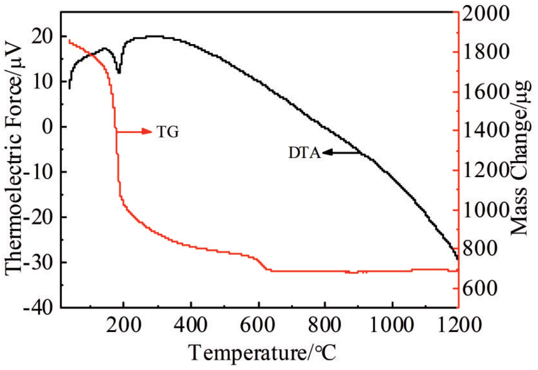

Fig.6 TG-DTA result of scandium sediment

conventional bulk materials, fine powder has a series of excellent physicochemical and surface and interface properties, which can achieve extraordinary effects. Fig. 10 shows the particle diameter of scandium oxide. It indicates that the particle size distribution is relatively concentrated. The particle size is mainly distributed between 6 and 8 μm. Meanwhile, Table 2 shows the cumulative distribution result. It clearly demonstrates that the D_{50} and D_{90} of the particle are 6.913 and 9.468 μm, respectively. Therefore, the submicron grade scandium is obtained by controlling reaction conditions.

The BET test was used to indicate the surface active properties of scandium oxide powder materials. The high specific surface area greatly increases the number of atoms on the surface and enhances the surface activity of the powder. Scandium oxide powder lacks the surface atoms of adjacent coordination, which is extremely unstable and easy to combine with other atoms. Thus, the binding force between nano-powder and application system increases, and the application effect of nano-powder is greatly enhanced. Fig. 11 and Fig. 12 show the absorption-desorption result and pore size distribution result, respectively. The specific surface area of scandium oxide is 373.952 m^2/g. The scandium oxide has a large specific surface area, which results in relatively good reactivity when reacted with other materials. Meanwhile, it can be concluded that the scandium oxide powder material has a certain micropore structure, and its single point average pore radius is 2.88 nm by analyzing the pore size result. Through the BET test analysis of scandium oxide, it can be concluded that the prepared scandium oxide powder materials have good surface activity.

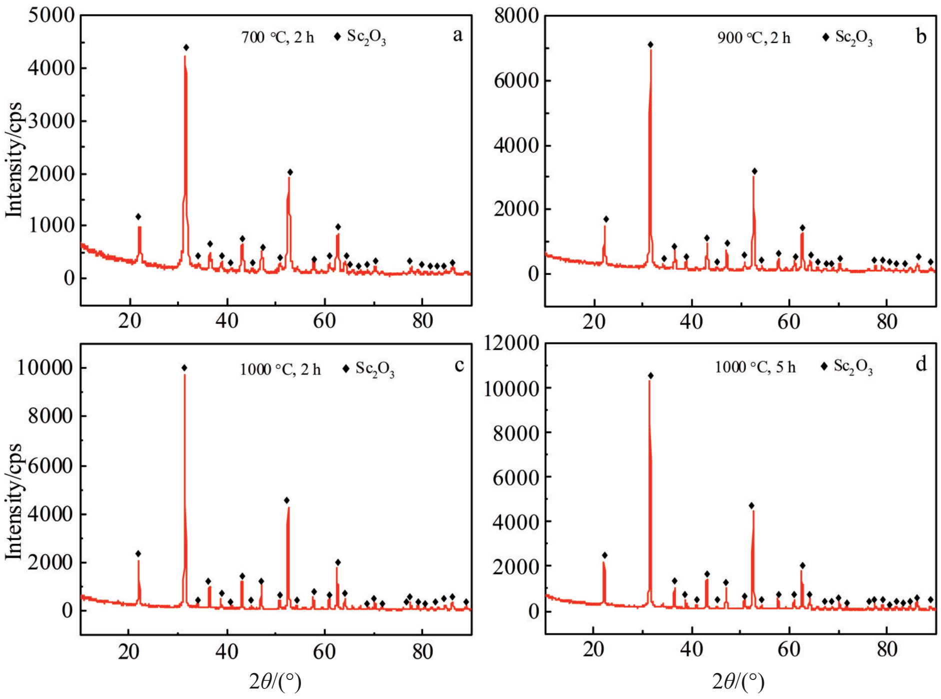

Fig.7 XRD patterns of scandium oxide obtained by roasting under different conditions: (a) 700 °C, 2 h; (b) 900 °C, 2 h; (c) 1000 °C, 2 h; (d) 1000 °C, 5 h

