Rare Metal Materials and Engineering
Volume 45, Issue 11, November 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(11): 2793-2797.

ARTICLE

Preparation of High Purity Rare Earth Metals of Samarium, Ytterbium and Thulium

Zhang Xiaowei, Wang Zhiqiang, Chen Dehong, Li Zongan, Miao Ruiying, Yan Shihong

General Research Institute for Nonferrous Metals, Grirem Advanced Materials Co. LTD., Beijing 100088, China

Abstract: High purity rare earth metals, including samarium, ytterbium and thulium, were prepared by vacuum reduction-distillation of each rare earth oxide with lanthanum metal. The results show that the rare earth metals of samarium and ytterbium with 4N-purity are obtained by direct vacuum reduction-distillation, and their purity is 99.99 wt% and 99.993 wt%, respectively, with respect to 75 impurities. There is a high concentration of reductant in thulium metal due to the higher reaction temperature and lower distillation velocity ratio of metallic thulium to lanthanum, so that the sublimation purification with lower temperature and high vacuum is needed. The purified thulium can reach a high purity of 99.995wt% with respect to 75 impurities. Therefore, the preparation of high purity reductant of lanthanum metal, especially of total amount control of metallic impurities, is the key step to obtain 99.99%-purity rare earth metallic samarium, ytterbium and thulium.

Key words: vacuum reduction-distillation; high purity rare earth metals; samarium; ytterbium; thulium

The highly volatile lanthanide metals, samarium, europium, ytterbium and thulium, are usually prepared by a vacuum reduction-distillation method, which is to reduce directly rare earth oxides with a non-volatile reductant such as lanthanum or cerium metal at high temperature. Generally speaking, the purity of reduction product can reach 99.5~99.9 wt%; it is well known that the purity of rare earth metals is closely related to the intrinsic property and the function of rare earth materials, so that the reduction product should be purified by vacuum distillation and/or sublimation to a high purity to meet the demands of materials technology development. Up to now, there are few researches concerning the preparation of volatile rare earth metals. Kazuyoshi[1,2] studied the fundamental on the production of rare earth metals (samarium, europium, ytterbium and thulium) by a direct reduction process, and found that the reactivity for reduction of each oxide was better in the order of europium oxide>ytterbium oxide>samarium oxide> thulium oxide; Z. Hao[3] prepared the metallic samarium by reducing samarium oxide with rich-lanthanum alloy, and the purity of reduction product is 99.78 wt% with respect to 10 impurities; W. Chen[4] prepared metallic europium by 2-step of distillation and ingot casting, and the concentration of oxygen is less than 300 μg/g; B. Wu[5] calculated the thermodynamic parameters of the reduction of metallic ytterbium by lanthanum or cerium, and prepared the metallic ytterbium with purity of 98.56wt% and 98.43wt%, respectively, by above two kinds of reductant with respect to 12 impurities. The thermodynamic behavior of RE(rare earth) impurities and non-RE impurities has been discussed, and some technical measures to improve purity degree of metallic ytterbium has been proposed[6]; G. Busch[7] purified europium with ultra high vacuum distillation in a simple quartz apparatus, and the total concentration of impurities (including gases) was found to 170 μg/g A. M. Ionov[8] compared the purification effects of samarium, europium, ytterbium and thulium by three methods: sublimation of solid metal, sublimation through porous tungsten filter and distillation through liquid lanthanum or cerium metal, and high purity rare earth metal with residual

Received date: November 11, 2015
Foundation item: National Basic Research Program of China (2012CBA01207); National High Technology Research and Development Program of China (2011AA03A409)
Corresponding author: Zhang Xiaowei, Ph. D., Senior Engineer, General Research Institute for Nonferrous Metals, Beijing 100088, P. R. China, Tel: 0086-10-82241180, E-mail: 04202095@163.com

resistance ratio (RRR) of 300 were obtained, but concentration of impurities was not measured by chemical analysis, and the purity of metals has not been determined.

In the present study, europium metal is oxidized easily in the process of sampling and chemical analysis, so that others high purity volatile rare earth metals have been prepared.

1 Experiment

The first attempt with commercial metallic lanthanum was to reduce the samarium oxide, and a high concentration of Ca, Mg, Si, Fe and C impurities were found in the reduction product, because the purity of the commercial metallic lanthanum is about 99 wt%, and the above impurities are brought into the reduction product. Consequently, the key point in the preparation of high purity rare earth metals is to avoid the impurities introduced by starting materials, and the purification of the starting materials must be carried out firstly. During the whole preparation process, the operation environment must be kept clean through the whole preparation process.

