



Hydrogen in-situ refining method for preparing high purity gadolinium



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ABSTRACT

The removal of non-metallic impurities, especially oxygen and nitrogen, from the rare-earth metal gadolinium (Gd) is challenging, due to their strong affinity to Gd metal. Herein we present an effective approach to prepare high purity Gd via a novel hydrogen in-situ refining method. The final concentrations of oxygen and nitrogen could be reduced to 30 and 19 mass ppm, respectively. The changes of lattice parameters were derived from XRD; enthalpy values and gaseous speciation associated with the gas–solid physiochemical reactions were determined through a combination of DSC/MS measurements and thermodynamic calculations. The results show that oxygen and nitrogen can be efficiently removed by degassing Gd with dissolved hydrogen. The underlying mechanism for the refinement is discussed systematically in this paper.

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1. Introduction

Gadolinium (Gd) is one of the most attractive rare-earth (RE) metals, because of the good electrical conductivity, large magnetic moment, and high complexion reactivity [1–5]. However, Gd is so active and its intrinsic properties are highly sensitive to impurities; its application is viable only if the impurities are reduced to ppm level. Commercial pure Gd metal is generally prepared by fusion electrolysis of its fluorides, with further refinement by Electron Beam Melting (EBM) in an inert atmosphere or by distillation in vacuum to obtain the cast metal. Upon distillation, the metallic impurities can be easily removed by evaporation, and their concentrations can be reduced to several mass ppm [6,7]. However, it is of great difficulty to remove the non-metallic impurities, especially oxygen and nitrogen [8,9], because of their strong affinity with Gd. Moreover, the reduced metals are vulnerable to be contaminated by the trace gases in these processes. Therefore, commercial gadolinium often solidifies a large amount of non-metal impurities,

dramatically undermining its physical and chemical properties.

Now one fact established through observation is that any purification process must be performed under ultra-high-vacuum (UHV) conditions and hold for hundred hours [9]. Such stringent conditions raise the risks of recontamination for commonly used refining methods, such as electrotransport, fuse salt deoxidation, and external gettering method. Besides, these methods are often accompanied with high energy penalties and high environmental impacts. As a result, it is highly demanded yet still greatly challenging to develop a scalable, efficient and eco-friendly method to prepare Gd with high purity.

The interactions of RE metals with hydrogen have been studied over the last decades [10–13]. However, the role of hydrogen in purifying RE metals, especially in degassing has been rarely reported. Based on the physical and chemical fundamentals of RE metals with hydrogen, we report in this paper a simple but effective refining method to get high purity Gd. The applicability of hydrogen for the removal of oxygen and nitrogen in Gd was demonstrated. The degassing properties were assessed by quantifying the residual non-metallic impurities. The underlying mechanism associated with the refining process was investigated and discussed.

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2. Experiment

2.1. Sample preparation

Commercially pure gadolinium ingots were used as raw material. Each Gd specimen was cut into $\phi 5 \text{ mm} \times L30 \text{ mm}$ columns. Impurities on the surface of these columns during handling were removed mechanically. After that, the specimens were rinsed with distilled water, ethanol and acetone, respectively. Then, they were dried for use.

Experiments were carried out using a laboratory-scale vacuum tubular furnace. The samples were first annealed in vacuum ($300 \text{ }^\circ\text{C}$, 60 min) for activation. After the chamber was cooled down to room temperature, high purity hydrogen gas (99.999%) was introduced to the sample chamber slowly. It should be emphasized that hydrogen can react with Gd to form GdH_3 or GdH_2 powders [14,15]. Therefore, the flow rate of hydrogen must be carefully adjusted to avoid the formation of hydride powders. It takes about 3–5 days for the hydrogen treatment because of the slow kinetics at room temperature. Samples with different hydrogen contents could be obtained by controlling the total gas intake. Finally, the samples were annealed at $1100 \text{ }^\circ\text{C}$ in the vacuum chamber for dehydrogenation for 1–5 h; purified Gd were thus obtained.

2.2. Characterization

The crystal structures and lattice parameters of the Gd metal after absorbing and desorbing hydrogen were characterized by X-ray diffraction (XRD, Rigaku D/max 200 diffractometer, $\text{Cu K}\alpha$) at a scan rate of $2^\circ/\text{min}$. The non-metallic element contents were analyzed by an inert gas fusion-infrared absorption method using LECO TCH-600. The average concentration of several pieces was taken as the analytical value at a given experimental condition. Differential scanning calorimetry (DSC) measurement was performed on a Netzsch DSC 204 HP calorimeter. The gas composition was further analyzed by a Pfeiffer PrismaPlus Mass Spectrometer/Residual Gas Analyzer (MS/RGA). The experiments were performed in an inert gas flow (high purity argon, 99.999%, 50 mL/min, 1.0 bar).