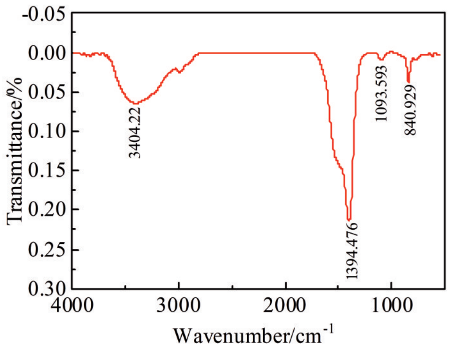

Fig.8 IR result of scandium carbonate precursor

Fig. 13 indicates the SEM morphologies of scandium oxide powder materials roasted at different temperatures and maintained for different time. It demonstrates that the

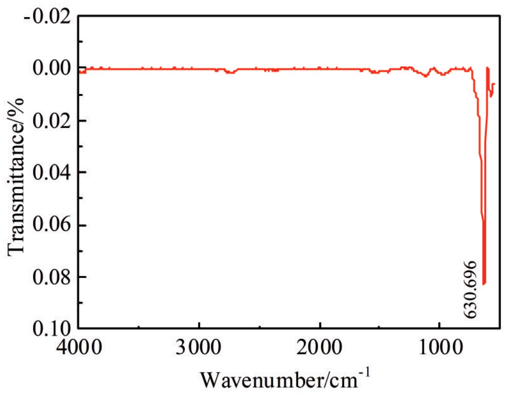

Fig.9 IR result of scandium oxide powder materials

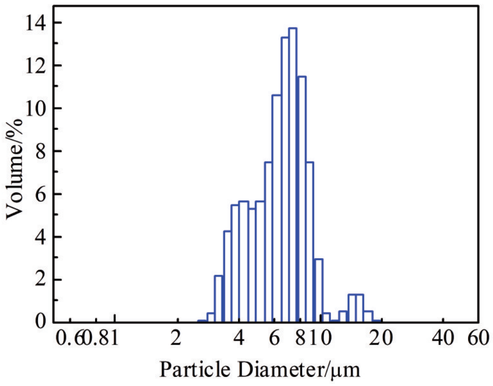

Fig.10 Laser particle size distribution of scandium oxide powder

Table 2 Laser particle size analysis results for scandium oxide powder

Cumulative distribution	D_{10}	D_{25}	D_{50}	D_{75}	D_{90}
Particle size/μm	4.083	5.271	6.913	8.219	9.468

