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Energy Procedia 71 (2015) 313 – 319
Energy Procedia

The Fourth International Symposium on Innovative Nuclear Energy Systems, INES-4

Experimental Study on Diffusion of Ni in Lead-bismuth Eutectic (LBE)

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Abstract

Lead bismuth eutectic (LBE) is considered as a spallation target and a coolant for the future accelerator driven system (ADS) or fast breeder reactor (FBR), due to its excellent properties. However, LBE is corrosive to structural materials like austenitic stainless steels if they are exposed to LBE directly. In order to study the corrosion phenomenon between the structural steel and liquid LBE, it is very important to investigate the characteristics of diffusion of such species in liquid LBE. A measurement of diffusion coefficient of Ni and Cr in liquid LBE was carried out by using a capillary tube in our study. The inner diameter of the thin ceramic tube was 2 mm, which was filled with liquid LBE and Ni powder was added at the top end. The tube was kept at constant temperature (550°C-650°C) for diffusion of Ni in an electric furnace. Then, the LBE rod in the tube was cooled down and cut into several pieces. Ni concentrations were measured from Ni contents in nitric acid solution by means of the inductively coupled plasma mass spectrometry (ICP-MS). In our experiment, because the element of Ni, Pb and Bi was highly separated in the ion exchange process, it is helpful to improve the accuracy of the experimental result. From the experimental data of Ni concentration, the diffusion coefficient in LBE was obtained.

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Keywords: Diffusion, Nickel (Ni), Lead-bismuth Eutectic (LBE), Diffusion Coefficient, FBR, ICP-MS

1. Introduction

Lead-bismuth eutectic (44.5%Pb-55.5% Bi, LBE) has been one of the candidate coolants for lead-alloy-cooled fast reactor (LFR) and the candidate coolant and spallation target for the accelerator-driven transmutation system (ADS). However, LBE shows high aggressiveness for conventional structural steels. One of the corrosion

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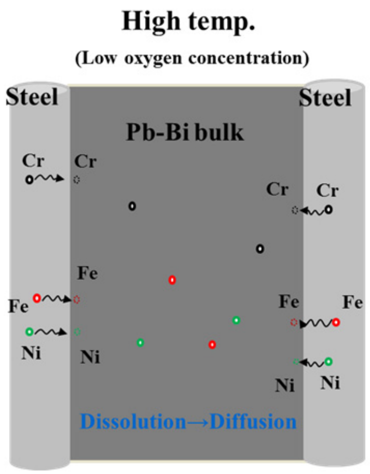
Selection and peer-review under responsibility of the Tokyo Institute of Technology
doi:10.1016/j.egypro.2014.11.884

phenomena is dissolution. The metallic elements of steels, such as iron (Fe), Chromium (Cr) and nickel (Ni), dissolute, then diffuse into the liquid LBE, before the concentration of these metals in the boundary that is between steel and LBE bulk becomes saturated. (Fig. 1)



Corrosion rate in Pb-Bi, J_M

$$\vec{J}^{LBE}_{diff,M} = -D_M \frac{C_{M,0} - C_M^{LBE}}{\delta}$$

D_M: diffusion coefficient of metal in LBE
$C_{M,0}$: concentration of metal at the interface between steel and LBE bulk
C_M^{LBE}: concentration of metal or oxygen in the bulk LBE
δ: thickness of diffusion boundary layer

Fig.1. Dissolution and Diffusion of metal elements into LBE.

The diffusion characteristics of dissolved elements from steels in the liquid LBE are important factor for prediction of corrosion rate in the dissolution type of corrosion as shown in Fig.1. Since Ni has the highest solubility in LBE among the elements in steels. Analytical estimate of the corrosion rate analytically requires the data of diffusion coefficient of Ni.

The diffusion coefficient of metallic elements in lead-alloy has been investigated by certain researchers. The diffusion coefficient of Fe in LBE at the temperature of 750°C was determined by using a rotating disk specimen, and the value was obtained as 2.27×10^{-5} cm^2/s [1]. The diffusion coefficients of Fe in LBE were determined to be 3.5×10^{-7} cm^2/s at 400˚C and 7.6×10^{-6} cm^2/s at 470˚C from the corrosion experimental data of ferritic / martensitic steel (T91) [2]. It was assumed that the corrosion rate of the steel was limited by Fe dissolution in the boundary layer of the liquid LBE. The diffusion coefficient of Fe in lead (Pb) was determined by analysing the grooving of grain boundaries in the liquid metal (3), and the empirical equation was obtained as

$$\log D = -5.31 - 2.5 / RT \quad (700˚C<T<1000˚C), \qquad (1)$$

where D (cm^2/s) is the diffusion coefficient of Fe in Pb, T (K) is the temperature of Pb, and R is the gas constant (8.31 J/ Kmol).