3. Results and discussion

3.1. Microstructural characterization

The XRD patterns of Gd metal with different hydrogen contents

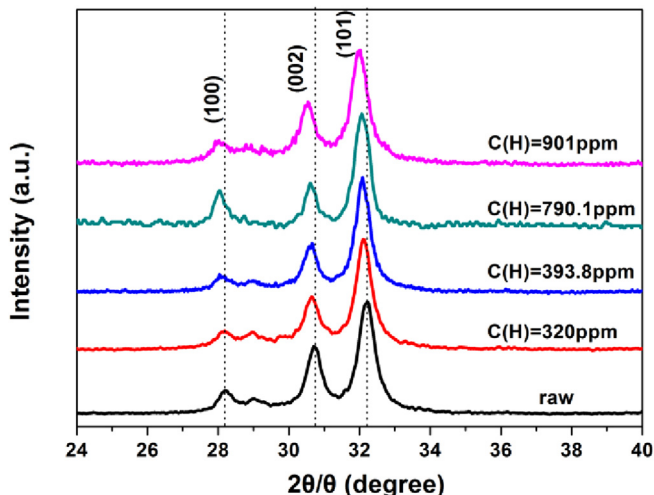


Fig. 1. XRD patterns of Gd with different hydrogen contents.

are shown in Fig. 1. To compare these data distinctly, three main peaks were chosen for comparison. The peaks at $2\theta = 28.2^\circ$, 30.7° and 32.2° are corresponding to the (101), (002), (100) diffractions of Gd metal, respectively. After the absorption of hydrogen, the Gd samples show systematic shift to the low-angle direction in their XRD patterns comparing to the raw material; the deviation value increases with the rise of hydrogen content. When the hydrogen content rises to 901 ppm, the deviation value reaches 0.2° . Neither GdH_2 nor GdH_3 can be detected in XRD. These results indicate that the hydrogen atoms are totally dissolved in the Gd body, inducing considerable lattice distortions.

To study the phase transformation of Gd metal during the hydrogenation/dehydrogenation process, Gd metal with 901 mass ppm hydrogen was annealed at $1100 \text{ }^\circ\text{C}$ for 300 min. Fig. 2 shows the XRD patterns of the raw, hydrogenated and dehydrogenated Gd samples. All the crystallite peaks of the hydrogenated sample move to the low-angle direction, while those of the dehydrogenated one shift back to the original positions in perfect accordance with the raw metal. The lattice constant, volume and density of unit cell were calculated correspondingly, as illustrated in Fig. 2. The lattice parameter of the hydrogenate sample significantly expands from 5.781 \AA to 5.834 \AA , and contracts to 5.761 \AA after desorption. Accordingly, the density decreases from 7.94 g/cm^3 to 7.79 g/cm^3 , then increases back to 7.90 g/cm^3 . The reversible change in the lattice parameters is evident that the hydrogenation/dehydrogenation in Gd proceeds in a reversible manner with the controlled hydrogen content; hydrogen atoms can be regarded as an ideal random interstitial solution in the metal [16].

3.2. Effect of hydrogen on the removal of oxygen and nitrogen in Gd

Fig. 3 shows the changes of oxygen and nitrogen concentrations in Gd after annealed at $1100 \text{ }^\circ\text{C}$ for 300 min as a function of the hydrogen contents. To better assess the experimental data, we define the removal degree (RD) in terms of % for each impurity by Eq. (1):

$$\text{RD} = \frac{100(X_0 - X_f)}{X_0} \quad (1)$$

where, X_0 and X_f represent the initial and final concentration of the impurities, respectively.

Fig. 3 clearly demonstrates the effect of deoxidation and denitrogenation using hydrogen. Keep in mind that the oxygen and nitrogen concentration of the raw metal were 187 and 97 mass ppm, respectively. After degassing the Gd sample with 420 mass ppm of

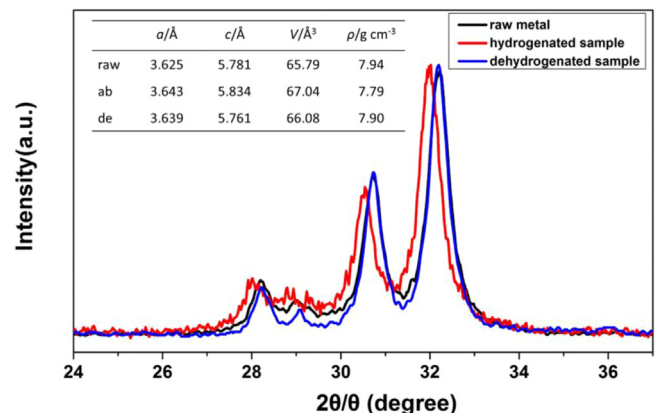


Fig. 2. XRD patterns of the raw, hydrogenated and dehydrogenated Gd samples.

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