Solid-state Reaction Studies in Al$_2$O$_3$–TiO$_2$ System by Diffusion Couple Method

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In order to study the formation mechanism of Al$_2$TiO$_5$, the solid-state inter-reaction between Al$_2$O$_3$ and TiO$_2$ under Ar atmosphere was investigated in the temperatures range from 1 723 to 1 873 K by the diffusion couple method. The phase of the inter-compound and the change of the concentration of Ti across the diffusion layers were confirmed by the electron probe microanalysis (EPMA). Based on the concentration profile of Ti element, the thickness of diffusion layers was obtained and the interdiffusion coefficients which were affected by temperature and concentration of Ti were calculated by the Wagner method. The experimental results indicate that the thickness of diffusion layers increases with the diffusion time. The magnitudes of interdiffusion coefficients were in the range of $10^{-10}$–$10^{-12}$ cm$^2$/s and the range of diffusion activity energy $E_D$ was from 266.77 kJ/mol to 309.96 kJ/mol.

KEY WORDS: interdiffusion; diffusion couples; titanium dioxide; aluminium oxides; diffusion activity energy.

1. Introduction

The polycrystalline Al$_2$TiO$_5$ ceramics are one of the excellent material for thermal shock resistance. Due to the low thermal expansion,$^{1)}$ low Young’s modulus and high melting point of 1 333 K, they had been used as an insulation material in engine components such as piston bottom, port-liners, and turbochargers etc.$^{2)}$ There has been some investigations on the synthesis and properties of Al$_2$TiO$_5$. Hans Wohlfromm$^{3)}$ studied the formation of Al$_2$TiO$_5$ by sintering the Al$_2$O$_3$/TiO$_2$ multilayers in the temperature range from 1 473 to 1 773 K, and it was found that TiO$_2$ played an important role in the initial growth of Al$_2$TiO$_5$. In the work by M. Nagano,$^{4)}$ coprecipitation method was applied to prepare the Al$_2$TiO$_5$ in air in the temperature range of 1 573 to 1 773 K. A fine grained-structure was obtained at 1 573 K, but resulted in large-grained and cracked microstructures at 1 673 and 1 773 K. Addition of ZrO$_2$, BaO or ZrSiO$_4$ was effective in suppressing the thermal decomposition of Al$_2$TiO$_5$.

Moreover, Non-metallic inclusions of (Al, Ti) oxide were found in the steel containing Ti and the formation of (Al, Ti) oxide, such as Al$_2$TiO$_5$, TiO$_2$, Ti$_2$O$_3$, can be utilized as nuclei for MnS and the intragranular ferrite, which improve the toughness and strength of steel.$^{5)}$ Generally, in the process of steel making, Ti is added as an alloying element after the deoxidation process by Al. The angular Al$_2$O$_3$ inclusions formed during Al deoxidation, which will be evolved to spherical inclusion after the addition of Ti.$^{6)}$ In addition, the excess addition of Ti may cause the nozzle clogging, specially for Ti bearing Al-killed steel. Therefore, it is necessary to study the reaction mechanism between Al–Ti oxides to understand above problems better. In-Ho JUNG et al.$^{7)}$ presented the optimized phase diagram of Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ system for Ti-Bearing and Al-killed steels.$^{7)}$ Cong Wang et al.$^{8)}$ reported that the effect of Ti addition on the transient behavior of inclusion. Morphological change of inclusion was found when Ti/Al ratio reached 0.5. Min-Ki Sun et al.$^{9)}$ studied that various Al and Ti deoxidation techniques had influences on the morphology and chemistry compositions of inclusions.$^{1)}$

Most researches were related to the formation of Al$_2$TiO$_5$ or Al/Ti oxides, however, the solid-state reaction kinetics of Al$_2$O$_3$–TiO$_2$ system was studied rarely. In the present study, the diffusion between Al$_2$O$_3$ and TiO$_2$ was processed by a diffusion couple method in the temperature range from 1 723 to 1 873 K under Ar atmosphere. The influences of time and temperature on the formation of intermediate products were investigated. The kinetic parameters, interdiffusivity and apparent activation energy, were calculated.

