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Investigation of oxygen diffusion behavior in terbium using $^{18}O_2$ isotopic tracking by high resolution SIMS

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ABSTRACT

High resolution secondary ion mass spectrometry (SIMS) analysis has been used to study the oxidation mechanisms when high purity terbium (Tb) metal is exposed to corroding environments containing $^{18}O_2$ isotope. The diffusion coefficients for ^{18}O in Tb at a natural atmosphere can be calculated, which plays an important role in subsequent purification and application in industry. Clear evidence has been shown for the characteristic distributions of ^{18}O after the kinetic transitions. The migration behavior is correlated with the existence of defects in the metal which allow the corrosions occur as localized nucleation. A set of ionization model has been developed to describe the oxidation process.

Application of rare earth metals terbium (Tb) has been studied for many years, like magnetic properties, optical properties, and purification technology [1–3]. However, it is also known that interstitial impurities on ppm level, especially oxygen, can seriously destroy these intrinsic properties. Moreover, Tb has high chemical affinity with oxygen, which makes the store process become a bothersome problem [4]. Therefore, the oxidation mechanisms of Tb need to be investigated deeply to promote academic and economic operations. The lack of literature on oxidation mechanisms of rare earth metals make this particular experiment more interesting.

Isotopic tracer technique has been widely used in the research of oxidation of Zr, Ni, Co [5–7], and even some semiconductor materials [8,9]. However, the study on the oxidation field of rare earth metal has been rarely reported so far. Changes in the oxide microstructure and composition have not been identified. The characteristics of the electrochemical barrier layer at the metal oxide interface are not yet clear. Tb has high chemical activities, which makes the $^{18}O_2$ tracking experiments more difficult.

High resolution secondary ion mass spectrometry (SIMS) analysis has previously been used to analyze crack chemistry in reactor steels, and grain boundary segregation in nickel [10,11]. NanoSIMS has a high lateral resolution (<100 nm) while still maintaining good sensitivity, and can easily distinguish isotopes. In this paper we report results of high resolution SIMS analysis of Tb oxidation in an $^{18}O_2$ enriched environment.

Samples were cut from high purity Tb cast ingot with 6 mm × 6 mm × 2 mm cuboids as shown in Fig. 1. Subsequently samples were placed in a laboratory-scale vacuum tubular furnace, containing vacuum system and ^{18}O pipeline. Samples were firstly annealed in vacuum (300 °C, 60 min) for activation. When the temperature of the chamber fell to room temperature, ^{18}O gas (98% purity) was introduced into the sample chamber. As the ^{18}O content is significantly above the natural abundance, ^{18}O signals can be used to track the location where new oxide is grown at different stages of the oxidation process.

In order to prepare specimens for NanoSIMS analysis, every oxidized sample was stuck using epoxy resin in a single column to expose the cross section of the metal oxide interface on one polished face. The columns were cut into pieces to fit the NanoSIMS holder (Φ10 mm × L3 mm), and samples were ground flat using silicon carbide paper down to 7000 grit. Cs^+ ions were used to achieve steady state conditions. Analysis was achieved by continuously scanning the area of interest with a large, defocused beam for approximately 40 min Images of 12 μm × 12 μm were acquired with a resolution of 256 × 256 pixels. Color merge images can be created using Image J with the Open MIMS plugin. Images present the ratio of isotopes. The brightness of the image gives an

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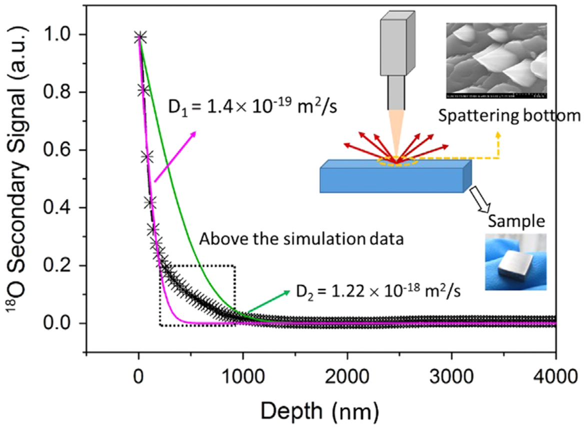

Fig. 1. SIMS depth profiles of $^{18}O^-$ in Tb and the diffusion coefficient at room temperature. Experimental set-up used for SIMS. Primary ion beam was positioned at the corner of the sample. SEM image of the spattering bottom could be clearly seen.

indication of the counts at each pixel.

For the investigation of O diffusion in Tb, samples were oxidized at 29 °C in the atmosphere with 20% $^{18}O_2$ (0.2 atm) to simulate the natural conditions. The oxidation duration was 24 h. Fig. 1 shows the ^{18}O isotope depth profile and the corresponding SEM image of the spattering bottom. The solution conditions fit well with the semi-infinite medium model developed by Crank [12]. Inside the media diffusion is described by

