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Study on the calcination experiments of rare earth carbonates using microwave heating

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Abstract: The heating behavior and effect of experimental parameters like holding time, calcination temperature and microwave power on the weight loss of the mixed rare earth carbonate using microwave heating have been studied, also characterized by X-ray diffraction, thermogravimetry-differential scanning calorimetry, scanning electron microscopy (SEM), particle analysis and Fourier transform infrared (FT-IR). The results show the following: rare earth oxides are obtained at 850°C for holding 1 h; FT-IR analysis indicates that the vibration absorption peak of carbonate disappears after calcination using microwave, confirming the feasibility of microwave calcination for the rare earth carbonates; SEM shows that the rare earth oxides have the characteristics of better and finer particles, have better dispersion and have surface that is more loose and porous than that of products using conventional calcination; particle analysis indicates that average size (D_{50}) of microwave heating is 1.52 μm, which is smaller than conventional calcination of 7.6 μm.

Keywords: microwave calcination; rare earth carbonates; rare earth oxides.

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1 Introduction

Rare earths (REs) are known as a treasure of new materials in the 21st century. Benefiting from their unique optical, electronic, magnetic and catalytic properties [1–5] due to the particular electronic configuration, RE compounds have been widely used in the preparation of functional materials and drawn research attention in recent years [6–8]. The ongoing development of advanced technologies, the continuous expansion of the scope of application of REs in the high-tech fields and the demand for RE materials are increasing rapidly. The traditional process of extracting RE from leach liquor is usually treating it by chemical precipitation with oxalic acid or ammonium carbonate as precipitant, forming RE oxalate or carbonate, followed by washing, filtering and calcining into RE oxides. Rare earth carbonate is used as a kind of main product on the current market, and its production technology is quite mature. However, the calcining process is time-consuming and reagent-consuming, and the serious disadvantage is that it pollutes the environment using coal as the combustion source. Thus, exploring a kind of new technology for calcination of RE carbonates to produce RE oxides is particularly important.

Microwave (MW) heating has the characteristics of quick velocity, selectivity heating, non-pollution and convenience to achieve automatic control and has been widely employed in metallurgy, chemical industry, medicine and food areas as a kind of green highly efficient method [9–13]. Deng et al. [14] added Ce, Nd, Gd, Y, Dy and Lu into the amorphous alloy of Cu-Zr-Al to research the product performance, and the results indicated that the glass transition temperature is reduced and performance of glass formation and alloy mechanical properties are improved through adding the rare earth elements (REEs). Jahangiri et al. [15] synthesized strontium carbonate ($SrCO_3$)

by MW heating, and the results showed that morphology and heating time have significant effect on product size; the optical properties of the samples are affected by synthesis conditions. But few literature have been reported about the calcination process of RE carbonates using MW heating. Therefore, the above features will contribute to the MW heating in the fields where calcination of RE carbonates applies extensively.

Utilizing the outstanding advantages of MW calcination over conventional calcination in calcination efficiency, calcination time and efficiency of heat energy, the effect of holding time, calcination temperature and MW power on calcinating RE carbonates using MW heating is studied. It has great significance in energy conservation and emission reduction, which improves production efficiency for RE smelting enterprises.

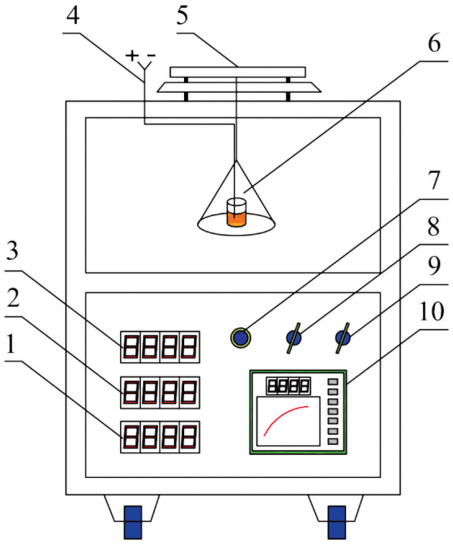

Figure 1: Schematic of a microwave heating system.
1-power controller; 2-ampere meter; 3-voltmeter; 4-thermocouple; 5-electronic balance; 6-materials; 7-power switch; 8-start switch; 9-stop switch; 10-computer system.