2. Experimental

The analytical reagent grade TiO$_2$ (>99%) was used for diffusion experiments, which was pre-dried at 393 K for 4 h in a drying oven under forced convection. The powers of TiO$_2$ were pressed to pellet of 10 mm diameter and about 5 mm thickness in a stainless steel die under 500 MPa. The prepared pellets of TiO$_2$ were put into the muffle furnace and sintered at 1 773 K for 12 h in air atmosphere. The purchased Al$_2$O$_3$ sheets (the relative density 99.4%) were

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cut into the same as TiO$_2$ pellets. The samples of Al$_2$O$_3$ and TiO$_2$ were ground and mechanically polished. Then the polished surface was clean in alcohol by ultrasonic.

To obtain a good contact between TiO$_2$ and Al$_2$O$_3$ pellets, the diffusion couple was fixed in a clamp made by Al$_2$O$_3$ with a constant load. The diffusion experiments were carried out in a SiC-heated furnace, and temperature was controlled by a B-type thermocouple. After reaching the target temperature, the diffusion couple was gradually pushed into the constant temperature zone. The diffusion couple was preheated for 20 min from the room temperature zone to the constant temperature zone. The gas flow of high purity argon was 400 ml/min. The diffusion experiments were performed with the conditions presented in Table 1. After the desired heat treatment, the diffusion couples were quenched in air atmosphere to the room temperature rapidly.

The completed samples were mounted into the epoxy and triethanolamine mixture (the mass ratio of 9 to 1). The treated samples were cut perpendicular to the contact plane with a diamond saw. One side of the pellet was polished with the SiC sand paper and diamond polishing paste (size of W1.5), the flatness of polished diffusion interface was observed by an optical microscope, then cleaned by ultrasonic in ethyl alcohol. The quantitative analysis of the composition profile was by electron probe microanalysis (EPMA, JEOL JXA-8230). Pure metal aluminum and titanium used as the standard material. An electron volt of 20 kV and specimen current of $10^{-8}$ A were used for the analysis. The peak concentrations of Al, Ti and O ions were measured with $1/1000$ interval near the interface of the diffusion couple. The thickness of the diffusion layers were determined by the diffusion profiles.

### 3. Results and Discussion

#### 3.1. Al$_2$O$_3$–TiO$_2$ System

Figure 1 shows the phase diagram of Al$_2$O$_3$–TiO$_2$. When the temperature is in the range from 1556 to 2073 K, the inter-compound in the diffusion is the only phase of Al$_2$TiO$_5$, below 1556 K, Al$_2$TiO$_5$ decomposes into Al$_2$O$_3$ and TiO$_2$. The reaction can be expressed as Eq. (1): $20^\circ$

Al$_2$O$_3$ ($\alpha$) + TiO$_2$ (rutile) = Al$_2$TiO$_5$ ($\beta$) .......................... (1)

As shown in Fig. 3, the thickness against the square root of diffusion time represents a linear relation, described by Eq. (3):

$L = 1.59 \times 10^{-7} t^{1/2}$ .................................. (3)

This linear relationship indicates that the rate controlling step in this reaction of Al$_2$TiO$_5$ formation could be the interdiffusion of Ti and Al ions. $^{22}$

#### 3.2. Growth of Intercompound, Al$_2$TiO$_5$

The multilayer structure after thermal treatment at different temperatures for 7.2 ks is shown in Fig. 2. The dark side of the view was Al$_2$O$_3$ and the light side was TiO$_2$. From the diffusion profiles of elements, the molar ratios of Al:Ti:O in Al$_2$TiO$_5$ phase. Besides, Al$_2$TiO$_5$ was so brittle that the diffusion interface resulted in cracking as shown in Fig. 2(d). The crack appeared after the dropping of Al$_2$TiO$_5$.

