Characterizations of the thermal decomposition of nano-magnesium hydroxide by positron annihilation lifetime spectroscopy

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Abstract

The thermal decomposition behavior of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) nanopowders was investigated by positron annihilation lifetime spectroscopy (PALS), X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetry (TG-DSC) analysis, high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). It was indicated that the microstructural changes started from 300 °C were earlier than the phase transformation from hexagonal $\text{Mg}(\text{OH})_2$ nanopowders to face-centered cubic MgO occurred at about 380 °C during decomposition process. The variation of positron annihilation parameters revealed the production of new vacancy defects and the aggregation of vacancy clusters in grain boundary areas and microvoids between particles due to the removal of H_2O and rearrangement of interface atoms. A positron trapping model was proposed to help further understand the changes of microstructure and interfacial defects during $\text{Mg}(\text{OH})_2$ thermal decomposition.

Keywords: Positron annihilation; structural defects; decomposition; magnesium hydroxide

1. Introduction

Nano-magnesium hydroxide ($\text{Mg}(\text{OH})_2$) is widely used in many industrial fields, such as flame-retardant [1], water treatment [2], biomedicine [3], and as the most important magnesium oxide (MgO) precursor [4, 5]. As nano- MgO has high efficiency in antibacterial agents [6], catalysts [7], adsorbents [8], and optoelectronic materials [9], many different synthetic methods were developed to obtain MgO nanoparticles, such as microemulsion-based oil/water interface precipitation [10], hydrothermal reaction [11] and chemical precipitation [12]. Calcining or drying kinds of modified $\text{Mg}(\text{OH})_2$ precursor is an easily accessible and cost-effective method to obtain MgO [13]. Pilarska et al. synthesized a plate morphology of poly(ethylene glycols)-modified $\text{Mg}(\text{OH})_2$ particles and the calcinate MgO could be used as insulating materials because of its permittivity ϵ' independent of frequency [5]. The resulting MgO properties strongly depend on the shape, agglomeration state, preparation process and decomposition process of $\text{Mg}(\text{OH})_2$ [4, 14]. However, in recent years, few work paid attention to the thermal decomposition behaviour of nano- $\text{Mg}(\text{OH})_2$.

The decomposition of $\text{Mg}(\text{OH})_2$ is generally viewed as a two-phase process occurred in the temperature range of 280~450 °C. The resulting MgO structure from $\text{Mg}(\text{OH})_2$ decomposition maintains a distinct crystallographic relationship with original $\text{Mg}(\text{OH})_2$, which is $(0001) \text{Mg}(\text{OH})_2 \parallel (111) \text{MgO}$ and $[11\bar{2}0] \text{Mg}(\text{OH})_2 \parallel [10\bar{1}] \text{MgO}$ [15]. Several kinds of decomposition mechanism have been proposed from kinetics, energetics, morphology and crystallography. A phase-boundary controlled mechanism was that the decomposition reaction proceeded by the advance of an interface two-dimensional reaction from the perimeter to the center of basal plane of hydroxide crystal [16]. In a homogenous mechanism, the migration of H_2O molecules from the planes to the surface was thought to control the structure change of $\text{Mg}(\text{OH})_2$ to MgO [17]. The nucleation and development of MgO in two directions of interface was considered more acceptable because it could successfully describe the kinetics of $\text{Mg}(\text{OH})_2$ decomposition [18]. McKelvy et al. [19] also discovered that the lamellar nucleation and growth processes governed dehydroxylation of lamellar $\text{Mg}(\text{OH})_2$. However, the atomic-scale nature (defects) of the decomposition process is lack of attention. The defects information in atomic-scale are important to the properties of MgO , e.g. the new introduced defects in MgO produced by $\text{Mg}(\text{OH})_2$ decomposition

contributed to the luminescence of MgO [4], and the interfacial defects in MgO nanocrystals were related to its ferromagnetism [20].