Moreover, the diffusion coefficient of silver (Ag^{110}) in LBE was obtained by using the capillary method by Niwa et al [4]. The empirical equation was determined as

$$\log D = -7.93 - 0.78 / RT \quad (435\ ˚C <T<610˚C). \qquad (2)$$

However, there is no measured data about the diffusion coefficient of Ni in the lead-alloy by means of situ measurement.

In this present study, the diffusion coefficient of Ni in LBE was obtained using the capillary method, which is the use of a thin crucible containing LBE and the diffusion species. The main advantage of this method is the diffusion coefficient is measured in situ without subsequent analytical calculation. The concentration of Ni in LBE is measured by using ICP-MS (7700 series) and the diffusion coefficient of Ni in LBE, the temperature range from 550 ˚C to 650 ˚C, is determined from the concentration profile of Ni which diffuses in the liquid LBE.

2. Experiment

2.1. Diffusion experiment

The preparation process of the diffusion test tube of a ceramic crucible containing LBE and Ni powder inside is showed in Fig.2 (a). Ni powder (purity: 99.9%, diameter of Ni particles: 10-20μm, Nilaco Co.) was used as a solute, and LBE was used as a solvent. In this experiment, Ni powder and the solid LBE were placed into a glove box filled with N_2 gas. A ceramic crucible tube made from 40%SiO_2-56%Al_2O_3 was used as a capillary tube for the diffusion experiment. The inner diameter of this crucible tube was 2 mm, and the length was 120 mm. The crucible was filled with liquid LBE that was heated up to 150 ˚C in the glove box. Then, Ni powder was put at the top surface of the liquid LBE. After that, the crucible, which was filled with LBE and nickel powder, was placed into a capsule made of stainless steel tube. Finally, this capsule was closed and removed from the glove box into a long electric furnace which had already heated up to the test temperature (550 ˚C - 650 ˚C). The capsule was kept in this high temperature furnace for 3.5h or 7h. After testing time, the capsule was cooled down to the room temperature quickly in the air and the temperature profile of the crucible during this experiment process is shown in Fig.3. The temperature was taken at three spots (top, middle and bottom) along the capillary tube (Fig.2 (b)). Due to the electric furnace was long enough, three temperature profiles of the crucible were typically the same and the heat up time was approximately 15 minutes.

The solid LBE rod where Ni diffused was taken out from the crucible, and cut into small pieces, approximately 1mm per cut, as shown in Fig.4.

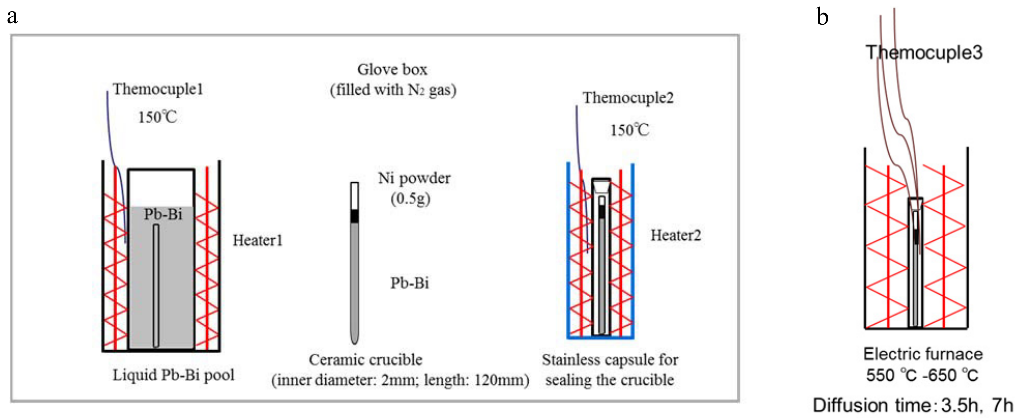


Fig.2. (a) Procedure of the diffusion test by using a thin ceramic crucible; (b) High temperature (550 -650˚C) electric furnace