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is the relative ^{18}O concentration, x is the position as measured from the interface, D is the diffusion coefficient at room temperature, t is the time at that temperature. The diffusion coefficients for ^{18}O can be estimated by fitting the signal values to the expression

$$C(x,\, t) = C_l + \frac{C_0 - C_l}{2}\left(1 - erf\frac{x}{k}\right) \tag{2}$$

where $k = (4Dt)^{1/2}$. The samples were totally put into the $^{18}O_2$ atmosphere, the secondary signal on the surface can be set as one, and the initial concentration is zero. Since the ^{18}O concentration is proportional to the intensity of the secondary ions, simulations are used directly to estimate the diffusion parameters of the system in Fig. 1. As can be seen in Fig. 1 (dotted line), a first approximation $D = 1.4\times 10^{-19}$ m^2/s is assumed to be constant in a region of about 200 nm from the substrate surface. Inside the metal, the following measured ^{18}O isotopic fraction values are not fit the tendency of the simulation diffusion profile. The experimental concentration curve locates between the D_1 and D_2 profiles, indicating the inner diffusivity value is faster than 1.4×10^{-19} m^2/s while slower than 1.22×10^{-18} m^2/s. The literature on the diffusion coefficients of oxygen in solid rare metals is limited. This value is in the same range as La and Gd reported by Madelung in 1982 [12,13]. The possibility that this isotopic values come larger than the conventional simulation data in the inner region is ascribed to the single dimensionless parameter $\frac{x}{\sqrt{4Dt}}$. The formula considers that both the distance and time are proportional to the square root of time and ignores heterogeneous diffusion bring by the potential defects. It indicates that the diffusion model involves two different regions.

In order to determine the ^{18}O transport mechanism deeply, samples were oxidized in pure $^{18}O_2$ atmosphere with 1 atm for 1 h. Fig. 2(A) shows a typical oxidation process from (a) to (h), and simultaneous mapping of ^{18}O shows the distribution of this isotope. The analysis of the diffusion data shows that ^{18}O distributes on the surface nonuniformly at beginning, exhibits discrete localized corrosion with time going and nucleates in an uneven form on the grain boundary. Fig. 2(B) displays the 3D plot, the oxidation layer finally grows like the rugged hills. The detected results illustrate that the ^{18}O migration is a heterogeneous diffusion process. To research the development of the “rugged hills” , we further prepared a sort of Tb samples oxidized in 1 atm pure $^{18}O_2$ with 12 h, 48 h and 72 h.

Typical data from samples oxidized for different times are shown in Fig. 3. The position and thickness of the oxide readily shape up after 12 h and increase to about 4 µm after 72 h, as a band of high concentration running parallel to the metal/oxide interface. The typical concentration profiles as a function of the distance from the samples can be obtained by the SIMS instrument in the linescan mode. The profiles display two platforms with the oxidation time increased. As it knows the first one means the oxide coating, while we consider the second platform as the ions interface in view of Tb^{3+} and O^{2-}.

Based on the detect data, oxidation includes initial nucleation stage and oxide layer growth stage. At the first stage, ^{18}O diffuses into Tb basic metal conventionally via localized point and line defects, like vacancies, interstitials or dislocation to nucleation, as shown in Fig. 2. After the oxide layer formed, it will thicken more with time increased, including different ions movement.

The SIMS detect data (Fig. 3) show that Tb belongs to the

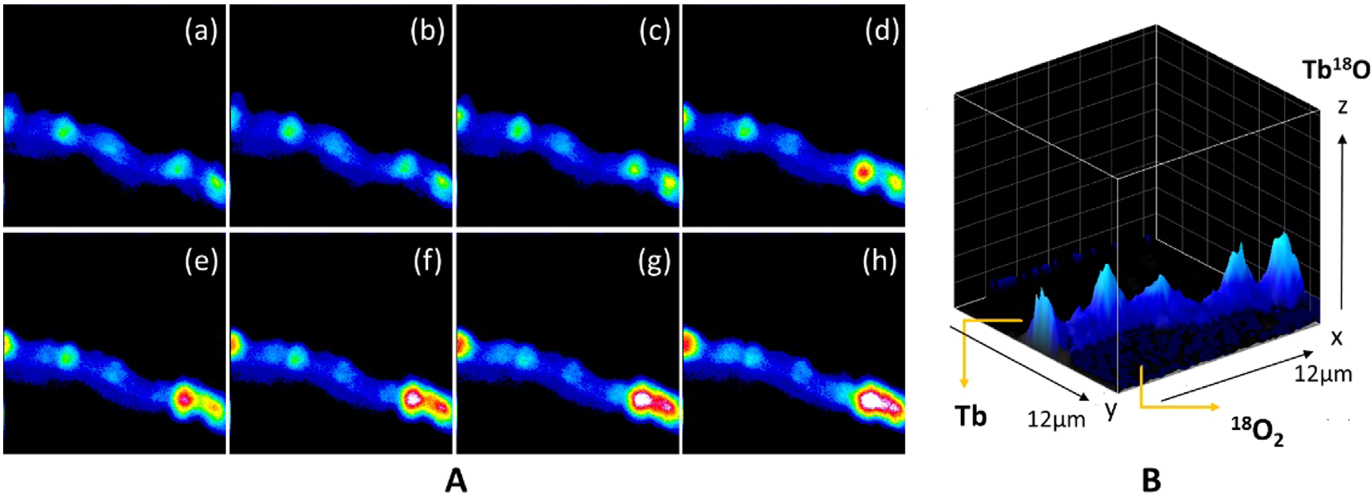

Fig. 2. Typical images (A) and the accordance 3D plot (B) of the oxidation process at 1 atm indicating the relative locations of $^{18}O^-$ signals in Tb.