Rare Metal Materials and Engineering
Volume 45, Issue 10, October 2016
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(10): 2509-2512.

ARTICLE

A New Process of Manufacturing "Oxygen-free" Gd

Li Li[1], **Li Guoling** [1,4], **Xu Li** [2], **Xiong Yifu**[3], **Li Xingguo**[1]

[1] Peking University, Beijing 100871, China; [2] Future Science & Technology Park, State Grid Smart Grid Research Institute, Beijing 102211, China; [3] Institute of Materials, Mianyang 621907, China; [4] Qingdao University, Qingdao 266071, China

Abstract: "Oxygen-free" Gd was fabricated by hydrogen plasma arc melting (HPAM). The HPAM is more different than the traditional Ar plasma arc melting (PAM) in Oxygen removal. It is attributable to the hydrogen atoms dissociated and activated in high temperature HPAM. In addition an increased diffusion of oxygen in Gd-O solid solution to the surface also plays an important role in removal of oxygen. The substances are confirmed by optical emission spectroscopy (OES), which are involved in the plasma like Ar I, Ar II and H I and some possible reactions. The effect of H with thermodynamic estimation was discussed in detail.

Key words: Gd; hydrogen; oxygen; HPAM

In recent years, rare earth (Gd) materials and compounds are characterized by a variety of particular physical and chemical properties, which means possibilities for wide applications as functional materials, therefore, the rare-earth metals (Gd) and compounds have been known to be widely used in permanent magnets[1] and corrosion resistance materials[2]. At the same time, rare earth element addition in Cu(Mg)-based alloys is applied extensively to refine grain size and to improve the mechanical properties[3,4]. However, almost all rare earth metals show sensitivity to oxygen, including the dissolution of very small amounts of oxygen [5]. Oxygen, in particular, has no benefit to the physical properties of them. But, there are many technological difficulties and complex problems due to high chemical reactivity of RE. Now, the preparation and characterization of plasma arc melting (PAM) have been widely reported as a practical and useful melting method for various refractory metals. Sometimes, it can be used to eliminate non-metallic impurities from some metals. It has been found, however, that an addition of H_2 significantly improves the removal of some nonmetallic elements from refractory metals such as Mo and Cr[6,7]. Many important factors of the hydrogen plasma arc melting, such as thermal, chemical and physical explaining have not been reported so far. The research related with these processes is of great importance, both for the development of manufacturing rare earth technology and for extending the applications of these metals. For these considerations, we reported how to deal with the relation between rare earth and oxygen in the present work, laying the foundation for characterizing the preparing process of "oxygen-free" Gd thermally and chemically. Optical emission spectroscopy (OES) was used for plasma processes, which can identify the species in the plasma by analyzing optical radiation of excited plasma species [8]. This technique enabled us to know the status of Ar and H, But it has been seldom used for analyzing the details of the HPAM process now. So, we evaluated the effect of H by the emission spectra which contained a whole quantity of information.

1 Experiment

Commercial Gd (above 99.5 wt% in purity by the supplier) was used as starting material and the purity of Gd was raised up to 99.96% after Ar-H_2 PAM. Samples were refined by plasma arc melting, and the detailed constitution of the furnace has been described in elsewhere [9]. The plasma

Received date: October 14, 2015
Foundation item: Project of the Ministry of Science and Technology of China (2012CBA01207, 2010CB631301); National Natural Science Foundation of China (U1201241, 11375020, 21321001)
Corresponding author: Li Xingguo, Professor, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China, Tel: 0086-10-6765930, E-mail: xgli@pku.edu.cn

torch is a dc arc discharged type with a maximum power of 35 kW. Gd (10 g) and Y (10 g) were placed on the water-cooled copper crucible by Ar-H_2 (20 vol%) plasma arc under atmospheric pressure. The samples were turned upside down and melted for uniform refining. The melting time was total time. The flow rate of the plasma generating gas introduced to the chamber was constantly 5 L/min. "Oxygen-free" Gd are still big challenges. An O-N analyzer was used to determine the oxygen concentrations in Gd before and after melting.

Oxygen concentrations were estimated by repeating measurements several times for each isotope. An OES (AvaSpec-2048FT-SPU, measured from 181 nm to 1100 nm in 0.8 nm steps) was used to obtain emission spectra of the Ar-H_2 PAM. The laboratory-scale plasma arc furnace is schematically shown in Fig.1.