The preparation of high purity samarium, ytterbium and thulium includes two steps, the first step is to prepare high purity reductant, lanthanum metal; the second step is to direct reduction-distillation rare earth oxide by lanthanum in vacuum atmosphere, and the subsequent vacuum distillation/ sublimation purification. The schematic diagram of equipment is shown in Fig.1.

Gaseous impurities, including carbon, oxygen, hydrogen and nitrogen, were analyzed by interstitial gas analysis (IGA), and other impurities were analyzed by glow discharge mass spectrometry (GDMS).

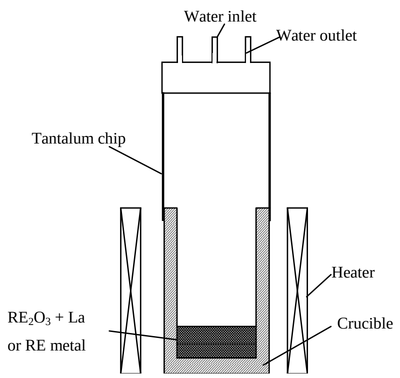

Fig.1 Schematic diagram of reduction-distillation and purification

2 Results and Discussion

2.1 Preparation of Lanthanum

Metallic lanthanum is prepared by metallothermic reduction of fluoride with calcium. LaF_3 is obtained by the dry method, the anhydrous HF is passed over the La_2O_3 at 650~700 ℃ for 16 h, and then the mixture of LaF_3 and Ca are packed into the tungsten crucible, an excess of 10% of Ca more than stoichiometric amount. The crucible is located in the vacuum induction furnace, and heated to 1400~1600 ℃ for about 2 h under the protection of argon gas, and poured into a tungsten mould. In the solidification process of the crude lanthanum metal, some inclusions will be entrapped, such as LaF_3 and CaF_2, and excess reductant will be left in the matrix metal, but the above inclusions and impurity can volatilize easily, so that the poured metal is re-melted at 1400~1500 ℃ in the vacuum environment to remove above volatile inclusions and impurities.

The refined metallic lanthanum was sampled and analyzed, as seen in Table 1. The GDMS analytical results indicate that the amount of metallic impurities is 185 μg/g, the concentration of impurities of Ca and F are both less than 5 μg/g, but the crucible impurities, such as W and Ni, reach 79 and 58 μg/g, respectively, and the amount of above two impurities is about 74% of the total metallic impurities in lanthanum metal, which are introduced in the procedure of fluoridation in nickel tube and reduction in tungsten crucible.

According to the Handbook[9], the saturated vapor pressures of W and Ni are much lower than that of samarium, ytterbium and thulium, so that they will be removed in the vacuum reduction-distillation or subsequent distillation/sublimation process, and the rare earth metal will not be contaminated.

As stated above, lanthanum metal, obtained by vacuum melting, can satisfy the request of preparation of high purity rare earth metals.

2.2 Preparation of high purity samarium

To evaluate the contamination degree of reductant (lanthanum) to the reduction product (samarium), or the separation degree in the distillation purification, a dimensionless ratio of distillation velocity of metallic samarium to lanthanum, has been considered, as shown in Fig.2.

The dimensionless ratio is greater than 1.2×10^7 at 1200 ℃, and it is found that the distillation velocity ratio is decreased gradually with the temperature increasing, and this curve also confirms the research result of Kazuyoshi[1], which is low temperature distillation is beneficial to obtain high purity rare earth metals. However, considering the metling point of reactants and products and the reaction rate, a proper reduction temperature should be chosen. In the process of high vacuum distillation purification, it is the best to distill or sublimate at low temperature, so the residual reductant

Table 1 Analytical results of lanthanum metal (μg/g)

Sc	Y	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
<0.005	6.7	1.2	<0.5	0.39	<0.05	<0.05	2.3	1.6	<0.05
Ho	Er	Tm	Yb	Lu	Si	Ca	Mg	Fe	Mn
<0.05	<0.05	<0.05	<0.05	<0.05	3.8	5	<0.05	4.6	0.03
Al	Ti	Ni	Co	Cu	Pb	Zn	Sn	Cd	Ta
3.3	0.85	58	0.02	1.1	0.24	<0.05	<0.05	<0.05	<1
Zr	Pt	Nb	Cr	W	Mo	Na	F	S	P
0.16	<0.05	<0.05	<0.05	79	15	0.08	<5	1.7	0.005