The principle of operation of positron annihilation lifetime spectroscopy (PALS) is to measure the spectrum of time intervals between start signals, generated by detecting prompt gamma rays following the emission of positrons, and stop signals from one of the annihilation gamma photons. A positron is the antiparticle of an electron, and it can get trapped by defects without positive charge, i.e. by vacancies or other open volume defects. Positrons can also get trapped by negative ions or by solute aggregates with higher positron affinity than the host atoms. Thus PALS is a unique and valuable technique to characterize the vacancy-type defects and open volume defects in solid based on the detection of γ -radiation [21, 22], which convey information of the lifetime of positrons. In addition, the correct identification of defects with PALS requires the knowledge of accurate positron lifetimes for the various kinds of defects, which can be provided by first-principles calculations. In most studies, positron lifetimes are calculated using a simple practical method proposed by Puska and Nieminen [23, 24] based on density function theory (DFT), where the electron and positron densities are determined without imposing self-consistency.

PALS method has been successfully used to study advanced semiconductor [25, 26], nano-ceramic [27] and nano-porous material [28]. In hydrogenation-modified TiO₂, a huge number of oxygen vacancies introduction were found by PALS measurements, which retarded the charge recombination and improved the photocatalytic activity of TiO₂ [26]. In report of Dutta et al. [29], PALS results revealed that high temperature annealed ZnO semiconductor had a better crystallinity (or lower defect concentration). But no reports about the thermal decomposition of nanomaterials by PALS were found. Therefore, in this work, the thermal decomposition of Mg(OH)₂ nanopowders with different temperatures annealing were investigated by using PALS technique, X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetry (TG-DSC) analysis, high resolution transmission electron microscopy (HRTEM), and scanning electron microscopy (SEM). The changes of microstructure and interfacial defects before and after decomposition from Mg(OH)₂ to MgO were discussed.

2. Experimental

2.1 Sample preparation

Nano-sized $\text{Mg}(\text{OH})_2$ powders (~30 nm particle size) synthesized by chemical coprecipitation with a purity of 99.9% were purchased from Beijing DK Nano Technology Co. LTD, China. After being milled in agate mortar, nanopowders were pressed into tablet under a static pressure of about 10 MP for 4 min. The tablet had a diameter about 10 mm and a thickness about 2 mm. The isochronally annealing experiments were carried on these samples at different temperatures in the range of 100~520 °C in air for 2 h. The heating rate was about 5 °C/min.

2.2 Characterization

The PALS measurements were performed on annealed samples immediately after cool down in air. In the measurements, PALS is a conventional fast-fast coincidence system with a time resolution of about 280 ps. The isotope positron source was ^{22}Na with intensity about 7.4×10^5 Bq, which was sealed between two Kapton films. During the measurement, the positron source and two identical samples were set as a sandwich structure placed between two gamma ray detectors. Each positron annihilation spectrum was collected with a total count of 1×10^6 and analyzed by LT Version 9 program [30] to decompose several lifetime components. Before sample measurements, the spectrum of pure Si single crystal was measured to determine the components of positron annihilation in the source and Kapton films.

XRD (Bruker D8 Advance, Cu $K\alpha$) was performed on samples annealed at different temperatures. The thermal decomposition behavior of the as-received $\text{Mg}(\text{OH})_2$ nanopowders were studied by thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis (NETZSCH STA 449C) in a temperature range of 20~800 °C with heating rate of 5 °C/min under N_2 flow. The micromorphology of samples before and after annealing was characterized using HRTEM (JEM-2100, JEOL, Japan) and SEM (Sirion 200, FEI, Netherlands).

2.3 Theoretical calculation

The theoretical positron lifetimes of perfect $\text{Mg}(\text{OH})_2$ and MgO lattices with and without vacancy defect were calculated, by using atomic superposition (ATSUP) method based on density function theory (DFT) [24]. In calculation models, the space group of $\text{Mg}(\text{OH})_2$ and MgO are $D_{3d^3} - \bar{P}3m1$ and $Fm - 3m$, respectively. The experimental lattice parameters of brucite structure $\text{Mg}(\text{OH})_2$ and rock-salt structure MgO were $a=b=3.147$ Å, $c=4.768$ Å, and $a=b=c=4.217$ Å, respectively. Perfect $\text{Mg}(\text{OH})_2$ lattice was modeled by a $4 \times 4 \times 2$ supercell, which contained a total of 160

atoms. Perfect MgO lattice was modeled by a $2 \times 2 \times 2$ supercell, which contained a total of 64 atoms. The vacancy-type defects of V_{Mg} , V_{OH} and $V_{\text{Mg-OH}}$ in $\text{Mg}(\text{OH})_2$ lattice and V_{Mg} in MgO lattice were constructed by removing the atoms of Mg, OH, and Mg-OH from the interior of perfect lattices, respectively.