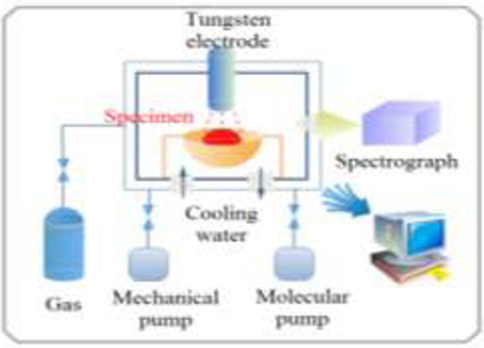

Fig.1 Experimental setup

2 Results and Discussion

Gd was melted after melting Y upside down as an external getter. It has been reported that rare earth metals (RE = Gd, Tb, Dy, Er) containing 1 wt% oxygen can be deoxidized either by calcium or yttrium metal [10]. So Y can react with O in the chamber which will promote diffusion of O in Gd to the surface. For the description of experimental data, the removal efficiency of O is defined by Eq. (1):

$$\text{Removal efficiency}=100\%\ (C_i - C_f)/C_i \quad (1)$$

where, C_i and C_f are the initial and final concentrations of O, respectively.

Fig.2a shows the dependence of removal efficiency of oxygen under the different H_2 contents in the plasma gas. Rapid increasing of removal efficiency occurs by Ar-H_2-PAM compared with by Ar PAM. It is found that Ar-20H_2 PAM provides excellent deoxidation. It has also been reported that refining effect gradually decreased with increasing the hydrogen content over 20%, because of the unstable plasma arc at higher hydrogen content [7]. Fig.2b~2d show the relations between oxygen concentrations and removal efficiency with the melting time. Concentration of oxygen is decreased with the melting time; however the removal efficiency is increased at the same time. Then, concentration of oxygen is reduced more rapidly by Ar-H_2 PAM compared with by Ar PAM even when external getter Y is used. Removal efficiency is up to 94.7% by Ar-H_2 PAM compared with Ar-PAM (41.1%) and Ar-PAM + Y (65.6%) melted for 30 min.

Fig.3 shows the removal efficiency of oxygen at different currents with optical spectra taken at 65 and 120 A. The spectra show some species like Ar I, ArII and H I. Some possible reactions are observed and they are presented as follows:

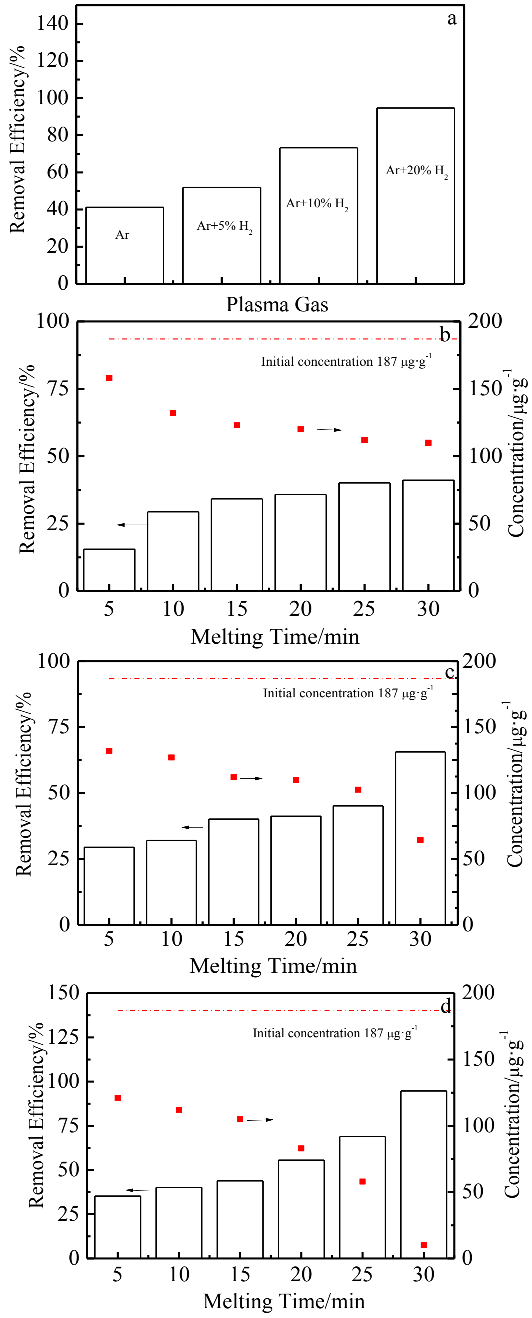

Fig.2 Relation between removal efficiency and content of H_2 during melting (a); removal efficiency and concentration change of oxygen as a function of melting time refined by Ar-PAM (b), Ar-PAM + Y(c), and Ar-20%H_2 PAM + Y (d)