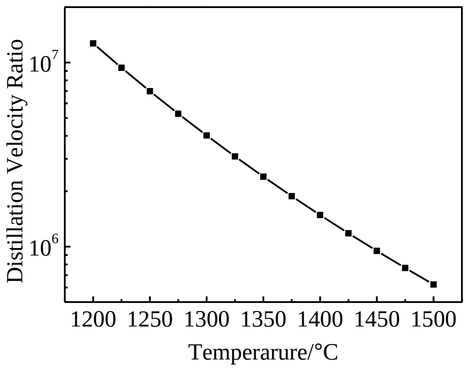

Fig.2 Dimensionless ratio of distillation velocity of samarium to lanthanum

can be removed effectively. However, on the other hand, if the distillation temperature is too low, the smaller distillation velocity of rare earth metal will prolong the distilled or sublimate time, and the purification efficiency will be reduced significantly.

In the experiment, the reduction-distillation experiment has been conducted at 1300~1400 ℃ for 2 h under 10^{-4} Pa. During the reduction-distillation process, the reduction product of metallic samarium is evaporated from the reaction chamber, and then condensed to obtain the solid metal product.

The analytical results of samarium metal are listed in Table 2, since the condenser is made by Mo slice, the concentration of Mo is as high as 14 μg/g; and the metallic impunities of W and Ni, as the major impurities in the reductant, has been separated successfully in the distillation process and left at crucible bottom, whose concentration is decreased to 0.1 and 0.01 μg/g, respectively; the concentration of La reductant is 3.1 μg/g; the amount of gaseous impurities, including carbon, oxygen, hydrogen and nitrogen, is less than 45.06 μg/g, the amount of 75 impurities is less than 99.13 μg/g, and the purity of samarium metal is 99.99 wt%.

2.3 Preparation of high purity ytterbium

The dimensionless ratio of distillation velocity of metallic ytterbium to lanthanum is shown in Fig.3. At 1200 ℃, the dimensionless ratio is larger than 5×10^8, which is one order of magnitude larger than that of samarium. It is predicted that the concentration of reductant in ytterbium is much less than that in samarium; and the same rule is found that the distillation velocity ratio of ytterbium to lanthanum is decreased with the temperature increasing.

The reduction-distillation experiment was conducted at 1400~1500 ℃ for 2 h under 10^{-4} Pa, the reduction product was sampled and analyzed, and the analytical results are listed in Table 3. The impurity of Ca is 5.2 μg/g, which is introduced by the reductant and ytterbium oxide, and the concentration of Ca in above starting materials is 5 and 2.5 μg/g, respectively. Owing to the high vapor pressure of Ca, it is evaporated and condensed on the condenser with the matrix metal; the second major impurity is Sm, 3.1 μg/g, which is introduced by the oxide ytterbium; and the concentration of reductant is very low, about 0.26 μg/g. It well agrees with the analytical result

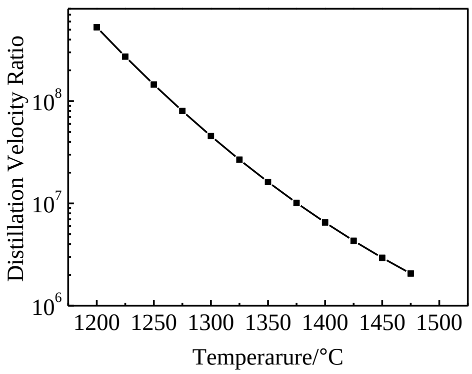

Fig.3 Dimensionless ratio of distillation velocity of ytterbium to lanthanum

Table 2 Analytical results of samarium metal (μg/g)

Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy
<0.01	<0.01	3.1	<0.01	<0.01	0.07	0.08	<0.01	<0.01	0.09
Ho	Er	Tm	Yb	Lu	Si	Ca	Mg	Fe	Mn
0.06	0.14	0.11	0.16	<0.01	<0.05	<0.1	<0.05	2.3	0.07
Al	Ti	Ni	Co	Cu	Pb	Zn	Sn	Cd	Ta
0.08	<0.01	<0.01	<0.01	0.11	<0.5	<0.05	<0.1	<0.1	<10
Zr	Pt	Nb	Cr	W	Mo	C	S	N	O
<0.05	<0.1	<0.01	0.11	<0.1	14	15	0.06	<10	20
Li	Be	B	F	Na	P	Cl	K	V	Ga
<0.01	<0.01	<0.01	<1	<0.05	<0.05	<0.1	<0.1	<0.01	<0.05
Ge	As	Se	Br	Rb	Sr	Ru	Rh	Pd	Ag
<0.1	<0.1	<0.5	7.9	<0.05	<0.05	<0.05	<0.05	<0.5	0.05
Sb	Te	I	Cs	Ba	Hf	Re	Os	Ir	Au
<0.05	<0.5	<0.1	5	<0.05	0.11	<0.05	<0.5	<0.01	<5
Hg	Tl	Bi	Th	U					
<0.1	<0.01	<0.05	0.005	0.005					