2 Materials and methods

2.1 Decomposition principle of RE carbonates

Moisture is lost at 150–200°C when RE carbonate is heated (as Equation (1)). Rare earth carbonates start decomposition gradually when the temperature continues to rise (by following Equation (2)).

$$RE_2(CO_3)_3 \cdot nH_2O = RE_2(CO_3)_3 + nH_2O \quad (1)$$

$$RE_2(CO_3)_3 = RE_2O_3 + 3CO_2\uparrow \quad (2)$$

2.2 Experimental materials and equipment

Mixed RE carbonates are obtained from RE liquor after precipitation in the *in situ* leaching process in Guangxi. The material is not treated, and its initial moisture content is 75% which is measured using a standard hot-air oven at 105°C by retaining the samples for 24 h from three replicate measurements. The main chemical components are shown in Table 1. It can be noticed that the content of RE oxides in the mixed RE carbonates is 43.7%. In addition, it also contains a small amount of Al_2O_3, CaO and MgO.

Microwave heating equipment is shown in Figure 1. The MW heating experiments are carried out in a lab-made MW muffle furnace, and the MW equipment consists of four sections: two magnetrons at the frequency of 2.45 GHz and 1.5 kW power, which are cooled by water circulation as MW sources; a waveguide for transporting MWs; a resonance cavity to manipulate MWs for a specific purpose; and a control system to regulate the temperature and MW power. The inner dimensions of the MW cavity are 260 mm in height, 420 mm in length and 260 mm in width. Continuous temperature measurement during MW heating is a major problem, so a thermocouple (connected to the computer system) with a thin layer of aluminum shielding can be employed to measure temperature and placed at the closest proximity to the material. The Al_2O_3 crucible is employed as the container for RE carbonates; it does not absorb MW.

Differential thermal – thermogravimetric experiment is performed by a STA449F3 analyzer (NETZSCH, Germany); IR spectra are measured with an Affinity-1 FT-IR spectrometer (Shimadzu); RE contents are measured by a Prodigy High Dispersion ICP Spectrometry (Leeman Labs, USA); Scanning electron microscopy (SEM) is done with a model of FEI Quanta 200, and particle analysis is performed by a model of Rise-2002 laser particle size analyzer (Jinan Rise Science & Technology Co., Ltd.).

Table 1: The main chemical composition of RE carbonate (mass fraction %).

SO_4^{2-}	Al_2O_3	Fe_2O_3	SiO_2	CaO	MgO	REO
0.89	2.26	0.063	2.07	2.49	0.24	43.7

2.3 Experimental method

The experiments are carried out as follows: the samples placed in a crucible are put in the MW muffle furnace and then heated at different power levels and calcination times. On starting the heating experiments and after each 15-min interval, the weight of the material (W_t) is noted down until the weights of the samples become constant.

The weight loss is calculated according to Equation (3):

$$\eta = \frac{W_i - W_t}{W_i} \times 100\% \quad (3)$$

where η is the weight loss; W_i is the initial weight, and W_t represents the weight of sample at time t.

3 Results and discussion

3.1 Differential thermal analysis of RE carbonates and temperature curve in MX field

The differential thermal analysis curve of RE carbonates is shown in Figure 2. The heating rate is 10°C/min with argon atmosphere, and RE carbonates are heated from room temperature to 1000°C. Figure 3 reveals the effect of MW calcination time on temperature behavior at 2.1 kW when the weight is kept at 1000 g.

