

KINETICS OF LIQUID PENETRATING INTO GRAIN BOUNDARY^①

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ABSTRACT The kinetic equation of liquid penetration was derived from the suppositions that the solid-liquid interface energy is less than half of the grain boundary energy and the penetration is controlled by the diffusion of solute. The equation, verified by the existed experiment, showed that both thermodynamics and kinetics of liquid penetrating into grain boundary are dependent on solid-liquid interface energy.

Key words: interface interface energy wetting penetration

1 INTRODUCTION

The interactions between solid and liquid exist in the processing and application of materials. The liquid penetrating into grain boundary, one of the interactions, is a key mechanism for various phenomena in materials. In the corrosion of refractory by slag, slag melt penetrates along the grain boundary, and the isolated grains are easily swept into the slag melt. The isolation of grains by liquid phase initiates the cracking of the welded materials and embrittles the materials cooled by metal melts in a nuclear reactor. On the other hand, the liquid penetrating along grain boundary is beneficial to powder sintering. But, the liquid penetration was seldom analyzed kinetically^[4].

Thermodynamically, the equilibrium distribution of liquid at grain boundary depends on the interface energy^[5]. In case the solid-liquid interface energy (γ_{SL}) is less than half of grain boundary energy (γ_{SS}), the liquid can completely penetrate into grain boundary. If $1/(2\gamma_{SS}) < \gamma_{SL} < \sqrt{3}/3\gamma_{SS}$, the liquid phase can penetrate completely into grain edge but not into grain boundary. If $\gamma_{SL} > \sqrt{3}/3\gamma_{SS}$,

both grain edge and grain boundary can not be completely penetrated by the liquid. In the present paper, the kinetic equation for liquid penetrating into grain boundary was derived from the suppositions that the penetration is controlled by the diffusion of solute and $2\gamma_{SL} < \gamma_{SS}$.

2 KINETICS MODEL OF LIQUID PENETRATING INTO GRAIN BOUNDARY

2.1 Mechanism and Suppositions

When a polycrystal exists in equilibrium with a liquid, the grain boundary of the polycrystal, unlike the plain surface, is not in equilibrium. Since the interface tensions on the grain boundary are not balanced by each other, there is additional pressure. Then, the chemical potentials of components on the grain boundary are greater than that of components on the solid plain surface, and the concentrations of the components of solid phase in the equilibrium liquid near the grain boundary are correspondingly higher than the concentrations near the solid plain surface. The difference between the concentrations near the grain

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boundary and near the surface results in the diffusive transfer, and the solid components on the grain boundary dissolve into the liquid and deposit on the solid surface. With the dissolution and deposition, the configuration of the solid-liquid interface changes.

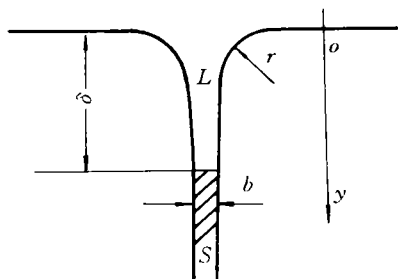


Fig. 1 Schematic drawing of liquid penetrating into grain boundary

b —the width of grain boundary, s —grain boundary as solid phase, L —liquid phase, δ —the depth of liquid penetrating into grain boundary, r —the radius of the curved surface

In case the solid-liquid interface energy or tension (γ_{SL}) is greater than half of grain boundary energy or tension (γ_{SS}), the grain boundary tension can be balanced by the solid-liquid interface tension at the equilibrium dihedral angle of the liquid. In this case, the components on grain boundary can not continue to dissolve in advance, and the configuration of the solid-liquid interface changes further by the dissolution and deposition of the components at the solid surface sites with different curvatures. The process is analogous to the formation of grain boundary groove during heat treatment^[4].

In case $2\gamma_{SL} < \gamma_{SS}$, grain boundary tension can not be balanced by the solid-liquid interface tension, and the chemical potentials of the components on the grain boundary are always higher than that of the components on the polycrystal surface. As shown in Fig. 1, the components on the grain boundary dissolve continuously and the liquid completely penetrate into the grain boundary. In general, grain boundary energy is related to the orientation of adjacent grains. But the large angle grain boundary, which amounts to 80 percent

of all grain boundaries in polycrystal, has a definite grain boundary energy^[5]. For the derivation of the kinetic equation of the liquid penetration, the following suppositions are taken: 1) the liquid is composed of components A and B , and the polycrystal is composed of component B . 2) the solid-liquid interface energy and grain boundary energy are not related to the orientation of grain in polycrystal. 3) the rate of liquid penetration is controlled by the diffusion in the liquid.