3. Results and discussion

3.1 XRD analysis

The XRD patterns of $\text{Mg}(\text{OH})_2$ nanopowders annealed at different temperatures are shown in Fig. 1. The results show that below 400 °C, the nanopowders are still hexagonal $\text{Mg}(\text{OH})_2$ and no MgO or other intermediate phases are observed. But above 400 °C, the structure of nanopowders transforms from hexagonal $\text{Mg}(\text{OH})_2$ to face-centered cubic MgO. The decomposition reaction

occurred at a temperature between 350 °C and 400 °C. This result is consistent with an in-situ XRD measurement for $\text{Mg}(\text{OH})_2$ nano-flakes [31]. The average grain size of each sample is estimated from full width at half maximum (FWHM) of the diffraction peaks by Scherrer equation [32]. The obtained values as a function of annealing temperature are shown in Fig. 2. It can be observed that the average grain size increases slightly from the original 33 nm to about 40 nm below 350 °C, then rapidly decreases to about 25 nm up to 400 °C, and finally increases again with the annealing temperature. The slight increase before decomposition is caused by the agglomeration and growth of $\text{Mg}(\text{OH})_2$ nanoparticles under lower temperature heating due to the higher surface energy of $\text{Mg}(\text{OH})_2$ nanoparticles. The rapid decrease corresponds to the decomposition process with MgO product formation. The new formed MgO products with small size coincide with the report of Yoshida et al. [33]. The final increase could be explained as the growth of MgO crystals under higher temperature annealing [34]. The results obey the mechanism of MgO nucleation and growth during $\text{Mg}(\text{OH})_2$ decomposition.

3.2 TG-DSC analysis

The TG-DSC measurement was carried out to analyze the thermal decomposition behavior of the as-received $\text{Mg}(\text{OH})_2$ nanopowders. The TG and DSC curves are both shown in Fig. 3. A significant weight loss from 97.2% to 70.8% appears in the temperature range of 300~400 °C, which corresponds to the decomposition process

from Mg(OH)₂ to MgO accompanying with H₂O removal. For Mg(OH)₂ nanoparticles, the stage of weight loss generally has a little difference varying from synthesis methods and different structure of Mg(OH)₂ [4, 31, 35, 36]. The corresponding DSC curve only shows one obvious endothermic peak at about 380 °C, which means the maximum rate of weight loss at the temperature. It indicates that the phase transformation from Mg(OH)₂ to MgO occurred at about 380 °C, which is consistent with the result of XRD. As we know, during thermal decomposition the endothermic is to broke the ionic bond of Mg(OH)₂, but before decomposition the endothermic could induce agglomeration and growth of some Mg(OH)₂ nanoparticles as reflected in Fig. 2. It has been suggested that during thermal decomposition, MgO structure formed in Mg(OH)₂ parent crystals with certain orientations according to a gradual change of the diffraction patterns from Mg(OH)₂ to MgO [16, 17]. Hence, the weight loss and grain size change during decomposition would inevitably induce a maze of microstructure in nanoparticles.

3.3 Analysis of positron annihilation lifetime spectra

In order to the details of microstructural change for Mg(OH)₂ nanoparticles during thermal decomposition, we performed positron annihilation lifetime measurement on samples annealed at different temperatures. The obtained positron annihilation spectrum was the convolution of the time-dependent positron decay spectrum

$$L(t)=\sum_i I_i \exp(-t / \tau_i) \quad (2)$$

and the Gaussian resolution function of the spectrometer, where τ_i is the positron lifetime in different annihilation sates and I_i is the corresponding relative intensity. Fig. 4 illustrates the positron lifetime spectra of samples annealed at different temperatures. The spectra were analyzed by using LT Version 9 program [30]. For all the samples, three positron lifetime component τ_1 , τ_2 , and τ_3 with corresponding relative intensities I_1 , I_2 and I_3 were obtained. These parameters as a function of annealing temperature are shown in Figs. 5(a)-(f), respectively. The shortest lifetime τ_1 has a slight increase from 199±7.8 to 208±4.8 ps while I_1 increases evidently in 300~400 °C. In the same temperature range, the second lifetime τ_2 shows an evident increase from 420±18 to 452±14 ps, while I_2 significantly decreases from 38% to 28%. All the samples yielded a long lifetime τ_3 , which increases in 300~400 °C, while the corresponding relative intensity I_3 decreases from the values about 4.5% to about