It can be noticed from Figure 2 that there is a strong endothermic peak at 70°C on the differential scanning calorimetry (DSC) curve due to the evaporation of adsorbed water in the samples. Rare earth carbonates start decomposition after 300°C, and heat is released. As can be seen, the thermogravimetry (TG) curve continuously declines, and the weight loss is about 90% of the total mass loss under 230°C. It is mainly caused by the loss of free water [16], and this process conforms to the drying stage of RE carbonates in MW field. The mass loss at 230–1000°C may be explained by the removal of combined water and partial decomposition of CO_3^{2-}. Total mass loss of RE carbonates is 76.79%, less than 80.73% under MW heating when the temperature is 1000°C. It may possibly be because conventional heating uses heat conduction and radiation from outside to inside. However, the materials are directly heated through MW energy dissipation within the samples when using MW heating. According to the electromagnetic properties of different materials, it can be timely and effective to generate heat throughout the interior of the materials. Thus, MW heating has obvious advantages such as faster rate and higher efficiency than traditional heating [17, 18].

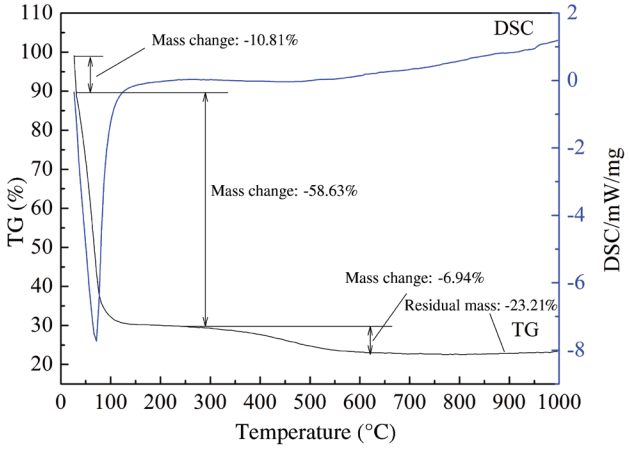

Figure 2: DSC and TG curves of RE carbonate.

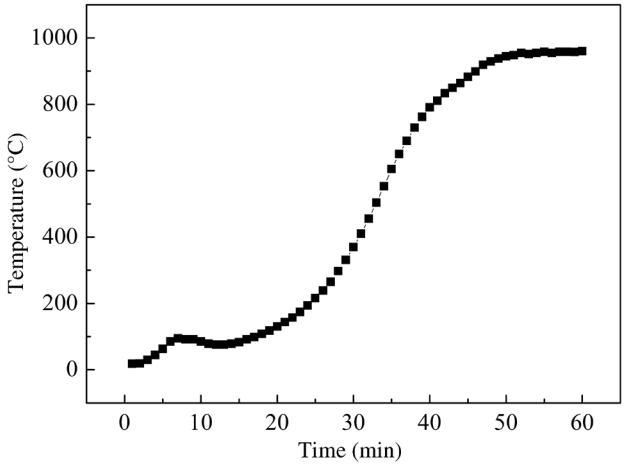

Figure 3: Heating curve of RE carbonate with calcination time in the microwave field.

Combined with TG curve in Figure 2, the relationship between MW calcination temperature and time of RE carbonates in Figure 3 is divided into two stages: drying stage and calcination stage. The drying stage is from 0 to 15 min, and the free water and combined water are removed (as shown in Equation (1)). The moisture is considered as a strong MW absorbing material because the dielectric constant of water is 78.54 at room temperature [19]. However, the MW absorbing properties of carbonates are regarded as weak. Based on the selectivity of MW heating, the moisture is heated preferentially after absorbing MW. Rare earth carbonates are not decomposited in drying stage. With the increase of MW calcination time, RE oxides are obtained after 15 min (following Equation (2)). The heating rate is accelerated with the content increase of RE oxides. Usually, the RE oxides have better MW absorbing properties than that of RE carbonates [20]. The process of calcination has reached thermal balance after 50 min; as can be seen, MW calcination of RE carbonates is feasible.

3.2 Effect of MW calcination time and temperature on the weight loss

The effect of calcination time and temperature on the weight loss at 2.1 kW is shown in Table 2. It can be seen that weight loss increases with increase in holding time and temperature. Rare earth carbonates are converted to oxides completely under temperature of 850°C and heat preservation 1 of h. The weight loss changes slowly if beyond the conditions and until the weight loss is 85.75%.

