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Purification of terbium by means of argon and hydrogen plasma arc melting

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ABSTRACT

The refining of terbium (Tb) by plasma arc melting using pure Ar and Ar + H_2 mixture was examined, respectively. The temperature distribution and gas flow of the plasma arc during the melting process were simulated. The residual metallic impurities were examined by inductively coupled plasma-atomic emission spectrometer. Experimental results show that both methods of argon plasma arc melting (APAM) and hydrogen-argon plasma arc melting (HAPAM) can lead to a good removal of metallic impurities despite of high initial concentrations. HAPAM displays a better refining effect of Tb metal. Activated hydrogen atoms dissociated in high temperature plasma arc, bringing on special chemical interactions, are supposed to be the cause for the wonderful refining effect. The detailed behaviors of impurities and hydrogen atoms are discussed systematically in this study.

1. Introduction

The interests in rare earth metals, alloys, and compounds have been raised from the needs in the advanced technology fields [1–4]. Terbium (Tb) is one of the most important rare-earth materials for modern society, which is widely used in industry, such as biological material, fluorescent powder and heavy metal glasses [5–8]. Recently, remarkable development of advanced electronics industry requires higher purity materials, therefore, the demand for high-purity Tb metal (above 99.9 mass%) is expected particularly [9,10]. However, currently, the purities of commercial pure Tb is only about 98–99 mass% at most and it contains a large amount of metallic impurities (the other rare earth elements and Fe, Cu, Ni, Al, Ca, etc.) [11]. The poor purity cannot meet the demands already. It is urgent to develop more efficient and practical methods for Tb purification.

For this purpose, hydrogen-argon plasma arc melting (HAPAM) has been reported to be available for purification of some refractory metals, such as Zr, Ta, Ti, Cr and Hf [12–16]. Plasma is in non-equilibrium state, composed of electronics, cations and neutral particles, and can be widely used in melting, milling and alloying [17–19]. Different from the traditional argon plasma arc melting (APAM) method, H_2 is introduced into the plasma-generating gases in HAPAM, Ar and H_2 are both used as plasma-generating gases. However, HAPAM has been rarely reported for the purification of rare earth metals so far. As Tb is a kind of rare-earth materials with high melting point, high vapor pressure and high chemical activity, the possibility of purification of Tb becomes an important pointer for HAPAM using on rare-earth materials.

In the present work, the refining of Tb using plasma arc heating has been examined. The purification properties have been identified by quantifying the residual metallic elements in high purity metals. The simulation of the high-density arc provides a good understanding about this simple and practical refining method.

2. Experiment

Commercial Tb (above 99.3176 mass% in purity) was used as the experimental material. Experiments were carried out using a laboratory-scale plasma arc furnace equipped with a transfer arc type plasma torch. Fig. 1 shows the details of the constitution. Tb

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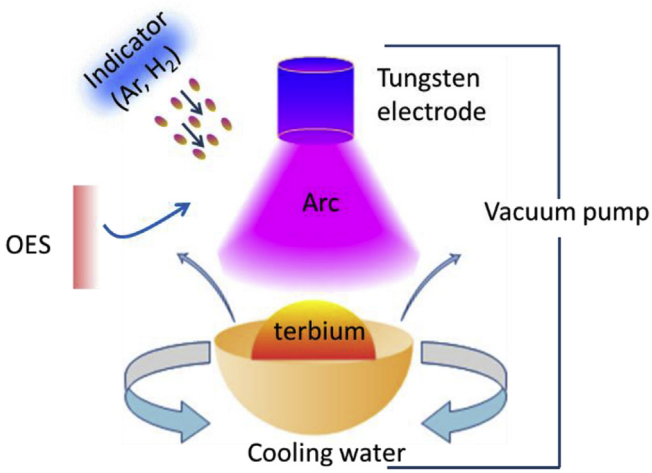

Fig. 1. The schematic diagram of the experimental equipment.

was placed on the water-cooled copper crucible, 25 mm in diameter and 6 mm in depth, and then melted by Ar and Ar + H_2 plasma arc respectively. The purities of Ar and H_2 were 99.9995% and 99.9999% respectively, and the volume ratio could be controlled by the gas flow indicator. The flow rate of the gas introduced to the plasma torch was constantly 5 L/min. The current of plasma arc was changed from 40 to 120 A. The distance between the tip of the plasma torch and the melted specimen was about 5 mm. All the samples were melted for 30 min in this study. For uniform refining, the specimen was melted again by turning upside down after first melting. The weight of each sample was fixed at about 20 g. An optical emission spectroscopy (OES) was used for obtaining emission spectra during the experiment. Inductively coupled plasma-atomic emission spectrometer (ICP-AES) was used for precise analysis of impurity contents in Tb specimens.

