Nickel in Terbium Metal and Its Characterization by Laser Induced Breakdown Spectroscopy-Original Position Statistic Distribution Analysis

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Abstract

The application of terbium involved in giant magnetostriuctive materials, phosphors, magneto-optical storage materials, magneto-optical glass, and so on. The requirement of content of nickel is stringent for most of the materials. The distributions of nickel in terbium by Laser induced breakdown spectroscopy-original position distribution analysis (LIBS-OPA) and the reason of difficult removal of nickel by vacuum distillation but easy removal by SSE had been mainly discussed in this paper. Terbium ingot prepared by electron-beam smelting after vacuum distillation was processed into rod of 0.76 cm in diameter and 15 cm in length. The solid state electrotransport (SSE) experiment was done to the rod at 1100°C and 450 A cm⁻² for 100 h under UHV (10⁻¹⁰ Pa) conditions. LIBS-OPA was used to acquire the local distribution of nickel in terbium after SSE purification in this study. The result of this study showed that nickel particles transported by the passing current from anode to cathode. This result was consistent with the result of glow discharge mass spectrometry (GDMS) analysis to the whole rod. LIBS-OPA is a promising approach which could be used to analyze the distributions of micro and trace impurities in other metals and alloys.

Highlights:
1. Distribution of Ni in terbium after SSE had been obviously observed by LIBS-OPA.
2. Nickel in Terbium is difficult to be removed by vacuum distillation, but after Solid State Electrotransport (SSE) for relative long time, content of Nickel can be greatly reduced.
3. The main reason of the difficult removal of nickel by vacuum distillation and easy removal by SSE had been discussed in detail in this study.

Keywords: Rare earth metal; Nickel; Terbium; Laser induced breakdown spectroscopy-original position statistic distribution analysis (LIBS-OPA)

Introduction

Pure materials based on rare earth metals are desired in order to investigate their intrinsic or unknown properties, and when used as magnetic refrigerant and magnetostriuctive materials, especially in the case of gadolinium, terbium, and dysprosium. The presence of impurities may affect the basic properties of pure metals [1]. However, the preparation of pure rare earth metals is difficult due to their high activity. As the noble metal of rare earth metals, terbium has the same chemical activity as other rare earth metals. For more than 100 years, due to the scarcity and precious of terbium, it has not been applied for a long time. In recent 30 years, with the rapid development of electronic information industry, terbium based functional materials emerge and has shown its unique importance [2]. The application of terbium mostly involved in the field of high technology, such as giant magnetostriuctive materials, coating materials, target materials, phosphors, magneto-optical storage materials, magneto-optical glass, and so on. Therefore, metal terbium has an attractive prospect for development [3]. Whether it is phosphor, coating material, giant magnetostriuctive material or target material, the content of nickel is required the lower the better, at least less than 10 ppm. Due to its ferromagnetism, the requirement of content of nickel is more stringent especially for giant magnetostriuctive materials. Therefore, the study of nickel as impurity is particularly important. Typically, vacuum distillation is the effective purification method for terbium of 99.9% [4]. Vacuum distillation is somewhat inadequate when the metal is needed for higher purity. This is because vacuum distillation may not be able to effectively separate metal impurities, such as nickel, owing to the same stage of vapor pressures and distillation rates as that of the terbium. In the past decades, solid-state electrotransport (SSE) has been used as an effective purification tool to acquire high purity rare earth metals [5-7]. SSE is a phenomenon whereby both host and impurity atoms within a metal migrate under the influence of an electrical field. In rare earth metals, the movement of the host atoms is slow compared with that of many impurity atoms, resulting in an effective redistribution of the impurity atoms within the host. In practice, SSE simply involves the passage of a high direct electrical current along a rod or strip of metal held in a suitable container under vacuum or an inert gas. The current both heats the sample and induces the electromigration of certain impurities. The impurities amenable to electrotransport will migrate towards one end of the sample, leaving the remainder of enhanced purity [8]. Electrotransport is effective for removal of most impurities, including nickel. Therefore, in this paper, SSE was used as the deep purification method to further separate the nickel impurities after the vacuum distillation of terbium.