Table 2: Relationship between holding time, temperature and weight loss.

Holding time (min)	Temperature (°C)						
	650	700	750	800	850	900	1000
0	76.82	77.2	77.95	78.48	79.33	80.16	80.73
30	78.41	78.96	79.13	79.53	81.36	81.47	81.52
45	79.2	79.74	79.82	80.21	83.77	83.8	83.81
60	80.62	81.13	81.67	81.75	85.72	85.72	85.73
90	81.94	82.26	82.6	82.83	85.73	85.75	85.75
120	82.73	82.91	83.15	83.44	85.75	85.75	85.75
240	83.48	83.3	83.92	85.02	85.75	85.75	85.75
260	83.65	83.75	84.12	85.31	85.75	85.75	85.75

In addition, the holding time has no significant effect on the weight loss. Generally, the production requirements can be achieved with heat preservation of 1 h using MW heating.

3.3 Effect of MW power on the weight loss

The effect of MW power on the weight loss at 850°C and heat preservation of 1 h is indicated in Figure 4. It can be found that the weight loss increases with the increase of MW power when MW power is less than 2.1 kW. However, the variation of weight loss is slow if MW power is more than 2.1 kW. It may be because the specific heat capacity c_p and MW absorption coefficient μ of materials are constant within a certain temperature range. According to the law of conservation of energy, the larger the MW power P of material's absorption, the higher the material's temperature [21]. Rare earth carbonates decomposition is considered an endothermic reaction. Improving the MW power contributes to the decomposition of RE carbonates. Therefore, the weight loss is higher with MW power increase. Based on the analysis, the optimal condition for MW power is 2.1 kW.

3.4 X-ray diffraction analysis

The materials before and after calcination are analyzed by X-ray diffraction (XRD). Figure 5 is the raw material graphics for RE carbonates. The XRD picture of RE carbonates after calcination at temperature 850°C, MW power 2.1 kW, heat preservation 1 h and sample mass 1000 g is shown in Figure 6.

As can be seen from Figure 5, the raw materials of RE carbonates are of sub-crystal structure, and diffraction peaks are more chaos. Figure 6 shows that the RE oxides have better crystallization, and the crystal structure is

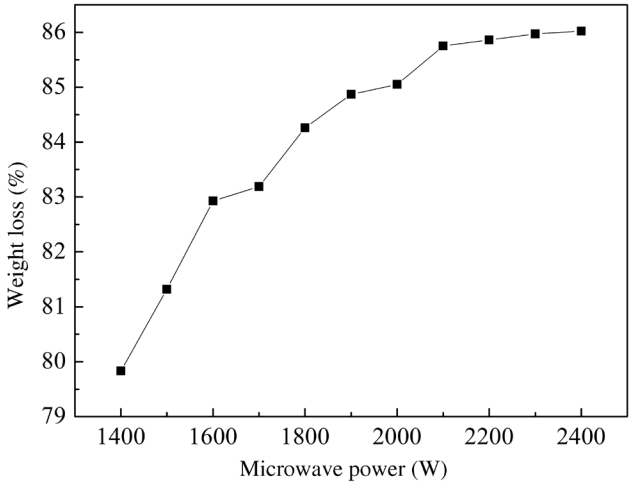

Figure 4: Effect of microwave power on the weight loss.

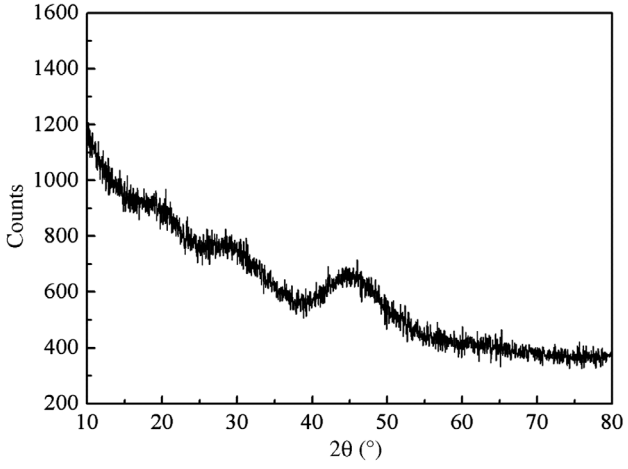

Figure 5: X-ray diffraction patterns of the mixed RE carbonate.