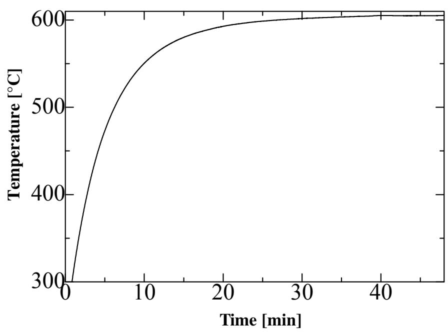


Fig.3. Temperature profile in the diffusion experiment

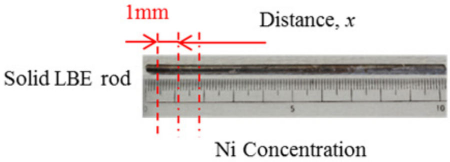


Fig.4. Solid LBE rod after 3.5h (7h) diffusion test and cooling

2.2. Measurement of Ni concentration in LBE

The solid LBE pieces were dissolved by nitric acid (61%, 1.38g/ml) and the concentration of Ni in per specimen was measured by using of the inductively coupled plasma mass spectrometry (ICP-MS).

In this measurement, taking account of the accuracy of analysis of Ni^{2+} concentration and the contamination from the large quantity of Pb^{2+} and Bi^{3+} in the specimen, Ni^{2+} ion was separated from large amount of Pb^{2+} and Bi^{3+} ions in each specimen by ion exchange before the measurement. The cation ion exchange resign was used and the system was shown in Fig.(5).a. In order to elute the Ni^{2+} from the mixture solution with Ni^{2+}, Pb^{2+} and Bi^{3+}, a test separation for a mixture sample solution with known amount of consistent: 10μg Ni, 100μg Pb and 100μg Bi was performed and the separation result is shown in Fig.5.(b). This methodology is called as ion exchange chromatography method.

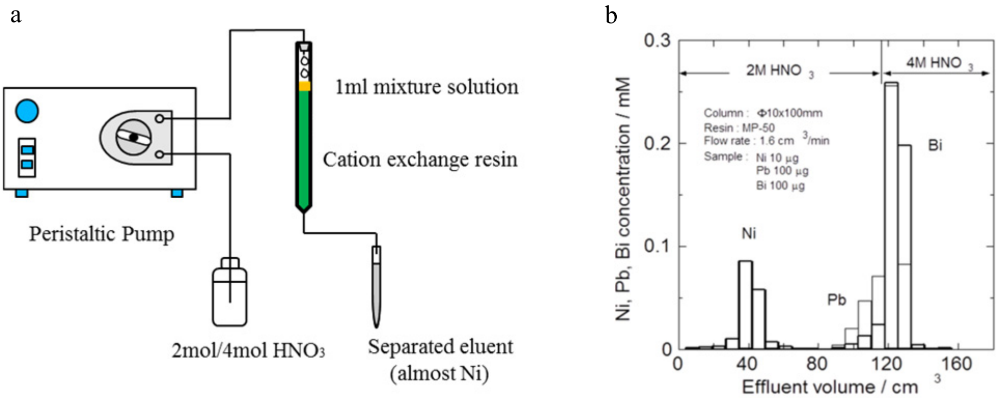


Fig. 5. (a) Ion exchange system; (b) chromatogram of Ni, Pb and Bi

It has been found that 99.2% of Ni^{2+} ion can be separated from the mixture solution by putting 80ml of 2M HNO_3; and Pb^{2+} and Bi^{3+} ions stuck to the resin can be cleaned by pouring 80ml of 4M HNO_3. Thus, this procedure was adopted to elute the Ni^{2+} in each specimen before the measurement. The amount of Ni^{2+} in each specimen can be calculated as follows:

$$m_{\mathrm{Ni}} = \sum_j C_{\mathrm{Ni},\,j} V ,$$

where m_{Ni} [μg] is the total amount of Ni^{2+}, $C_{\mathrm{Ni,\,j}}$ [ppb] is the concentration of Ni^{2+} measured by ICP-MS , V [mL] is constant volume for each column.

The concentration of Ni in each specimen w [wt%] was calculated from

$$w = m_{\mathrm{Ni}} / m ,$$

where m is the mass of the solid specimen [g].

2.3. Calculation of diffusion coefficient of Ni in LBE

The relationship between the Ni concentration in LBE, C and the diffusion coefficient of Ni in LBE, D, can be written in the following equation from Fick's second law

$$\frac{\partial C}{\partial t} = \mathrm{D}\frac{\partial^2 C}{\partial x^2}, \tag{3}$$

where t is the diffusion time and x is the distance from the interface between Ni and LBE.
The analytical solution of the equation (3) is expressed as

$$\frac{C - \mathrm{C}_0}{\mathrm{C}_B - \mathrm{C}_0} = 1 - \mathrm{erf}\left(\frac{x}{2\sqrt{\mathrm{D}t}}\right), \tag{4}$$

where C is the Ni concentration at the distance after the diffusion time t , C_0 is the Ni concentration at the infinity, and C_B is the Ni concentration at the boundary between the Ni powder and LBE. In this study, it was assumed that C_B was equal to the solubility of Ni in LBE C_s that was given by [5]

$$\log C_{s(Ni)}(wt\%) = 1.53 - 843/T(K)\,. \tag{5}$$

The theoretical concentration distribution is shown in Fig.6. From the experiment results, the diffusion coefficient was derived by using the least-squares method based on Fick's second law, Eq. (4).