3. Results and discussion

3.1. Removal of impurity elements from Tb

Impurity concentrations in Tb metal after plasma arc melting for 30 min under different plasma gases are shown in Table 1. Approximately, the initial purity of Tb is above 99.3176%, which contains plenty of impurities like Ca, Ti and Gd in 2100 ppm, 1270 ppm and 1330 ppm, respectively. When Ar is only used as the plasma gas, the final purity of Tb is up to 99.9122%. The main impurities are effectively discarded. The contents of Ca, Ti and Gd decrease to 100 ppm, 20 ppm and 10 ppm, respectively, which indicate that the thermal plasma provides excellent refining capability. Compared to the case of APAM, it can be seen that the HAPAM demonstrates a higher removal efficiency of impurities. After purified by 5% HAPAM, the total purity can reach to 99.9174%. Further removal of impurities can be achieved by increasing the contents to 10%. Not only the contents of none-RE impurities, such as Cr, Al and Ca, decrease to below 20 ppm, but also the RE impurities, such as Y, La and Sm, are significantly decreased. The final purity of Tb increases to above 99.9521%. However, too much H_2 is unpractical. When the H_2 content increases to 15%, the weight loss of Tb by evaporation will be very high with the production of TbH_3 or TbH_2 nanopowders. Accordingly, the final purity will be not very good. Thus, it is concluded that both methods of APAM and HAPAM can lead to a good removal of metallic elements despite of large initial concentrations, while 10% HAPAM displays the best purification result.

Table 1
Impurity concentrations (mass ppm) in Tb metal by APAM and HAPAM at 120 A.

Impurity	Commercial material	APAM	5%HAPAM	10% HAPAM
Mg	40	<10	<10	<10
Al	220	60	35	10
Ca	2100	100	100	20
Ti	1270	20	10	20
Cr	100	50	61	20
Mn	50	10	15	10
Fe	230	110	98	70
Co	10	10	<10	<10
Ni	110	10	43	30
Cu	240	190	137	51
Zn	10	<10	10	<10
Y	110	40	25	10
La	100	50	10	20
Ce	50	10	15	<10
Nd	160	50	81	40
Sm	50	30	10	20
Eu	50	10	10	<10
Gd	1330	10	49	10
Dy	40	30	35	30
Ho	190	40	36	40
Er	310	10	<10	<10
H	54	17.6	16	18.4
Purity (mass %)	>99.3176%	>99.9122%	>99.9174%	>99.9521%

Fig. 2 shows impurity concentrations in Tb metal after APAM for 30 min under different melting current. It can be seen all the main impurities finally drop to below 100 ppm. Furthermore, the removal degrees except Fe can be further improved by increasing the melting current. The results suggest that the elimination of metallic impurities from Tb metal deeply depends on the power of thermal plasma.

Fig. 3 shows the melting current dependence of main impurity concentrations in Tb under 10% H_2 in the plasma gas. On the basis of a comparison with data obtained using APAM, it is clear that the contents of Al, Ti, Cr and Y can be reduced dramatically below 30 ppm at only 60 A after 10% HAPAM. It reflects a higher efficiency for the removal process with H_2 concentration in the plasma gas. The contents of Fe reduce remarkably from 160 ppm to 70 ppm with the current increasing from 40 A to 120 A by HAPAM. The results indicate that active hydrogen plasma can effectively promote the removal effect.

3.2. Numerical analysis of plasma arc at various electrical currents

3.2.1. Governing equations and boundary conditions

It is clear that the plasma arc melting technology is an efficient refining method, and the removal degrees regularly depend on the applied currents. Therefore, we should focus on the specific temperature gradient of plasma melting and the following heat convection. To study the refining phenomenon deeply in present research, a numerical model of plasma arc at various values of the electrical current (I = 40, 60, 100 and 120 A) with Flow Analysis Simulation Tool (FAST [20–22]) has been developed. The arc configuration, which consists of the shaped tungsten cathode and water-cooled copper anode with a 5 mm gap, is shown in Fig. 4.

The mass conservation equations can be written in the generalized form,