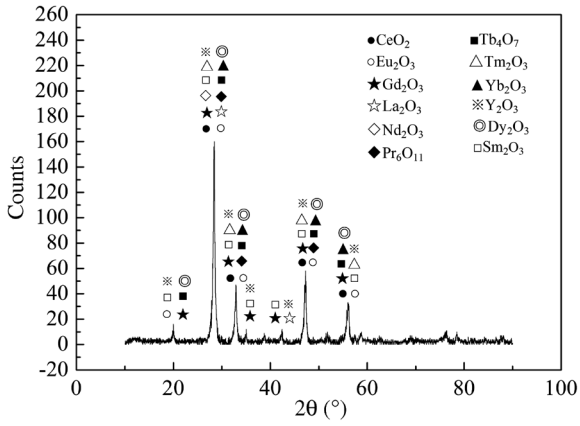

Figure 6: X-ray diffraction patterns of RE carbonate after calcination using microwave heating.

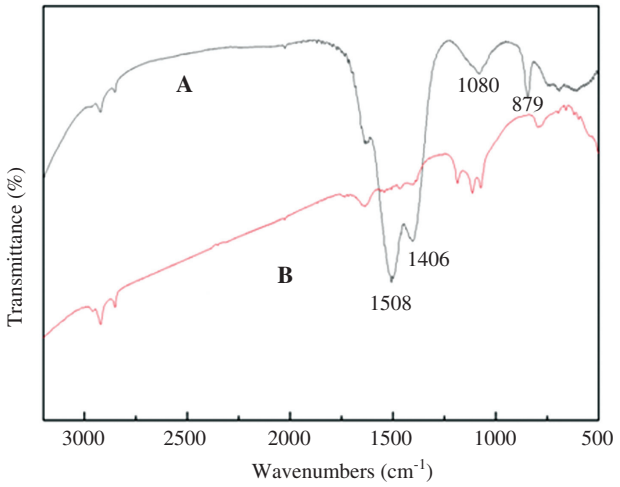

Figure 7: Infrared spectrum of RE carbonate before and after calcination using microwave.
(A) before calcination; (B) after calcinations.

relatively perfect. Rare earth elements contents after calcination are calculated through the GB/T18882.1-2008 of China in Table 3. According to Figures 6 and 7, RE carbonates are translated into RE oxides using MW calcination, further illustrating that it is feasible to prepare RE oxides by MW heating.

3.5 FT-IR analysis

The infrared spectrum of RE carbonates before and after using MW calcination is shown in Figure 7. The 1080, 879, 680 and 1415 cm^{-1} measurements are defined as the vibration and absorption frequencies of free carbonate ions, and 1080 and 879 cm^{-1} are treated as non-degenerate frequencies [22]. The absorption peak 1380–1495 cm^{-1} and 1420–1520 cm^{-1} are the stretching vibration frequencies of the CO_3^{2-} group. However, the absorption peak 870 cm^{-1} is the bending vibration frequency.

Free carbonate ions are regarded as a non-infrared active at 1080 cm^{-1}, and it can be observed in crystal field. Therefore, it can be inferred that a dipole could appear in the carbonate ions if the absorption and degenerate vibrations are found and absorption frequency is splitting at 1080 cm^{-1}. If the non-degenerate vibration absorption frequencies (1080 and 879 cm^{-1}) are split, it can be indicated that the non-equivalence of carbonate ions is present [22, 23]. The absorption frequencies 1415 cm^{-1} (1408 and 1506 cm^{-1}) of carbonate ions are confirmed to split in the formation of complex carbonate. The vibration absorption peaks of carbonate ions disappeared after using MW calcination, and it can be deduced that RE carbonates have been decomposed into oxides.