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In high purity metals prepared by distillation or SSE or other techniques, the contents of impurities determined by common approaches such as inductively coupled plasma mass spectrometry (ICP-MS), glow discharge mass spectrometry (GDMS), and residual resistance ratio (RRR) only indicate the general level of every element. Sometimes, the distribution of several important elements may reveal some more useful information. However, up to date the distribution of the impurities in rare earth metal remains elusive. In this study, LIBS-OPA was used for the first time to characterize the distribution of impurity of nickel in terbium.

**Experimental Section**

**Experimental principle**

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy, which uses a highly energetic laser pulse as excitation source. The laser focuses on the samples that are thus atomized and excited. In principle, LIBS can be used to detect all elements and analyze any matter regardless of its physical state, since all elements emit light of characteristic frequencies when excited at sufficiently high temperatures. If the constituents of a material to be analyzed are known, LIBS may be used to monitor the presence of impurities [9,10].

When a strong pulsed laser beam focuses on the measured sample, it generates a radiation intensity that exceeds the breakdown threshold of the elements; thus, this process will generate plasma in the local area. A spectrometer can be used to collect the emission signals generated by a plasma beam. A quantitative analysis named original position statistic distribution analysis (OPA) can be conducted according to the intensity of the emitted spectrum. OPA is used to analyze the distributions of impurities in metals, especially in steel [11,12].

When a sample is continuously scanned and excited in a determined surface (cm²), the synchronous collection of the laser spectrum corresponding to the examined position and analysis of the collected signals by means of mathematical statistics allows obtaining the distribution analysis of the impurity elements for a determined area of a metal material.

If the sizes of the samples are large enough (>2 × 2 cm²), OPA is sufficient, however when the areas of the samples are smaller, LIBS is necessary. Therefore, LIBS-OPA is used to collect the distribution information for smaller samples (<2 × 2 cm²).

**Sample preparation**

Terbium was prepared according to a similar method as that used for gadolinium by fluorination, reduction, melting, and distillation before SSE [13]. Then, it was refined by electron beam melting, and subsequently placed into a rod of 0.76 cm in diameter and 15 cm in length. The SSE experiment was carried out at 1100°C and 450 A cm⁻² for 100 h under UHV (10⁻⁷ Pa) conditions. In order to observe the distribution of the impurity elements, the terbium rod was cut in half along its radial direction after SSE. Then, one of the half-cylinders was picked and successively divided into small half-cylinders, which were eventually mounted into cylindrical samples with their longitudinal section exposed, as shown in Figure 1. One fragment named S1 was chosen to carry out the LIBS-OPA measurements. The scan area of the selected sample was 6 mm × 5 mm.

In order to realize the migration effect, both ends of S1 named S2 and S3 were as small as possible to conduct the GDMS tests. All tests except LIBS-OPA are GDMS tests conducted by the Evans Analytical Group in this study.

**Results and Discussion**

**LIBS-OPA results**

LIBS-OPA measurements were performed to acquire the distribution of nickel. The 2D contour map obtained as a result of the collected signals is displayed in Figure 2.

The different colors shown in the vertical bar on the right side indicated the different strength of the element. Accordingly, the strength weakened successively with the color changes from the top to the bottom in the right bar. Therefore, the content of the chosen element decreased in turn with the changes of color according to the same order. This means that in the same sample the concentration corresponding to the black areas is minimal, while the content relative to the gray areas is maximal. As it can be seen in the figure, in the case of Ni the color changed from cyan to green, yellow, and then orange gradually from right to left, corresponding to the enhancement of the spectral intensity. The direction of the increasing concentration was the right direction of electron transportation. During the solid-state electrottransport process, it was evident that the effective valence (Z*) of nickel was negative, similar to the electrons and most of the impurities. A negative Z* indicates that the transport takes place in the cathode to anode direction [8], in analogy to the transport in gadolinium [14].

**Verification of the results**

At the same time, to check the transportation pattern of Ni, the other Tb rod after SSE under the same condition was divided into 5 fragments. Contents of metallic impurities including Ni after SSE had been characterized by GDMS. Figure 3 demonstrated the changes of contents of Ni in different position.

From the figure, content of Ni increased from cathode to anode.
This trend is quite similar to the result characterized by LIBS-OPA except for the slight difference of content.