1.0%. The changes of positron lifetime components in 300~400 °C correspond to the average grain size decrease by XRD and obvious weight loss by TG-DSC as shown in Fig. 2 and Fig. 3. The fitted lines of lifetime components τ_2 and τ_3 for as-received and 400 °C annealed samples were also added in Fig.4. The τ_1 components were not indicated as a straight line, because they have no obvious increase and close to the time resolution. The slope of the straight line is according to $\lambda = \Delta \ln L(t) / \Delta t$ strictly. The λ represents annihilation rate, which is the reciprocal of the τ .

In addition, we calculated the theoretical lifetimes of perfect $\text{Mg}(\text{OH})_2$ and MgO lattices with and without vacancy defect using atomic superposition (ATSUP) method based on density function theory (DFT) [24] and the calculated results are shown in Table 1. The bulk lifetime of perfect $\text{Mg}(\text{OH})_2$ is about 176 ps, while the lifetime values of monovacancy V_{Mg} , divacancy V_{OH} and vacancy complexes $V_{\text{Mg-OH}}$ are 184, 189 and 215 ps, respectively. Similarly, the bulk lifetime of perfect MgO lattice is about 123 ps, while the value of monovacancy V_{Mg} is 174 ps. The calculated lifetime value for perfect MgO without defect is similar to the reported value of 119 ps by Puska et al. [37]. The experimental values of τ_1 are much higher than the theoretical values of bulk with monovacancy, but lower than that with vacancy complexes $V_{\text{Mg-OH}}$. Therefore, we suggest that much higher τ_1 of annealing $\text{Mg}(\text{OH})_2$ nanoparticles and decomposition product MgO in the present case are ascribed to positrons annihilating in bulk and some vacancies, vacancy complexes or small-size defects (such as divacancies), which are mostly located in grain boundary areas.

Positron annihilation lifetime is proportion to the size of defects and the relative intensity is proportion to the density of defects [24]. The increase of τ_1 and I_1 in 300~400 °C (see Figs. 5(a) and (d)) indicates that the number of vacancy defects in grain boundary areas increased significantly, while the size was almost no change. More vacancy defects were formed in product MgO due to the removal of H_2O and crystal type change during decomposition. In early performed [38, 39], similar longlived $\tau_2 \approx 0.4 \sim 0.6$ ns with an intensity $I_2 = 50\%$ have been detected in alkali halides, which was explained as being attributed to major processes (I) annihilation from a complex compound (e^+ -anion) and (II) annihilation with vacancy A-centers (crystal defects). In the present case, the second lifetime components τ_2 of $\text{Mg}(\text{OH})_2$ and MgO are attributed to positrons annihilating in the intersections of several interfaces or

some vacancy clusters in grain boundary areas. For MgO nanocrystals, the vacancy defects including vacancies and vacancy clusters were considered to be responsible for the ferromagnetism of crystals [40, 41]. According to the variation of τ_2 and I_2 , it can be inferred that during decomposition process, those vacancy clusters in $\text{Mg}(\text{OH})_2$ grain boundary areas gradually diffused together and aggregated into larger clusters with atoms rearrangement and grain boundary migration.