3.6 SEM analysis

Scanning electron microscope images of RE oxides after using conventional and MW calcination are shown in Figure 8. It can be seen that particle size of conventional calcination is significantly larger than that in MW heating, and dispersibility of RE oxides by MW calcination is enhanced in (A) and (B). The surface of RE oxides is dense by conventional calcination; however, a loose and porous structure can be found in RE oxides by MW calcination in (C) and (D). It may be explained by the heating of materials from inside to outside and by the characteristic of selectivity heating via MW heating. The process is integrality and homogeneity, and the temperature gradient

Table 3: REE after calcination using microwave (in REO).

REO	Y_2O_3	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3
Content (%)	27.70	22.37	5.26	5.41	20.01	4.40	0.62	4.79
REO	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	
Content (%)	0.63	4.26	0.71	1.97	0.27	1.43	<0.20	

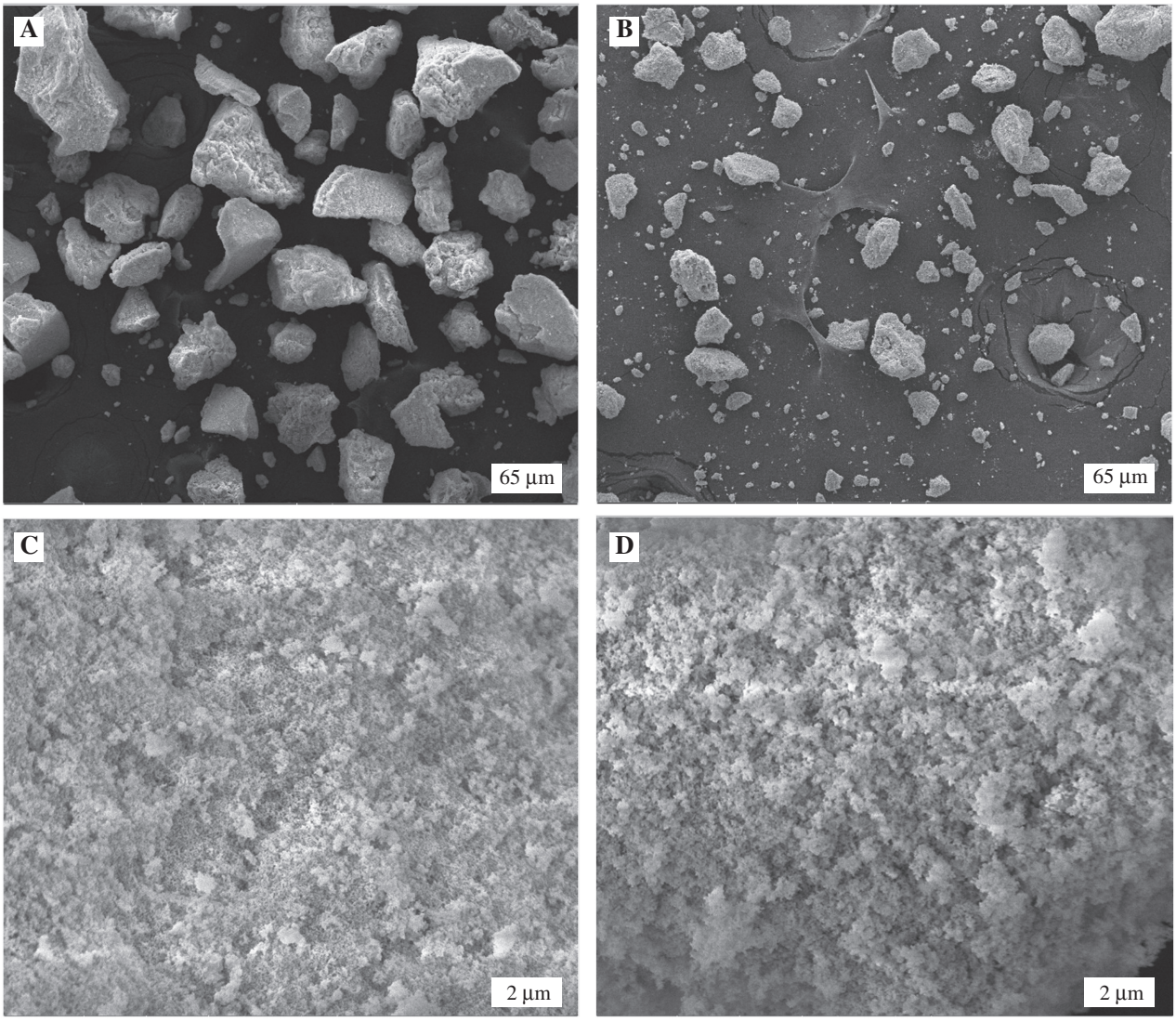

Figure 8: Scanning electron microscope images of RE carbonates using conventional and microwave calcinations. (A) and (C) conventional calcination; (B) and (D) microwave calcinations.

is avoided. The generated gas facilitates diffusion easily in the interior, resulting in more active sites than conventional heating to participate in the reaction; thus, the RE carbonates can react internally and externally. The inside temperature and outside temperature are similar using MW calcination, whereas temperature gradient is found significant in conventional calcination process.

3.7 Particle analysis