In the process controlled by diffusion, the components of solid and liquid on the interface are in equilibrium. In present paper, the equilibrium composition of the liquid on grain boundary is firstly derived from thermodynamics law, and the kinetic equation of liquid penetration is then derived from diffusion law.

2. 2 Equilibrium Composition (X_B) of Liquid on Grain Boundary

Take a system which consists of the liquid phase penetrating into grain boundary and the grain boundary with a width of b as solid phase. In the system, consider the isothermal equilibrium transformation between the solid and liquid phases, or, the dissolution and growth of solid phase. Since the volume change in the dissolution or growth is little, the process can be considered as an isothermal and iso-volume process. So, the change of work function (F) in the process equals to zero,

$$dF = dF^L + dF^S = 0 \quad (1)$$

where F^S and F^L are the work functions of solid phase and liquid phase respectively, dF^S and dF^L can be expressed as follows:

$$\left. \begin{aligned} dF^S &= -S^S dT - P^S dV^S \\ &\quad + \mu_B^S dn_B^S + \gamma_{SS} dA^S \\ dF^L &= -S^L dT - P^L dV^L \\ &\quad + \mu_B^L dn_B^L + \gamma_{SL} dA^L \end{aligned} \right\} \quad (2)$$

where S , T , P , V , γ , A , n and μ_B are entropy, temperature, pressure, volume, interface tension, interface area, mole number, and the chemical potential of component B respectively, and superscript S and L represent solid phase and liquid phase respectively.

$$\begin{aligned} \text{Since } dV^S &= -dV^L \\ dn^S &= -dn^L \\ dA^S &= -2dA^L \end{aligned} \quad (3)$$

and the chemical potentials of corresponding components in the two phases equal to each other,

$$\mu_B^S = \mu_B^L \quad (4)$$

from equations (1), (2), (3) and (4), the following equation can be derived:

$$P^S = P^L + \frac{\gamma_{SS} - 2\gamma_{SL}}{b} \quad (5)$$

As shown in Fig. 1, the width of solid phase or grain boundary is b . Take the thickness of solid phase as h ,

$$\begin{aligned} dA^S &= h d\delta \\ dV^S &= h b d\delta \end{aligned} \quad (6)$$

from equations (5) and (6),

$$P^S = P^L + (\gamma_{SS} - 2\gamma_{SL}) \frac{dA^S}{dV^S} \quad (7)$$

To express $\mu_B^S(P^S, T)$ by Talor's progression around P^L , and to take the one order item of the progression,

$$\begin{aligned} \mu_B^S(P^S, T) &= \mu_B^S(P^L, T) + (P^S - P^L) \\ &\quad \left. \frac{\mu_B^S}{P} \right|_{P=P^L} \\ &= \mu_B^{0S}(P^L, T) \\ &\quad + \frac{\gamma_{SS} - 2\gamma_{SL}}{b} V_B^S \end{aligned} \quad (8)$$

where V_B^S is the molar volume of solid component B . The chemical potential of component B in the liquid can be expressed by following equation.

$$\begin{aligned} \mu_B^L(P^L, T) &= \mu_B^{0L}(P^L, T) \\ &\quad + RT \ln \alpha_B \end{aligned} \quad (9)$$

From equations (4), (8) and (9), the following equation is derived.

$$\begin{aligned} \alpha_B &= \exp \left[\frac{\mu_B^{0S}(P^L, T) - \mu_B^{0L}(P^L, T)}{RT} \right] \\ &\quad \exp \left(\frac{\gamma_{SS} - 2\gamma_{SL}}{RTb} V_B^S \right) \\ &= \alpha_B^0 \exp \left(\frac{\gamma_{SS} - 2\gamma_{SL}}{RTb} \cdot V_B^S \right) \end{aligned} \quad (10)$$

where α_B^0 is the activity of component B in the equilibrium liquid near plain solid surface. If the activity coefficient does not vary with concentration, then

$$X_B = X_B^0 \exp \left(\frac{\gamma_{SS} - 2\gamma_{SL}}{bRT} \cdot V_B^S \right) \quad (11)$$

