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Impurities especially titanium in the rare earth metal gadolinium—before and after solid state electrotransport

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Abstract: Gadolinium was prepared by conventional procedures of fluorination, reduction, distillation and solid state electrotransport (SSE). The electronegativities of the metals were found to have an important influence on the electrotransport process and result of the impurity element. Meanwhile, titanium particles in the distilled gadolinium as major metallic impurities were studied by high resolution transmission electron microscopy (HRTEM) before and after solid state electrotransport. The results showed that impurities especially titanium transported from anode to cathode during SSE. In the metal before SSE, there were impurities of titanium in strip shape or embedded round shape. After SSE processing, titanium particles in the metal smaller than 50 nm in the cathode, but existed 6 to 10 times bigger in the anode.

Keywords: impurities; titanium; rare earth metal; gadolinium; solid state electrotransport

Gadolinium has no large-scale applications but has a variety of specialized uses, such as applications in the luminescence, electricity, magnetism, nuclear and especially in medicine.

High purity metals are desired when used for magnetostrictive and magnetic refrigerant materials, and when used for searching their intrinsic or unknown properties. However, the high purity metal cannot be achieved easily with regard to the highly active rare earth metals. During the past decades, preparation of the rare earth metals was introduced in detail by the researchers of the Ames Laboratory[1]. In recent decades, rare earth has been becoming a hot topic[2–4]. Solid state electrotransport (SSE) had been applied to rare earth metals since 1961[1], and the first material was yttrium. In 1972[5], electrotransport velocities of O, N and C in gadolinium were determined by Peterson and coworkers at Ames Laboratory. During these decades, purifications of all possible rare earth metals by SSE were studied by researchers at Ames Laboratory and University of Birmingham, United Kingdom[1,6–23] and interstitial impurities such as O, N and C were main topics in these papers. This may be attributed to the obvious effect of transport. Compared to the interstitial impurities, metallic impurities were less focused on. As for titanium, still less.

In this paper, SSE was studied from a particular perspective. Firstly, gadolinium was prepared from common gadolinium oxide (99%), and the final metal was obtained by fluorination, reduction, distillation and solid state electrotransport. And after that, the compositions of the metals before and after SSE were characterized by glow discharge mass spectrometry (GDMS). The microstructures of metallic impurities especially titanium in the metal and the metal itself were characterized by HRTEM, as well.

1 Experimental

1.1 Fluorination

Gd_2O_3 was fluorinated by continuously mixing with HF gas at 600 °C for 8 h in accordance with the following formula[24,25]:

$$Gd_2O_3(s)+3HF(g)=GdF_3(s)+3H_2O\,(g) \quad (1)$$

$$GdF_3(s)+H_2O(g)=GdOF(s)+2HF\,(g) \quad (2)$$

Here, formula (2) is a side reaction. To avoid the side reaction, multiple fluorinations are recommended. If high purity is desired, multiple fluorinations are essential.

1.2 Reduction

The product in the above step was reduced by calcium particles in the carbon tube furnace in the titanium crucible at 1500 °C for half an hour in the argon atmosphere[26].

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In the process, the product Gd and CaF_2 were layered according to the density difference as shown in Table 1. Thus the metal obtained layered in the bottom of the crucible and the slag layered in the top. Both of them could be easily separated.

Table 1 Some of the physical constants in the reduction

Material	m.p./°C	b.p./°C	Density
GdF_3	1231	2277	7.1
Gd	1313	3273	7.89
Ca	842	1484	1.55
CaF_2	1418	2534	3.18

* m.p.: melting point; b.p.: boiling point

1.3 Melting and distillation

The metal obtained was melted in the vacuum tantalum furnace at 1800 °C for half an hour, and distilled at 1725 °C for 20 h[17,27]. In the melting process, those volatile and high vapor-pressure impurities were eliminated. And the distillation removed most of those non- volatile and low vapor-pressure impurities from the metal.

1.4 Solid state electrotransport (SSE) processing

Solid state electrotransport device was designed and manufactured according to Refs. [28,29]. In this process, ultra high vaccum is essential[10,30]. In this study, the degree of vacuum was 5×10^{-7} Pa, approximately 4×10^{-10} Torr.