Table 3 Analytical results of ytterbium metal (μg/g)

Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
<0.05	<0.05	0.26	<0.01	<0.01	<0.01	3.1	0.94	<0.01	<0.01
Dy	Ho	Er	Tm	Lu	Si	Ca	Mg	Fe	Mn
<0.01	0.02	0.34	<0.5	<0.5	<0.05	5.2	0.29	0.23	<0.01
Al	Ti	Ni	Co	Cu	Pb	Zn	Sn	Cd	Ta
0.39	<0.01	<0.05	<0.01	<0.05	<0.05	<0.5	<0.1	<0.5	-
Zr	Pt	Nb	Cr	W	Mo	C	S	N	O
<0.1	<0.1	<0.05	<0.01	<0.1	<0.1	31	<0.05	<10	<10
Li	Be	B	F	Na	P	Cl	K	V	Ga
0.24	<0.01	0.05	<0.5	0.7	<0.05	0.75	0.35	<0.01	<0.1
Ge	As	Se	Br	Rb	Sr	Ru	Rh	Pd	Ag
<0.1	<0.1	<0.5	<0.5	<0.05	<0.05	<0.1	<0.1	<0.05	<0.1
In	Sb	Te	I	Cs	Ba	Hg	Re	Ir	Au
<0.1	<0.1	<0.1	<0.1	<0.1	0.4	<0.1	0.31	0.13	<0.5
Hg	Tl	Bi	Th	U					
0.1	0.01	0.01	0.005	0.005					

of distillation velocity ratio in Fig.3. The amount of 4 gaseous impurities is 51.05 μg/g, the amount of 75 impurities is less than 71.97 μg/g, and the purity of ytterbium metal is about 99.993 wt%.

2.4 Preparation of high purity thulium

The distillation velocity ratio of metallic thulium to lanthanum is shown in Fig.4. Considered that the reducing temperature of 1500~1600 ℃, the dimensionless ratio of distillation velocity is less than 10^5, which is greatly less than that of samarium and ytterbium, so the reductant of lanthanum in the reduction product may be higher than that in the other metals, and it will be removed in the subsequent sublimation or distillation purification process.

The experiment was carried out at 1500~1600 ℃ for 2 h under a pressure of 10^{-4} Pa, and GDMS analytical results of reduction product indicate that the concentration of impurity of reductant is about 1100 μg/g, and the amount of other 30 metallic impurities is less than 8 μg/g. Therefore, the removal of reductant is the key point of preparation of high purity metallic thulium.

Compared to other rare earth metals, the concentration of La impurity in thulium metal is greatly higher than that 0.26 and 0.94 μg/g in the metallic ytterbium and samarium respectively. The primary cause is that the vapor pressure of thulium is less than that of other metals, and the reduction temperature is higher than others.

Based on Fig.4, low temperature distillation or sublimation is beneficial to removal of lanthanum impurity; so some sublimation experiments were conducted at 1500, 1400, 1300 and 1200 ℃ for 2 h under 10^{-6} Pa. The concentration of lanthanum drops from about 1100 μg/g to 514 μg/g at 1500 ℃, and with decreasing the sublimation temperature, the concentration of lanthanum impurity declines to 274 and 71 μg/g with sublimation temperature of 1400 and 1300 ℃, respectively; when the sublimation temperature decreases to 1200 ℃, the concentration of reductant is sharply reduced to 6.2 μg/g, as seen in Table 4, the amount of 4 gaseous impurities is 39.02 μg/g, the amount of 75 impurities is 51.885 μg/g, and the purity of thulium metal is about 99.995 wt%.

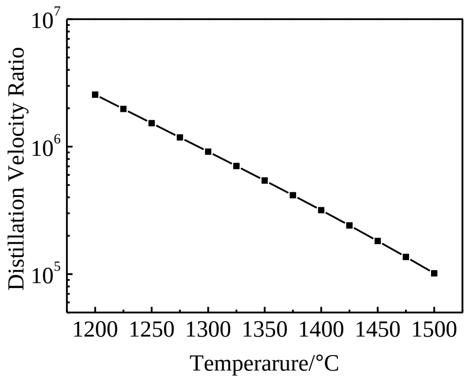

Fig.4 Dimensionless ratio of distillation velocity of thulium to lanthanum

Table 4 Analytical results of thulium metal (μg/g)

Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
<0.01	<0.01	6.2	<0.05	<0.05	<0.01	0.57	<0.1	<0.05	<0.05
Dy	Ho	Er	Yb	Lu	Si	Ca	Mg	Fe	Mn
0.43	0.15	0.03	0.03	<0.01	0.02	0.14	<0.01	<0.01	0.08
Al	Ti	Ni	Co	Cu	Pb	Zn	Sn	Cd	Ta
0.31	<0.01	<0.01	<0.01	0.16	0.02	<0.05	<0.05	<0.1	-
Zr	Pt	Nb	Cr	W	Mo	C	S	N	O
<0.01	<0.1	<0.01	0.02	<0.1	<0.05	11	0.02	<10	18
Li	Be	B	F	Na	P	K	V	Ga	Ge
<0.005	<0.005	<0.005	<0.5	<0.05	<0.01	<0.05	<0.01	<0.05	<0.1
As	Se	Br	Rb	Sr	Ru	Rh	Pd	Ag	In
<0.1	<0.1	<0.5	<0.01	<0.01	<0.05	<0.05	<0.05	<0.05	<0.1
Sb	Te	I	Cs	Ba	Hf	Re	Os	Ir	Au
<0.05	<0.05	<0.01	<0.01	<0.05	<0.05	<0.01	<0.05	<0.1	<0.5
Hg	Tl	Bi	Th	U					
<0.1	<0.05	<1	0.005	0.005					

3 Conclusions

1) High purity samarium and ytterbium can be obtained by direct vacuum reduction-distillation, and the amount of 4 gaseous impurities is 45.06 and 51.05 μg/g, respectively. The purity of above rare earth metals is 99.99 wt% and 99.993 wt%, respectively with respect to 75 impurities.

2) The concentration of reductant is high in the reduction product of thulium metal. After low temperature sublimation purification, the impurity of reductant can be removed successfully, and the purity of thulium metal can reach 99.995 wt% with respect to 75 impurities.

3) High purity lanthanum metal, particularly the total amount control of metallic impurities, is a critical step in the preparation of metallic samarium, ytterbium and thulium with 99.99% purity.

References

1 Shimakage K, Endou K, Sato T. *Mining and Metallurgical Institute of Japan*[J], 1990, 7(1): 1

2 Shimakage K, Endo K, Sato T *et al*. *Nippon Kinzoku Gakkaishi /Journal of the Japan Institute of Metals*[J], 1990, 54(1): 17

3 Hao Z, Jiang Y, Qin F *et al*. *Rare Earth*[J], 1992, 13(1): 47 (in Chinese)

4 Chen W, Liu S, Yang Q *et al*. *Rare Metals and Cemented Carbides*[J], 2005, 33(4): 17 (in Chinese)

5 Wu B, Zhang Y, Ding X. *Rare Metals and Cemented Carbides*[J], 1997, 25(9): 13 (in Chinese)

6 Wu B, Zhang Y. *Jiangxi Nonferrous Metals*[J], 1997, 11(2): 34 (in Chinese)

7 Busch G, Kaldis E, Muheim J *et al*. *Journal of Less Common Metals*[J], 1971, 24(4): 453

8 Ionov A M, Nikiforova T V, Rytus N N. *Vacuum*[J], 1996, 47(6-8): 879

9 Yaws C L. *Handbook of Vapor Pressure*[M]. Oxford: Elsevier Science and Technology, 1995

高纯稀土金属 Sm、Yb 和 Tm 的制备

张小伟，王志强，陈德宏，李宗安，苗睿瑛，颜世宏

(北京有色金属研究总院 有研稀土新材料股份有限公司，北京 100088)

摘　要：采用镧热还原蒸馏法对蒸气压较高的稀土元素 Sm、Yb 和 Tm 的制备进行了研究，制得了纯度达 4N 级的稀土金属 Sm 和 Yb，其纯度分别为 99.99%和 99.993%（质量分数，相对 75 种杂质元素）；对于稀土金属 Tm，由于还原温度较高，还原蒸馏产物中 La 的含量偏高，需要对其进行低温、高真空升华提纯，提纯后纯度达到 99.995%（同上）。结果表明，高纯度还原剂 La 的制备，尤其是 La 中金属杂质总量的控制，是获得 99.99%纯度 Sm、Yb 和 Tm 的关键步骤。

关键词：真空还原蒸馏；高纯稀土金属；钐；镱；铥

作者简介：张小伟，男，1982 年生，博士，高级工程师，北京有色金属研究总院，北京 100088，电话：010-82241180，E-mail: 0420295@163.com