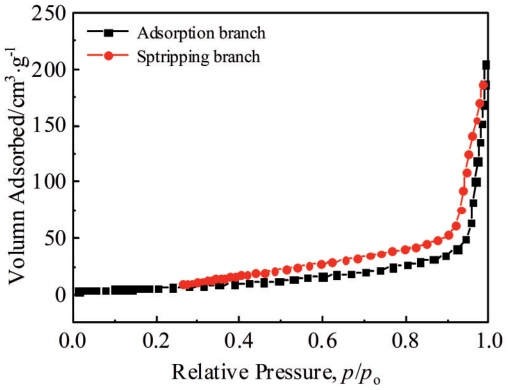

Fig.11 BET result (absorption-desorption) of scandium oxide powder materials

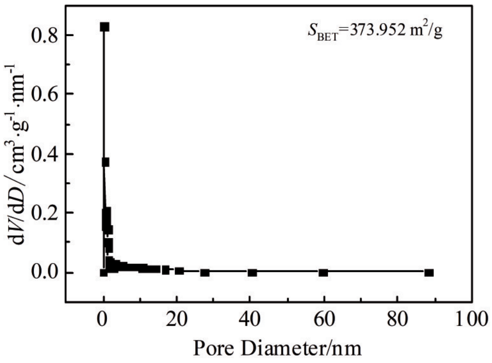

Fig.12 BET result (pore size distribution) of scandium oxide powder materials

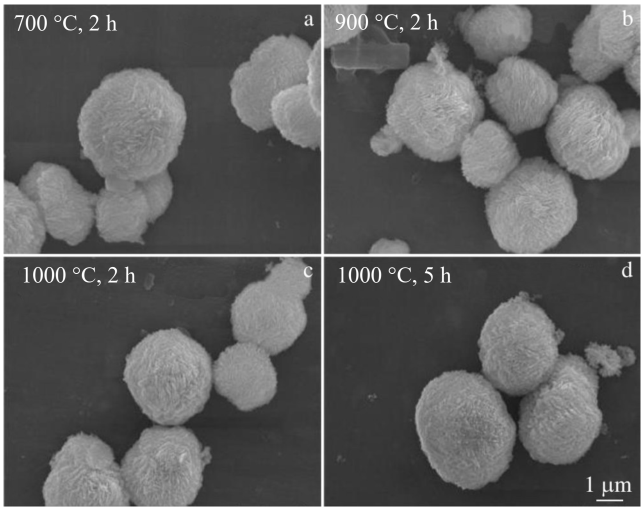

Fig.13 SEM morphologies of scandium oxide powder materials roasted under different conditions: (a) 700 °C, 2 h; (b) 900 °C, 2 h; (c) 1000 °C, 2 h; (d) 1000 °C, 5 h

scandium oxide has regular spherical microstructure. With the increase in temperature from 700 °C to 1000 °C for 2 h, the spherical structure of scandium oxide changes more completely, and the region of grain size is homogenized. Meanwhile, the particle size increases with the extension of thermal insulation from 2 h to 5 h. Therefore, the optimum roasting condition for preparing scandium oxide is 1000 °C for 2 h.

3 Conclusions

1) The spherical scandium oxide powder is obtained, and the appropriate reaction temperature is 30 °C. The amount of precipitant is that the feasible molar ratio of carbonate ion to scandium ion is 4. Meanwhile, the appropriate reaction stirring rate is 200 r/min.

2) The reaction pH has an important influence on the crystal structure of scandium sediment. The crystal of scandium is amorphous structure when the pH value is less than 6. When the pH value is 6, the crystal structure begins to form in the scandium sediment and the crystal structure is gradually improved. The scandium sediment has good crystal structure when the pH is 7.

3) The submicron grade scandium is obtained by controlling certain reaction conditions. The D_{50} and D_{90} of the particle is 6.913 and 9.468 μm, respectively. The BET result demonstrates that the specific surface area of scandium oxide is up to 373.952 m^2/g and its single point average pore radius

is 2.88 nm. Meanwhile, the SEM result demonstrates that the scandium oxide is regular spherical microstructure under suitable preparation conditions.

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碳酸氢铵沉淀法制备球形氧化钪

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摘　要：研究了碳酸氢铵沉淀法制备球形氧化钪粉的方法。在溶液中以$ScCl_3·XH_2O$为前驱体制备含钪的碳酸盐。研究了反应温度、沉淀剂量和搅拌速度对钪回收率的影响。通过粉末X射线衍射和激光粒子测定表征了pH值对含钪碳酸盐晶体结构和粒径的影响。结果表明，随着反应pH值的增大，含钪碳酸盐的结构由非晶结构变为结晶结构，初始变化pH值约为6时，氧化钪的晶体结构为立方结构。同时，在一定条件下，可以获得3.756–103.8 μm尺寸的钪沉积物颗粒。当pH值为7时，钪的D_{50}为6.634 μm。含钪碳酸盐被用作制备氧化钪的前体。TG-DTA结果表明，碳酸盐的分解温度趋于600 ℃左右。基于XRD和IR分析，可以得出，当煅烧温度为1000 ℃时，获得相对纯净的氧化钪粉体材料。同时，采用激光粒度分析仪、BET和SEM-EDS对所得氧化钪粉末进行表征。球形氧化钪粉末的微晶尺寸小于10 μm，表面积约为373.952 m^2/g。微观结构非常均匀，呈球形结构。

关键词：Sc_2O_3粉体；沉淀法；球形结构

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