The specimens used in the electrotransport measurement were rods with 11 cm in length and 0.8 cm in diameter machined from the distilled metal.

The experiment was carried out in the current density of 450 A/cm^2 at 1250 °C, above the temperature of the crystal transformation (1235 °C) of gadolinium from a structure of hexagonal close packing (h.c.p.) to β structure of body-centered cubic (b.c.c.)[31]. This transformation would result in the decrease of the efficiency of space filling and thus in the increasing of the volume for the crystal transformation part.

1.5 Characterization

For chemical analysis, all of the samples obtained were characterized by glow discharge mass spectrometry (GDMS).

High resolution transmission electron microscopy (HRTEM, Tecnai G^2 F30 S-TWIN) coupled with energy dispersed spectroscopy (EDS) was used to acquire the microstructures and morphologies of the metals.

2 Results and discussion

2.1 Photos of the gadolinium rod during the SSE processing

Photos of the gadolinium rod during the solid state electrotransport processing are shown in Fig. 1.

Non-uniform temperature distribution could be seen from Fig. 1(b). During the processing, the highest temperature appeared in the lower part of the rod. The ends of the rod are at a lower temperature than the center. The maximum difference can be 260 °C. This difference can make the impurities at the ends migrate more slowly than those in the center[10].

It is known that the electrotransport mobilities and diffusion coefficients for solutes such as C, N and O are considerably higher in β (b.c.c.) form than in α (h.c.p.) form, as shown in Fig. 2[31]. Because of the temperature difference of the whole rod, there should be two forms of gadoliniums that exist in our processing rod. From the dynamic-view, the transport mobilities and diffusion coefficients of the solutes are different in them. From the thermodynamic-view, the structure of the different parts with different forms should be different, as well. In this paper, the rods after SSE displayed different degrees of bending at the brightest part. It might be interpreted that the brightest part of the rod had a structure of b.c.c., which had low efficiency of space filling. Thus the volume of the b.c.c. part would increase, and meanwhile other part of the bar with h.c.p. form would remain unchanged during the process. This function would cause the bending of the whole rod, and even cause break in some serious cases. It is consistent with the results of Spedding and his research team[32]. In his paper, the atomic volume increased sharply when b.c.c. formed. Thermal expansion coefficient is an average of 8.9 at 400°C for gadolinium with same crystal form. The coefficient in *c*-axis (13.0) is more than twice as much as in the direction of *a*-axis (6.3).

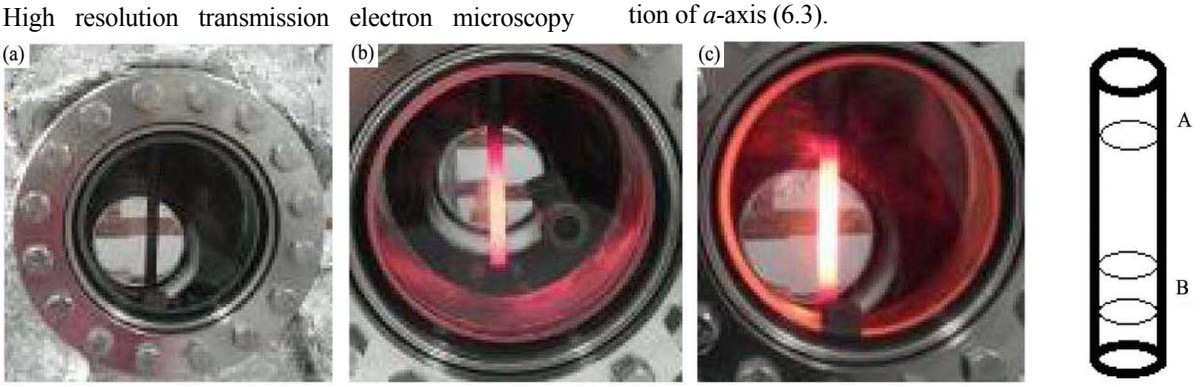

Fig. 1 Photos of the gadolinium rod during SSE processing
(a) Before electrotransport; (b) During heating process; (c) During thermal insulation