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Impurity distribution in metallic dysprosium during distillation purification

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Abstract: The distribution rules of impurities contents in distilled metallic dysprosium were researched, and a theoretical analysis was carried out. The research results indicated that, the content of impurity in distilled metal, such as Al and Fe, was lower in the initial stage, increased slowly in the middle stage, and increased rapidly in the last stage during the process of distillation purification. The calculated method of separation coefficient of impurity in crude metal by content of impurity in distilled metal was not suitable for high pure metals, and the modified separation coefficient was proposed, and it equaled 1/6.1 and 1/16.9 for impurity Al and Fe. The physical process of distillation was coincident with that of solidification essentially, and solute re-distribution theory in solidifying front could be used to describe the impurity distribution near evaporating surface. In the former stage of distillation purification, the diffusion of impurity in liquid metal could reach a quasi-equilibrium state, the calculated result of impurity content in distilled metal agreed well with experiments. In the latter stage of distillation process, the diffusion rate of impurity in liquid metal decreased, and the content in distilled metal was larger than the calculated result.

Keywords: vacuum distillation purification; distilled dysprosium; impurity distribution; modified separation coefficient; rare earths

High-purity rare earth metals have been widely used in high technique field, which is a key raw material of high-performance magnetostrictive material[1], magnetic refrigerant materials[2,3], superconducting materials[4–6], etc.. Vacuum distillation is an important method for purifying rare earth metals. Vacuum distillation is an important method for purifying rare earth metals, in this purification process, the impurities, with lower saturated vapor pressure than the matrix metal, can be separated at high temperature environment in vacuum distillation purification process. The impurities, with lower saturated vapor pressure than the matrix metal, can be separated at high temperature environment in vacuum distillation purification process.

Up to now, most previous studies focused on preparation of rare earth metals by vacuum distillation technology[7–14], measurement of distillation velocity[1,7,15,16], the effects of experimental conditions on purification[17,18], and few researchers used the separation coefficient to judge whether the impurity can be separated from the matrix metal[18–22]. Xi et al.[19] discussed the behavior of impurities in distillation purification of metallic terbium, the impurities with the separation coefficient β_i>1 (defined as $\beta_i=\gamma_i p_i^\theta/\gamma_m p_m^\theta$) can be evaporated preferentially, the impurities with the separation coefficient β_i<1 will be remained mostly in the crucible, and the impurities with β_i≈1 cannot be separated by vacuum distillation; Li et al.[18,20] considered that it is credible to use separation coefficient to judge whether the impurity can be separated or not, but due to the lack of the activity coefficient of impurity, β_i cannot be calculated accurately by the definition formula, but actually it can be obtained by another equation of $\beta_i=\alpha_i\sqrt{M_i/M_m}$, α_i is volatilization coefficient of impurity, determined by volatilization rate of impurity and matrix metal based experiment, and it is found that the impurities of Al, Cu, Cr and Co present a negative deviation in liquid scandium, and Ni and Si present a positive deviation; Pang et al.[21] calculated the volatile quantity of impurities in metallic neodymium, the theoretical quantity equated with the experimental results for the impurities with β_i>1, and there is a large error for the impurities with β_i>1; Zaiour et al.[22] discussed behavior of impurities in distillation process and the removal efficiency of submicron major impurities in tellurium can be characterized by studying the effective separation coefficient α, which is affected by both the evaporation rate and particle size. The above researches are all related on the separation coefficient to judge whether the impurities can be removed, however, the removal rate of the impurities and the distribution of impurities in distilled metal have not been studied.

In present study, a vacuum distillation purification ex-

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periment of metallic dysprosium was carried out, and the content of impurity was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), and the distribution rules of impurities were obtained, and the theoretical analysis of the distribution rules was discussed.

1 Experimental

The self-preparation metallic dysprosium (Dy) was used in the present experiment, the starting material consists of 20 casting ingots, every ingot is about 250 g, and the total amount of metal is 4.99 kg; 6 samples were sampled and analyzed by ICP-AES, and the average contents of impurities are listed in Table 1, and the purity of metallic dysprosium is about 99.87 wt.%.