2.3 Kinetic Equation of Liquid Penetrating Into Grain Boundary

As shown in Fig. 1, in case the penetration rate is limited by diffusion, there are following mass equilibrium equations at the contact site of liquid and grain boundary^[6],

$$\left. \begin{aligned} &\frac{A d\delta^S}{V^S} \cdot X_A^S - \frac{A d\delta^L}{V^L} \cdot X_A^L \\ &= - \frac{A D_A^L}{V^L} \cdot \frac{dX_A^L}{dy} \cdot dt \\ &\frac{A d\delta^S}{V^S} \cdot X_B^S - \frac{A d\delta^L}{V^L} \cdot X_B^L \\ &= - \frac{A D_B^L}{V^L} \cdot \frac{dX_B^L}{dy} \cdot dt \end{aligned} \right\} \quad (12)$$

where superscripts S and L represent solid (grain boundary) and liquid respectively, and subscripts A and B represent component A and component B respectively, and X is molar fraction. From equations (12),

$$\begin{aligned} \frac{d\delta^S}{dt} &= - \frac{X_A^L D_A^L + X_B^L D_B^L}{X_B^S - X_B^L} \\ &\quad \cdot \frac{dX_B^L}{dy} \cdot \frac{V^S}{V^L} \end{aligned} \quad (13)$$

X_B^L is represented by X_B . Since

$$\begin{aligned} X_A^S &= 0 \\ X_B^S &= 1 \\ X_B^L - X_B^0 &\ll 1 \end{aligned}$$

the following equation can be derived from equation (13),

$$\begin{aligned} \frac{d\delta}{dt} &= \frac{d\delta^S}{dt} \\ &= \frac{D_L}{1 - X_B^0} \cdot \frac{dX_B}{dy} \cdot \frac{V^S}{V^L} \end{aligned} \quad (14)$$

Suppose that the concentration of component B in the liquid varies linearly with the site in the penetrated grain boundary shown in Fig. 1 within the penetration depth (δ). Then

$$\frac{dX_B}{dy} = \frac{X_B - X_B^0}{\delta} \quad (15)$$

Where X_B and X_B^0 are the concentration of component B in the liquid at the 0 and δ sites of y coordinate, shown in Fig. 1.

Since $X_B^L < 1$, it can be inferred from the law of mass conservation and Fick's second law that the composition of the liquid varies in the range beyond the penetrated depth while the liquid penetrates into grain boundary^[6]. But since the dissolved amount of solid is very

small in the penetration and the component can diffuse in three directions at the 0 site of y coordinate, the effective range within which the liquid composition varies is near δ . In addition, the solid surface at the contact of grain boundary and plain surface, or at 0 site of y coordinate, becomes a curved surface by the dissolution and deposition, as shown in Fig. 1. The concentration of component B in the liquid in equilibrium with the curved surface can be expressed as follows:

$$X_B^r = X_B^0 \exp\left(\frac{\gamma_{sl}}{rRT} V_B^s\right) = X_B^r \quad (16)$$

where r is the curvature radius of the curve surface

According to equation (11) and (16),

$$\begin{aligned} X_B - X_B^r &= X_B - X_B^r \\ &= X_B^0 \left[\exp\left(\frac{\gamma_{ss} - 2\gamma_{sl}}{bRT} V_B^s\right) \right. \\ &\quad \left. - \exp\left(\frac{\gamma_{sl}}{rRT} V_B^s\right) \right] \end{aligned}$$

Since $r \gg b$, and in case r is not very small,

$$\begin{aligned} X_B^r &\approx X_B^0 \\ X_B - X_B^r &= X_B^0 \cdot \left[\exp\left(\frac{\gamma_{ss} - 2\gamma_{sl}}{bRT} V_B^s\right) - 1 \right] \quad (17) \end{aligned}$$

From the equations (14), (15) and (17), the following equation can be derived:

$$\begin{aligned} \frac{d\delta}{dt} &= \frac{D_L V^s}{(1 - X_B^0) V^L} \\ &\cdot \frac{X_B^0 \left[\exp\left(\frac{\gamma_{ss} - 2\gamma_{sl}}{bRT} V_B^s\right) - 1 \right]}{\delta} \quad (18) \end{aligned}$$

