

L e c t i o n 7

Phase equilibrium conditions

The processes of high temperature materials treatment are accompanied inevitably by phase transitions, including melting and crystallization, sublimation and condensation. Naturally the necessity appears to calculate the temperature fields taking into account the heat release or absorption connecting with phase transitions. Various phases can be in the equilibrium at the conditions established in thermodynamics.

If the system consists of two phases, then for each of them we can write the Gibbs equation

$$du_k = T_k ds_k - p_k dV_k + g_k dC_k, \quad (1)$$

where g_k are chemical potentials of phases, $C_k, k=1,2$ are mass fractions of substances in phases, so

$$g = g_1 C_1 + g_2 C_2. \quad (2)$$

Generally, phase is homogeneous regions in the system separated from each other by the interface. The chemical composition and physical properties change at the transition through the interface. The question on phase equilibrium transition is important problem in the phase transition theory and heat exchange.

If the interface is plane, then its energy characteristics do not effect on the equilibrium conditions. Therefore we can neglect the properties of this surface.

If the system is isolated (that is it does not change with environment by mass and energy), and do nothing work, then the its equilibrium condition leads to the equality $ds = 0$, and the n equalities are correct справедливы равенства

$$\begin{aligned} u &= u_1 + u_2 = const, \quad du_1 = -du_2, \\ V &= V_1 + V_2 = const, \quad dV_1 = -dV_2, \\ C &= C_1 + C_2 = const, \quad dC_1 = -dC_2. \end{aligned} \quad (3)$$

If s_1 и s_2 are the entropies of first and second phases, then the additivity condition allows to write down

$$ds_1 = -ds_2. \quad (4)$$

Expressing ds_1, ds_2 from (1), we shall find from (4)

$$\frac{1}{T_1} [du_1 + p_1 dV_1 - g_1 dC_1] + \frac{1}{T_2} [du_2 + p_2 dV_2 - g_2 dC_2] = 0.$$

Taking into account (3), we obtain

$$\left(\frac{1}{T_1} - \frac{1}{T_2} \right) du_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 - \left(\frac{g_1}{T_1} - \frac{g_2}{T_2} \right) dC_1 = 0. \quad (5)$$

Differentials du_1, dV_1 and dC_1 in (5) are independent. Then this equality takes a place, when the multipliers near by the differential equal to zero:

$$T_1 = T_2, \quad p_1 = p_2, \quad g_1 = g_2.$$

Therefore, the equilibrium condition of two phase one-component system consists in the following

$$g_1(T, p) = g_2(T, p) \quad (6)$$

и означает равенство химических потенциалов фаз при неизменных давлении и температуре.

Taking into consideration the properties of interface (the deduction of this condition is contained in thermodynamical textbooks) we come to the equilibrium conditions in the form

$$T_1 = T_f, T_2 = T_f, g_1 = g_2, \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 - \frac{\sigma_f}{T_f} d\Sigma_f = 0.$$

where Σ_f is interface area, σ_f is surface tension.

That is, at the equilibrium, chemical potentials of phases, their temperatures are the same; but the pressures connect by the equality

$$p_1 = p_2 + \sigma_f \frac{d\Sigma_f}{dV_1}. \quad (7)$$

It can be expand for deformable medium.

Clausius-Clapeyron equation

In the case of phase transition accompanied by heat release or adsorption, the Clausius-Clapeyron equation is correct. It has the form

$$\frac{dT_{ph}}{dp} = \frac{\Delta V_{ph}}{\Delta s_{ph}} = \frac{\Delta V_{ph} \cdot T_{ph}}{Q_{ph}}, \quad (8)$$

where $\Delta V_{ph} = V_2 - V_1$ и $\Delta s_{ph} = s_2 - s_1$ are difference between the partial mol volumes of phases and their mol entropies,

$$Q_{ph} = h_2 - h_1 = T_{ph}(s_2 - s_1) -$$

is difference in enthalpies of phases or transition heat. If $Q_{ph} < 0$, and phase 2 volume is large then phase 1 volume, then $dT_{ph}/dp < 0$, that is the phase transition temperature diminishes with the pressure. The equation (8) can be obtained from (6) without problems with the help of expansin the chemical potentials into series relatively to deviations of temperature and pressure on their equilibrium values.

Sometimes, the equation (8) can be integrated.

With the help of (8), ones can construct the state diagrams.

Stephen problem

The simplest problem on phase transition was formulated and solved by Stephen, when he has study the change of the arctic glaciers thickness. We have here the problem with motion interface, the rate of which are not known.

Assume that the liquid with initial temperature T_e touches with cold wall of temperature T_0 less then crystallization



Fig. 1

temperature $T_0 < \theta$. At $t > 0$, crystallization front starts from cold surface - the interface between liquid and solid phases (Fig.1). It is necessary to find the interface position for any time moment $x = \xi(t)$.