In the experiment, the existence of longlived component τ_3 with identifiable intensity confirms that positroniums could be formed in $\text{Mg}(\text{OH})_2$ nanoparticles. Generally, positronium is favorable formation in porous materials by catch one electron. Positronium has two kinds of spin states, the long-lived ortho-positronium (o-Ps, 142 ns) and the short-lived para-positronium (p-Ps, 125 ps). In condensed matter, the lifetime of o-Ps can be greatly reduced to 1~10 ns by picking up a surrounding electron and then annihilating with it. The process is called pick-up annihilation with the lifetime closely related to the size of the pore. The positroniums formation and annihilation in hydroxides compounds are very similar to those in porous materials and molecular system [39]. The existence of τ_3 and I_3 indicates that the as-received $\text{Mg}(\text{OH})_2$ nanoparticles contained a small number of microvoids before annealing. The increase of τ_3 in 300~400 °C demonstrates that larger size of microvoids were formed in MgO product by thermal decomposition. It has been known that during thermal decomposition of $\text{Mg}(\text{OH})_2$, the removal of H_2O would leave a periclase structure of MgO with many open volume microvoids between particles and irregular intercrystallite channels (cracks). These new formed open volume microvoids and cracks with larger size probably exceeded the detected range of PALS measurement, resulting in the decrease of I_3 .

In Fig. 5, the variation of positron lifetimes and corresponding relative intensities all start at 300°C. It indicates that the changes of microstructure and interfacial defects of $\text{Mg}(\text{OH})_2$ nanoparticles are earlier than the phase transformation from hexagonal $\text{Mg}(\text{OH})_2$ nanopowders to face-centered cubic MgO occurred at 380 °C during decomposition process. The changes of interfacial defects in nanoparticles are hard to be characterized by HRTEM or other traditional techniques. Schaefer et al. [42] once proposed a positron annihilation model to investigate the surface and interface of nanometer-sized polycrystalline Fe specimens based on positron lifetime spectroscopy. The model clearly illustrated the location of monovacancy (τ_1) in interface, vacancy

clusters (τ_2) at the intersections of several interfaces and larger voids (τ_3) at surface. Here, we suggest a possible positron trapping model for thermal decomposition of $\text{Mg}(\text{OH})_2$ nanoparticles on the basis of the model of Schaefer et al. The schematic of the model is shown in Fig. 6. For $\text{Mg}(\text{OH})_2$ nanoparticles and MgO product particles, positrons were trapped in the vacancies/vacancy complexes (τ_1) at grain boundary areas, the vacancy clusters (τ_2) at the intersections of several interfaces, and the larger open or closed microvoids or pores (τ_3) between particles, respectively. After thermal decomposition, more vacancies/vacancy complexes were formed in MgO products resulting in more positrons being trapped in these sites. Meanwhile, original vacancy clusters and microvoids aggregated into larger ones due to the rearrangement of atoms and the migration of grain boundaries. Positrons had a longer lifetime when annihilating in these larger-size vacancy clusters and microvoids. This model provides a further understand of the decomposition mechanism in atomic-scale and could be applied to some other tentative nanoparticles.

3.4 Micromorphology

Fig. 7 illustrates the TEM images of $\text{Mg}(\text{OH})_2$ nanopowders in as-received and 400 °C annealed $\text{Mg}(\text{OH})_2$ samples. The image of the as-received sample in Fig. 7(a) indicates a well crystallinity of $\text{Mg}(\text{OH})_2$ particles despite with some agglomeration. In Fig. 7(b), the annealed sample shows a porous and cracked structure due to the removal of H_2O and MgO crystallization during decomposition. The HRTEM images of annealed sample in Fig. 8(b) acquired in the area indicated by the red small box in Fig. 8(a). The lattice fringes are separated by a distance of 0.243 nm which is attributed to the (111) plane of cubic phase of MgO . The blurred crystal texture demonstrates the presence of some vacancy defects in MgO bulk. The internal interfaces containing vacancy complexes or small-size defects (divacancies) and vacancy clusters are located in disorientated regions between nanoparticles.

The SEM images in Fig. 9 show the micromorphology of $\text{Mg}(\text{OH})_2$ nanopowders in as-received and 350 °C and 400 °C annealed samples. The as-received $\text{Mg}(\text{OH})_2$ nanoparticles have an aggregation with no special morphology. The $\text{Mg}(\text{OH})_2$ sample annealed at 350 °C shows a “dissolution” phenomenon partially before decomposition. This evident microstructural change at 350 °C is consistent with the view of microstructural change ahead of phase transformation during $\text{Mg}(\text{OH})_2$ decomposition. For the 400 °C annealed sample, a large number of tiny crystals appear due to

nucleation and growth of MgO product, which is agree with the XRD and HRTEM results.