The schematic of distillation equipment is shown in Fig. 1. The starting material was placed into a tungsten crucible with dimensions of 115 mm in external diameter, 95 mm in inner diameter and 225 mm in height; considering that the melting point of Dy is 1407 ºC, a soaking temperature of 1500 ºC was maintained for 8 h under a pressure of 10^{-5} Pa, the temperatures of crucible were measured by an infrared radiation thermometer (RATMR1SBSF, Reytek, USA) through the sight hole in the furnace. In this period, the metallic dysprosium evaporated from liquid metal surface and condensed at the cooled collector (tantalum sheet, consists of a cylinder and a cover, with thickness of 0.1 mm, about 50 g), leaving high melting point and low vapor pressure impurities at the bottom of tungsten crucible.

In order to be convenient for discussing the distribution rule of the impurities, the height of collector was determined by the total amount of starting material, the height of collector was calculated by following equation $H=m_{Dy}/(\rho_{Dy}\pi(d_{Ex}/2)^2)$, where m_{Dy} is mass of metallic dysprosium, kg; ρ_{Dy} is density, 8550 kg/m^3; d_{Ex} is external diameter of crucible, m; which could guarantee the lower surface of the distilled metal to be at tungsten upper edge level.

2 Results

After distillation experiment, about 120 g grey powder was left in crucible bottom, and the total amount of deposited Dy and collector (tantalum sheet) was 4.92 kg, after machining off the collector, distilled metal was 4.86 kg, the longitudinal section of distilled metal is shown in Fig. 2, and the schematic diagrams in various distillation periods are indicated in Fig. 3. In initial stage of distillation purification, as seen in Fig. 3(a), the metallic vapor will condense on the inner surface of the cylinder and the cover sheet to form a thin metallic film; and then metallic atom will deposit on the surface of metallic film, seen in Fig. 3(b) and (c); as the distillation process continues, the evaporated metallic atom deposited on the cover sheet presents a truncated cone and deposited on the cylinder sheet presents a circular ring with a triangular section, as seen in Fig. 3(d).

In order to discuss the distribution rules of impurities, five samples were taken along the axial line in distilled metal successively (as seen in Fig. 2) after the experiment finished, and the size of every sample is 10 mm×5 mm×5 mm; 3 samples were taken for each position, the sample were dissolved by nitric acid, the impurities were determined by ICP-AES (PerkinElmer Optima 8100), the

Table 1 Content of 24 impurities in metallic dysprosium (mg/kg)

Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Ho	Er	Tm
<10	19	<10	<10	<10	<10	<10	36	117	68	<10	<10
Yb	Lu	Mg	Al	Si	Ca	Cr	Mn	Fe	Co	Ni	Cu
10	30	23	86	116	211	15	22	45	29	18	189

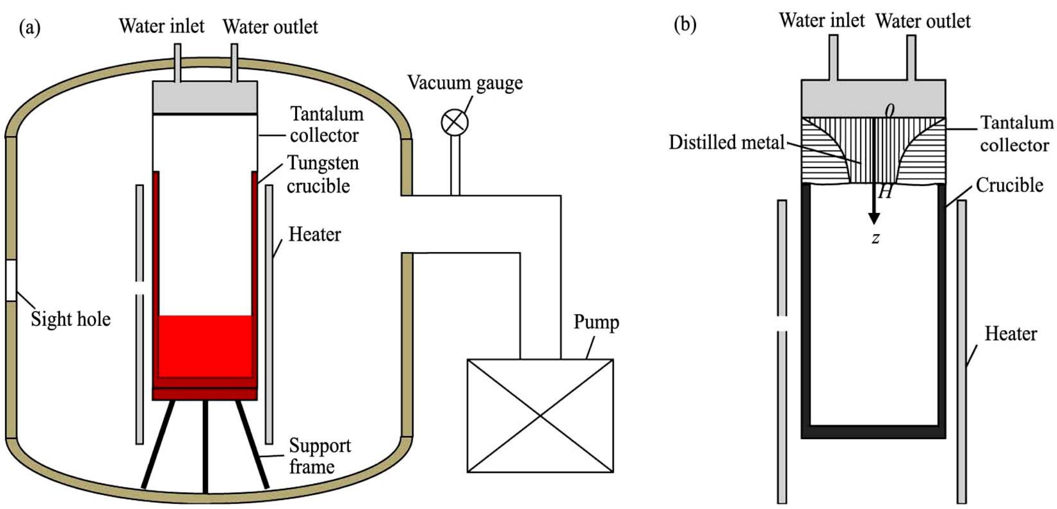

Fig. 1 Schematic of distillation equipment of metallic dysprosium before (a) and after (b) distillation