The average thickness of the Al$_2$TiO$_5$ layer ($\Delta x$) determined by the concentration of Ti and Al in Al$_2$TiO$_5$ phase is shown in Fig. 2. For getting the values of the Al$_2$TiO$_5$ layer thickness, ten measured values were averaged to obtain the average thickness ($\bar{L}$), which is listed in Table 2. The average thickness $\bar{L}$ can be calculated by Eq. (2).

$\bar{L} = \sum_{i=1}^{10} L_i / 10$  ........................................... (2)

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#### 3.3. The Calculation of the Interdiffusion Coefficient

Generally, traditional Boltzmann-Matano method can be used to calculate the interdiffusion coefficient by Eq. (4):
\[
D(c^*) = -\frac{1}{2t} \left( \frac{\partial c^*}{\partial x} \right)_{x=x'^*} \int_{x'}^{x'^*} x dc^* 
\]

Where \( D(c^*) \) is the diffusion coefficient at random position \( x'^* \) and \( c^* \) is the mole fraction, \( t \) is the diffusion time, \( c_1 \) is mole fraction at the Matano interface.

However, when the inter-composition generates, the traditional Boltzmann-Matano method is invalid because the diffusion profiles is discontinuous. For the complex binary system, Jost\(^{23}\) and Appel\(^{24}\) modified the Boltzmann-Matano equation, which can be expressed as Eq. (5):

\[
D(c^*) = -\frac{1}{2t} \left( \frac{\partial c^*}{\partial x} \right)_{x=x'^*} \int_{x'}^{x'^*} x dc^* \int_{x'}^{x'^*} x dc^* - (c_2^* - c_1^*)X \quad \ldots \quad (5)
\]

Fig. 2. Cross-sectional view of the diffusion interface after annealing for 7.2 ks at (a) 1 723 K, (b) 1 773 K, (c) 1 823 K, (d) 1 873 K.

Where \( c^* \) is the mole fraction of the interest at random position \( X \), \( c_1^e \) and \( c_2^e \) are the respective equilibrium concentrations of the diffusing species in the two phases in contact. The \( X \) is measured from the Matano interface \( (x=0) \), which is determined difficultly.

In order to reduce the error of Matano interface determining, the Wagner method was used to determine the variation of interdiffusivity. The Wagner equation\(^{25}\) is shown as Eq. (6):

\[
D(N_2^e) = \frac{\left( N_2^e - N_2^i \right) V_m \left( N_2^e \right)}{2t \left( \frac{\partial N_2}{\partial X} \right)_{x=x'^*}} x \left( 1 - Y' \right) \int_{x'}^{x'^*} \frac{Y'}{V_m} dx + Y' \int_{x'}^{x'^*} \frac{1 - Y'}{V_m} dx \quad \ldots \quad (6)
\]
Where $x^*$ is the distance at which $N_2^* = N_2^*$, $N_2^*$ is the mole fraction of Ti$^{4+}$ at random position which is the concentration of interest for interdiffusivity calculation, $N_2'$ is the initial mole fraction of Ti$^{4+}$ in TiO$_2$ and $N_2' = 0.33$, $N_2''$ is the initial mole fraction of Ti$^{4+}$ in Al$_2$O$_3$ and $N_2'' = 0$. $V_m$ is the mole volume of component, and $V_m(N_2^*)$ is the mole volume at concentration $N_2^*$. Because the change of the molar volume was so small that the equation can be revised as

$$D(N_2^*) = \frac{1}{2\tau(\partial N_2 / \partial x)_{x=x^*}} \times \left[ 1 - \frac{N_2'}{0.33} \int_{x}^{x^*} N_2^* dx + \frac{N_2'}{0.33} \int_{x^*}^{\infty} (0.33 - N_2^*) dx \right]$$

............................................ (8)

As shown in Fig. 4, the left side is Al$_2$O$_3$ and another side is TiO$_2$, the curve represents the concentration of Ti span the boundaries of Al$_2$TiO$_5$/Al$_2$O$_3$ and Al$_2$TiO$_5$/TiO$_2$. The first integral is expressed as the area A and the second integral is the area B. Compared with the method of modified Boltzmann-Matano, Matano interface is not necessary to confirm, which will make the calculation more convenient.