Integrate (18), the dependence of penetration depth (δ) on time (t) is derived as follows:

$$\begin{aligned} \delta^2 &= \frac{2X_B^0 D_L V^s}{(1 - X_B^0) V^L} \\ &\cdot \left[\exp\left(\frac{\gamma_{ss} - 2\gamma_{sl}}{bRT} V_B^s\right) - 1 \right] t \quad (19) \end{aligned}$$

3 DISCUSSION

It has been showed that the copper melt can penetrate completely into the grain boundary of iron polycrystal^[2]. Hongh R R^[7] *et al* measured the dependence of the depth of copper melt penetrating into the grain boundary of iron polycrystal on penetration time, as shown in Fig. 2. The depth is proportional to

the time's square root, which qualitatively verifies the derived kinetic equation. The parameters in the equation (19) are shown in Table 1. According to the equation (19), the width of grain boundary can be computed as 3.14 Å and 3.56 Å from Hongh's measurement of 1100 and 1130 °C respectively. In general, the width of grain boundary is the size of two or three atoms (or 3~4 Å)^[11], which is identical to the above computed value. To take the width of grain boundary as 3.56 Å, γ_{sl} at 1100 °C is computed as 3.62×10^{-1} J/cm², which is identical to the measured value. All of above comparison between computation and measurement verifies the equation (19). The equation can be used to quantitatively predict the time dependence of the penetration depth and to compute the interface energy by measuring the penetration depth. As to various solid-liquid systems, the parameters in the kinetic equation vary in some definite ranges. By the equation, the main factors influencing the penetration rate can be determined.

In the metallic systems, D_L is about 5×10^{-9} m²/s^[10], the molar volumes of various metals have almost the same value^[8]. Then, the penetration rate depends mainly on interface energy for various metallic systems.

In the oxide systems, the interdiffusion of the components in the melt is that of posi-

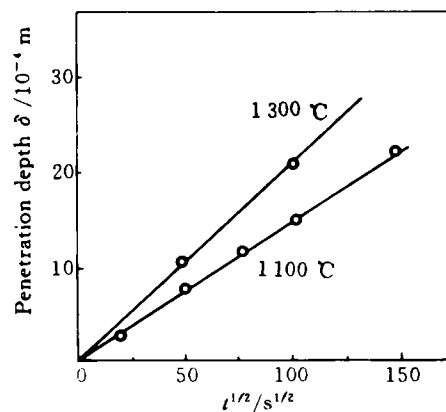


Fig. 2 The time dependence of the depth (δ) of copper melt penetrating into the grain boundary of iron polycrystal^[7]

Table 1 Parameters in the kinetic equation of liquid penetration

Temperature /°C	X_{Fe}^0	V_{Fe} / $10^{-6} \text{ m}^3 \text{ mol}^{-1}$	γ_{ss} / 10^{-1} J m^{-2}	γ_{sl} / 10^{-1} J m^{-2}	D_{Fe} / $10^{-9} \text{ m}^2 \text{ s}^{-1}$	D_{Cu} / $10^{-9} \text{ m}^2 \text{ s}^{-1}$	D_L / $10^{-9} \text{ m}^2 \text{ s}^{-1}$
1100	0.032	7.66	10.89	3.87	3.91	4.17	3.92
1130	0.036	7.66	10.72	3.01	4.30	4.50	4.31
reference	[8]	[9]	[2]	[7]	[10]	[10]	computed from D_{Fe} and D_{Cu}

tive ion under the electric neutrality. The interdiffusion coefficient is determined by the component with the smallest selfdiffusion coefficient . In the oxide melts containing SiO₂ or Al₂O₃ with small selfdiffusion coefficient, the interdiffusion coefficient is about 10⁻¹² m²/S; In the non-fused oxide melts, the interdiffusion coefficient is similar to that of metallic melts. Therefore, in oxide systems, the penetrating rate depends on both the interface energy and the component with low diffusivity.

4 CONCLUSION

The kinetic equation of liquid penetration into grain boundary derived from the diffusion as rate limiting step, is verified by the previous measurement, and can be used to predict quantitatively the dependence of the penetration rate on the various parameters and to compute the interface energy by measuring the penetration depth.

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