3. Results and Discussion

The experiment results of Ni concentration distribution in LBE at the temperature of 550 (time: 3.5h and 7h), 600 ˚C (time: 3.5h) were shown as plots in Fig.6. The solid line on the graph designates the fitting results of concentration distribution based on Eq. (4), with the proviso that the position of x=0 is shifted from the interface between Ni and LBE. The fitting results were compared with the experiment data with a parameter of the diffusion coefficient. The diffusion coefficient was determined from the value for the best fitting condition. From the fitting result, the diffusion coefficients of Ni in LBE can be determined at each temperature.

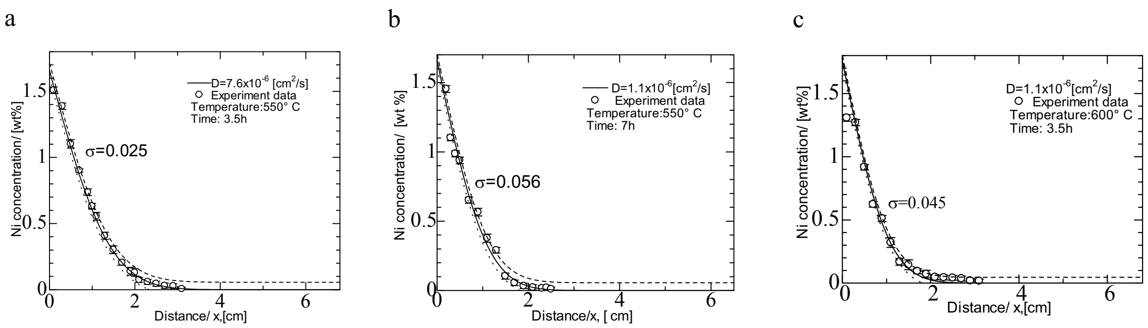


Fig.6. Measurement results of Ni concentration distribution in LBE with the theoretical curves of Eq.(4), (a)550 ˚C, 3.5h; (b) 550 ˚C, 7h; (c) 600 ˚C, 3.5h

For instance, the diffusion coefficient is 7.6×10^{-6}[cm^2/s] at 550 ˚C, 3.5h, and Table1shows all the experiment results. It is found that the measurement error of Ni concentration in this study was 0.02wt%, and the fitting error was under 0.1 (10%). As shown in Fig.3, if the decreasing rate of temperature was approximately the same as the rising rate, the sum of the heating and cooling times of 0.5h was not included in the diffusion time t, which gives a maximum error of 14% in the estimate of D.

Table1. Experimental results of diffusion coefficient of Ni in LBE

Diffusion time: 3.5h			
Temperature [˚C]	550	600	650
Diffusion coefficient [cm²/s]	7.5×10^{-7}	1.30×10^{-6}	6.0×10^{-6}

Diffusion time: 7h			
Temperature [˚C]	550	600	650
Diffusion coefficient [cm²/s]	1.1×10^{-6}	1.6×10^{-6}	9.0×10^{-6}

Fig.7 shows the Arrhenius plot of the experiment results of Ni diffusion coefficient in LBE. The diffusion coefficient increased by increasing the temperature of LBE. The results obtained with the diffusion time of 3.5 h are compared with those obtained with 7 h. It is found that the diffusion time had no effect on the result of diffusion coefficient.

The correlation of diffusion coefficients of Ni in LBE D_{Ni} (cm^2/s) with temperature can be obtained as

$$D_{Ni} = 179\exp(-\frac{1.49\times10^{6}}{\mathrm{R}T}) \qquad (500°C \le T \le 600°C) \quad , \tag{6}$$

where T (K) is the temperature of LBE, and R is the gas constant (8.31 J/ Kmol).