The results of interdiffusion coefficients calculated by Eq. (8) are shown in Table 3. At different position of boundary layer, the interdiffusion coefficients are different. $N_{Ti}=0.013$ presented the mole fraction of Ti ions in Al$_2$O$_3$ side. $N_{Ti}=0.125$ is the intermediate phase of Al$_2$TiO$_3$ and $N_{Ti}=0.25$ presented the TiO$_2$ side. According to Arrhenius equation, the plots of In D vs $T^{-1}$ for different mole fraction of Ti$^{4+}$ ions are shown in Fig. 5. The values of $E_D$ and $D_0$ are listed in Table 4.

As shown in Fig. 5, the magnitudes of interdiffusion coefficients were in the range of $10^{-10}$~$10^{-12}$ cm$^2$/s. The values in the phase of Al$_2$TiO$_3$ were larger than Al$_2$O$_3$ side and TiO$_2$ side. It is possible that vacancy defect concentration in the intermediate phase is more than that of two sides. In the Al$_2$TiO$_3$ phase, the interdiffusion phenomenon of Ti ions and Al ions is more frequent and the effect of temperature on the interdiffusion coefficient was obvious.

Many literatures reported the solid-solid reaction in diffusion systems belong to the type of A$_2$O$_3$–BO$_2$ system. The apparent activation energy value in Fe$_2$O$_3$–TiO$_2$ system obtained by Z. S. Ren was (92.14±26.34) kJ/mol during 1 323–1 473 K. The value in Al$_2$O$_3$–SiO$_2$ system reported by Davis and Pask was
Table 4. The values of ln D_0 and E_0 at different mole fraction of Ti^{4+}.

<table>
<thead>
<tr>
<th>N_{Ti}</th>
<th>ln(D_0) (cm²/s)</th>
<th>E_0 (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.013 ± 0.001</td>
<td>-9.63 ± 1.99</td>
<td>266.7 ± 10.29</td>
</tr>
<tr>
<td>0.125 ± 0.01</td>
<td>-7.55 ± 0.69</td>
<td>280.3 ± 16.14</td>
</tr>
<tr>
<td>0.25 ± 0.01</td>
<td>-6.35 ± 1.49</td>
<td>309.96 ± 22.22</td>
</tr>
</tbody>
</table>

(2) The vacancy mechanism was applied to interpret the solid-solid reaction of Al₂O₃–TiO₂ system. The diffusion coefficients increase with the temperature and the rate controlling step in this reaction of Al₂TiO₅ formation could be the interdiffusion of Ti and Al ions.

(3) The apparent diffusion activation energy is calculated by the Arrhenius equation. The values were 266.77 ± 10.29 kJ/mol in Al₂O₃ side, 280.31 ± 16.14 kJ/mol in the phase of Al₂TiO₅, and 309.96 ± 22.22 kJ/mol in TiO₂ side.

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4. Conclusions
The diffusion couple method was used to investigate the solid-solid reaction in the system of Al₂O₃–TiO₂ in the temperature range of 1723–1873 K.

(1) The Wagner method was applied to calculate the diffusion coefficients and the order of magnitudes in Al₂O₃–TiO₂ system was in the range of 10⁻¹⁰–10⁻¹² cm²/s.

(2) The vacancy mechanism was applied to interpret the solid-solid reaction of Al₂O₃–TiO₂ system. The diffusion coefficients increase with the temperature and the rate controlling step in this reaction of Al₂TiO₅ formation could be the interdiffusion of Ti and Al ions.

(3) The apparent diffusion activation energy is calculated by the Arrhenius equation. The values were 266.77 ± 10.29 kJ/mol in Al₂O₃ side, 280.31 ± 16.14 kJ/mol in the phase of Al₂TiO₅, and 309.96 ± 22.22 kJ/mol in TiO₂ side.