As can be seen in Figure 8, the particle size after MW heating is smaller than in conventional calcination. However, SEM does not specify the size of particles when using conventional and MW calcination. The size distributions of RE carbonates after MW calcination and conventional calcination at temperature of 850°C, MW power 2.1 kW, heat preservation 1 h and sample mass 1000 g are shown in Figure 9. It can be seen that the size distribution of RE carbonates after conventional calcination exhibits an abnormal distribution, with the average size (D_{50}) of 7.6 μm; it shows a normal distribution when using MW calcination, with D_{50} of 1.52 μm, which is smaller than conventional, indicating that MW calcination has a role of refinement. It may be explained by the heating of materials from the inside to outside in MW field. The internal molecules produce oscillation and then generate heat due to friction.

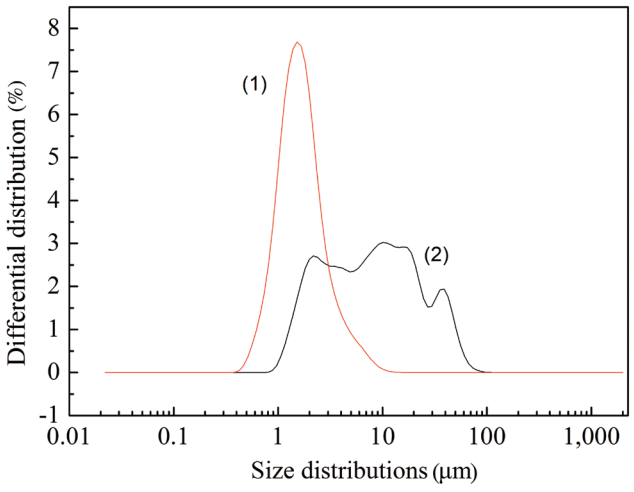

Figure 9: Size distribution of RE carbonates using conventional and microwave calcinations.
(1) microwave calcination; (2) conventional calcination.

4 Conclusions

1. When calcination temperature and heat preservation are 850°C and 1 h, respectively, the weight loss is increased with increase in the holding time and temperature. Weight loss increases with the increase in MW power, and the variation of weight loss is slow when MW power is more than 2.1 kW.
2. FT-IR indicates that the vibration absorption peak of carbonates disappeared after MW calcination; with the XRD analysis after MW calcination, RE carbonates are translated into RE oxides via MW heating, the products have better crystallization, and the crystal structure is relatively distinct.
3. Scanning electron microscopy and particle analysis indicate that particle size of RE oxides after MW calcination is smaller than in conventional calcination; the dispersibility of the former is better and has a loose and porous structure on the surface of RE oxides.

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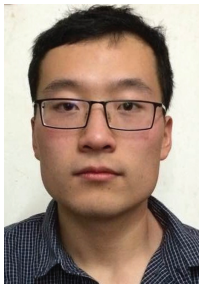

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