The present experiment result of diffusion coefficient of Ni in LBE is compared with the experiment result of diffusion coefficient of Ag [4] in Pb-Bi (56.2%Pb-43.8%Bi). It is found that the diffusion coefficient of Ni is much lower than that of Ag. In comparison with the diffusion coefficient of Ni in LBE calculated from Stokes-Einstein equation and Sutherland-Einstein equation expressed by

$$D = \frac{\kappa T}{N\pi r\eta}, \tag{7}$$

where κ is the Boltzmann constant, T is the temperature, r is the atomic diameter of Ni. N is equal to 6 for the Stoke -Einstein equation and 4 for the Sutherland-Einstein equation. η (Pa s) is the viscosity of LBE given by [5]

$$\eta = 4.94\times10^{-4}\exp(754/T). \tag{8}$$

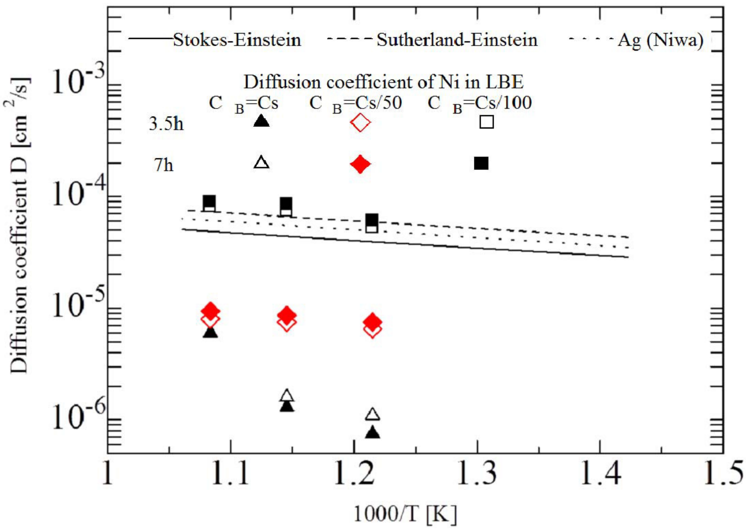


Fig.7.Diffusion coefficients of Ni, compared with that of Ag in Pb-Bi (43.8%-Bi) and calculation results from Stokes-Einstein equation and Sutherland-Einstein equation.

It is found that the present result is much lower than the calculated results from Stokes-Einstein equation and Sutherland-Einstein equation. One of the reasons is considered as the assumption of Ni concentration at the boundary between Ni powder and liquid LBE. At this boundary, Ni concentration was assumed to be the solubility of Ni in LBE calculated by Eq. (5) for the determination of the diffusion coefficient in this study. However, the solubility of Ni in LBE is much higher than those of Ag and Fe, since it is considered to be the overall solubility including both of the concentration of dissolved Ni as Ni atoms and the content of solid Ni compounds formed in LBE during the dissolution. The solid compounds that are lighter than LBE float near the surface of LBE due to the buoyancy force without descending. Only the dissolved Ni may diffuse downward in LBE in the vertical capillary tube. Therefore, it is probable that the compounds have influence on the value of diffusion coefficient. Thus, the real concentration of Ni atom at the boundary expressed in Eq. (4) should be lower than the solubility C_s given by Eq. (5).

The diffusion coefficients were determined with the assumption of $C_B = C\text{s}/50$ and $C_B = C\text{s}/100$. When C_B is equal to Cs/100, the concentration of Ni atomic at the boundary is in the same order of magnitude of the solubility of Ag in LBE. The results are shown in Fig. 8. It is found that diffusion coefficients determined by using $C_B = C\text{s}/100$ have a good agreement with the calculated results from Stokes-Einstein equation and Sutherland-Einstein equation. It suggests that there is necessity to consider the solid compounds of Ni, Pb and Bi during the investigation of Ni diffusion phenomena in LBE.

4. Conclusion

The methodology of measurement of Ni concentration in LBE using the ion exchange chromatography and ICP-MS has been established. Based on this methodology and Fick's second law, the diffusion coefficients of Ni in LBE at 550, 600 and 650 ˚C were determined experimentally by using capillaries tube. A correlation of diffusion coefficient of Ni was obtained. However, it was much lower than the calculated results from Stokes-Einstein equation and Sutherland-Einstein equation and the diffusion coefficient of Ag in Pb-Bi (56.2%Pb-43.8%Bi). In consideration of the solid compounds of Ni, Pb and Bi at the boundary between Ni powder and liquid LBE during the dissolution, It is found that diffusion coefficients determined by using $C_B = C\text{s}/100$ have a good agreement with the calculated results from Stokes-Einstein equation and Sutherland-Einstein equation. This parametric study on Ni concentration in LBE at the boundary layer suggests that it is necessary to take a consideration of the compounds during the investigation of diffusion phenomena.

Acknowledgements

The author would like to express their gratitude to Mr. S. Matsui for his assistance in the present experiment, and Mr. T. Yano for his fruitful discussion in this study.

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