4. Conclusions

PALS, XRD, TG-DSC, HRTEM and SEM were employed to investigate the thermal decomposition behavior of $\text{Mg}(\text{OH})_2$ nanopowders. The XRD and TG-DSC results demonstrate that the decomposition of $\text{Mg}(\text{OH})_2$ happened in the temperature range of 300~400 °C and the phase transformation from $\text{Mg}(\text{OH})_2$ to MgO occurred at 380 °C. The PALS results indicate that the microstructural changes of $\text{Mg}(\text{OH})_2$ nanopowders are earlier than the phase transformation occurred at 380 °C. During decomposition from $\text{Mg}(\text{OH})_2$ to MgO, new vacancy defects were produced, and the vacancy clusters in grain boundary areas and microvoids between particles aggregated into larger size due to the removal of H_2O and rearrangement of interface atoms. A positron trapping model for thermal decomposition of $\text{Mg}(\text{OH})_2$ nanopowders has been proposed to further understand the atomic-scale decomposition mechanism. The blurred crystal texture in MgO product observed by HRTEM shows the presence of some vacancy defects.

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Figure captions:

Fig. 1 XRD patterns of $\text{Mg}(\text{OH})_2$ nanopowders annealed in air at different temperatures.

Fig. 2 The average grain size calculated from full width at half maximum of the diffraction peaks by Scherrer equation as a function of annealing temperatures.

Fig. 3 TG and DSC curves of $\text{Mg}(\text{OH})_2$ nanopowders in the temperature range of 25~800 °C with a heating rate of 5 °C /min.

Fig. 4 The original positron lifetime spectra of $\text{Mg}(\text{OH})_2$ annealing samples, with fitting lines of as-received sample (blue) and 400 °C annealed sample (red).

Fig. 5 The positron lifetimes (a) τ_1 , (b) τ_2 , (c) τ_3 and the corresponding relative intensities (d) I_1 , (e) I_2 , (f) I_3 of $\text{Mg}(\text{OH})_2$ nanopowders as a function of annealing temperature.

Fig. 6 Schematic of positron trapping model for the thermal decomposition from $\text{Mg}(\text{OH})_2$ nanoparticles to MgO. The hatching indicates the orientation of lattice planes. The various trapping sites are attributed to the positron lifetimes (1) τ_1 , interfacial vacancies/vacancy complexes at grain boundary areas, the atomic structure shown in the inset, (2) τ_2 , vacancy clusters at the intersections of several interfaces, (3) τ_3 , open and closed microvoids in particles.

Fig. 7 Low-magnification TEM images of $\text{Mg}(\text{OH})_2$ nanoparticles (a) the as-received sample and (b) the 400 °C annealed sample.

Fig. 8 (a) High-magnification TEM (HRTEM) image of $\text{Mg}(\text{OH})_2$ nanoparticles annealed at 400 °C and (b) Magnified HRTEM image with lattice fringes separated by 0.243 nm corresponding to the (111) plane of MgO.

Fig. 9 SEM images of $\text{Mg}(\text{OH})_2$ nanopowders annealed at different temperatures, (a) as-received, (b) 350 °C, (c) 400 °C.

Figures:

Figure. 1

Figure. 2

Figure. 3

Figure. 4

Figure. 5

Figure. 6

Figure. 7

Figure. 8

Figure. 9

Tables:**Table 1** The experimental lifetime τ_1 (ps) of as-received Mg(OH)_2 nanoparticles and decomposition product MgO annealed at 520 °C, and calculated lifetimes (ps) of perfect Mg(OH)_2 and MgO lattices with and without vacancy defect.

Sample	Experimental lifetime τ_1 (ps)	Theoretical lifetimes τ_1 (ps) with and without vacancy defect			
		bulk	V_{Mg}	V_{OH}	$V_{\text{Mg-OH}}$
Mg(OH)_2	199 ± 7.8	176	184	189	215
MgO	208 ± 4.8	123	174	/	/

MgO(NP)₂ nanoparticle

MgO powder particle

- ① Interfacial vacancies/vacancy complexes (x_1)
- ② Vacancy clusters (x_2)
- ③ Open and closed microvoids (x_3)