Analysis and discussion

In the raw material constituted of terbium oxide, the content of nickel was less than 0.05 ppm. Owing to the use of nickel liners during the fluorination of oxides, the content of Ni increased to 18-20 ppm. After reduction, melting, and multi-distillation, the content of nickel decreased to around 8 ppm. In sample S3, the content of Ni was 7.8 ppm. At this time, the separation of nickel from terbium further would be very difficult by common purification, in view of the nature of nickel and terbium.

Usually, vacuum distillation is the most common method to refine metals. Normally, the distillation temperature of terbium is around 1575°C [15]. In order to describe the degree of separation further, modified separation factor [16,17] defined as \( k \) was introduced, which is a dimensionless ratio of distillation velocity of impurity element to the matrix metal, defined as:

\[
k = \frac{E_i}{E_m}
\]  

(1)

Where \( E_i \) and \( E_m \) are the distillation velocities \((g/(cm^2 \cdot s))\) of impurity and matrix metals, respectively, defined as the following formula,

\[
E = 4.37 \times 10^{-4} p \sqrt{\frac{M}{T}}
\]  

(2)

Where \( M \) is atomic mass, and \( T \) is temperature \((K)\). And \( p \) was calculated from the following equation [18]:

\[
\log \frac{p}{Pa} = 5.006 + A + BT^{-1} + C \log T + DT^{-1}
\]  

(3)

Figures 4 and 5 respectively compare vapor pressure \((p)\) and distillation velocity \((E)\) of Ni and Tb in the different temperature from 1100°C to 1950°C. Both of them increase with the temperature rises. Especially after 1700°C, the increase trends become more rapid.

From Figure 4, their vapor pressures kept in the same order of magnitude above 1300°C. 1430°C which is close to the melting point of Ni \( (1453°C) \) exists as a critical point. In this point, both of them are identical. The \( pNi \) is lower than \( pTb \) below this point; and it is higher when above this point. From Figure 5 their distillation velocities always keep in the same order of magnitude in the whole temperature range.

Further on, the ratio \( k \) was plotted to the temperature range above-mentioned. The ratio increases gradually with the temperature rises. Obviously, \( k \) changes little during the range in this study. Compared to other easily removed impurities, it is larger. That is, nickel will be distilled simultaneously. To achieve better separation, the value should be at least \( 10^{-2} \) orders of magnitude. From the figure, it is equal to 1 under 1774°C. Obviously, it’s impossible to separate them near this temperature by distillation. In order to achieve separation, lower temperature should be selected for distillation or direct sublimation extending processing time (Figure 6).

Therefore, the removal of nickel by common purification methods is relatively hard. However, in this study, the content of Ni was only around 3.5 ppm (for sample S2), i.e., less than half of S3, after SSE. This may be attributed to the effect of the electrical field. Following the introduction of an electrical field, the nickel particles were dragged by the electrons to the direction of the anode, according to the so called electron wind effect. On the other hand, the electronegativity of nickel \((1.91)\) is much higher than that of the terbium \((1.2)\). It will lead to the better purification effect because of its nuclei having larger...
attraction with outer electrons. This attraction will result in the nuclei being pulled ahead with the passing electron [10]. At the same time, the time required for SSE is much longer compared with other methods of purification, thus the effect could be remarkable. Therefore, SSE is a valuable method for the impurities which is difficult to remove, such as Ni, Al, Si, Ti, and so on.

Using the same method, Al, Fe, Si, Ti and other metal impurities difficult to move in Tb had been characterized. Similar conclusions had been obtained. Thus, LIBS-OPA is an effective method to show the distribution of trace and micro metallic impurities in terbium. This approach gave some light to the distribution analysis of impurities in solid state metals and alloys other than iron and gadolinium and dysprosium [19-21].

Conclusions

In summary, we demonstrated an approach to assess the distributions of Ni in terbium by LIBS-OPA. By collecting the spectral signals in combination with mathematical statistic results, a distribution analysis was realized. The transportation of impurities of nickel particles from cathode to anode under the action of a direct electrical field was directly observed by LIBS-OPA. Furthermore, this transportation allows the removal of more than half of the impurities that are generally difficult to eliminate. The study provides a better insight into the microcosmic world of metals in solid state electrotransport. The reason of difficult removal of nickel in terbium by distillation but easily by SSE had been discussed in detail at the same time in this study. This approach may be applied to other rare earth metals and alloys in addition to steel and terbium, and the results can be used to guide further preparation and purification.

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