Mathematical formulation of this problem has the form

$$\begin{aligned} c_1 \rho_1 \frac{\partial T_1}{\partial t} &= \lambda_1 \frac{\partial^2 T_1}{\partial x^2}, \quad 0 \leq x \leq \xi(t); \\ c_2 \rho_2 \frac{\partial T_2}{\partial t} &= \lambda_2 \frac{\partial^2 T_2}{\partial x^2}, \quad x \geq \xi(t). \\ x = 0: \quad T_1 &= T_0; \\ x \rightarrow \infty: \quad T_2 &= T_e; \\ x = \xi(t): \quad \lambda_1 \frac{\partial T_1}{\partial x} - \lambda_2 \frac{\partial T_2}{\partial x} &= L \rho_1 \frac{d\xi}{dt}; \quad T_1 = T_2 = \theta; \\ t = 0: \quad \xi &= 0; \text{ there is liquid only.} \end{aligned}$$

Index 1 relates to solid phase, 2 – to liquid one.

In the simplest formulation of Stephen problem it is taken $\rho_1 = \rho_2 = \rho$.

We seek the solution of one-dimensional problem in the form

$$T_i = A_i + B_i \Phi\left(\frac{x}{2\kappa_i \sqrt{t}}\right), \quad (9)$$

where $\Phi(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dy \equiv \text{erf}(z) = 1 - \text{erfc}(z)$.

Boundary conditions allow determining the constants $A_i, B_i, i = 1, 2$ and the rate of interface motion.

From the conditions at $x = 0$ and $x \rightarrow \infty$ we shall find

$$A_1 = T_0; \quad A_2 + B_2 = T_e. \quad (10)$$

We have from the boundary conditions in interface

$$T_0 + B_1 \Phi\left(\frac{\xi}{2\kappa_1 \sqrt{t}}\right) = T_e - B_2 \left[1 - \Phi\left(\frac{\xi}{2\kappa_2 \sqrt{t}}\right)\right] = \theta. \quad (11)$$

The last relation can be true for any time, hence we should taken

$$\xi = 2\mu \sqrt{\kappa_1 t}, \quad (12)$$

where $\kappa_1 = \lambda_1 / (c_1 \rho_1)$, and μ is constant that can be found from remind condition. That is, the interface moves as \sqrt{t} . As a result we find

$$B_1 = \frac{\theta - T_0}{\Phi(\mu)}, \quad B_2 = \frac{T_e - \theta}{1 - \Phi\left(\mu \sqrt{\frac{\kappa_1}{\kappa_2}}\right)};$$

$$\frac{\exp(-\mu^2)}{\Phi(\mu)} - \frac{\lambda_2 \sqrt{\kappa_1} (\theta - T_e) \exp\left(-\frac{\kappa_1}{\kappa_2} \mu^2\right)}{\lambda_1 \sqrt{\kappa_2} (\theta - T_0) \left(\Phi\left(\mu \sqrt{\frac{\kappa_1}{\kappa_2}}\right) - 1\right)} = \frac{\mu L \sqrt{\pi}}{c_1 (\theta - T_e)}. \quad (13)$$

In particular case, when the liquid temperature equal to melting temperature, the equation for μ takes the simple form

$$\mu \Phi(\mu) \exp(\mu^2) = \frac{c_1 (\theta - T_0)}{L \sqrt{\pi}}. \quad (14)$$

The roots of this equation could be found graphically or approximately.

Elements of theory of two-phase zone

Two component systems with solid solutions are examples of the systems with the interval of melting temperature (Fig.2), for which the theory of two – phase zone was suggested.

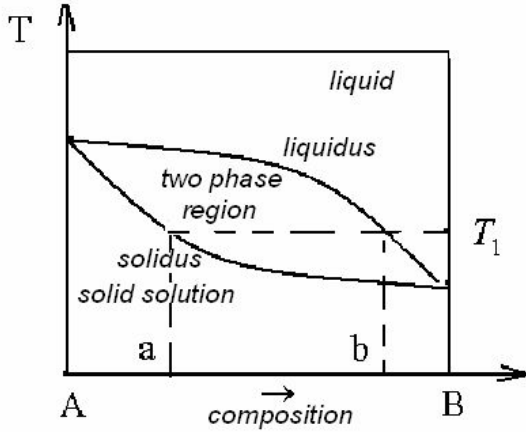


Fig.2

Here, the melting temperature of component A diminishes at component B addition; the melting temperature of component B increases with concentration A growths. .

The curves of solidus and liquidus conjugate in the points corresponding to pure substances A and B . There is one phase solid solution below the solidus – curve, there is the one phase liquid solution above the liquidus-curve. Between these curves, the two – phase mixture is located. Here solid and liquid phases exist together.

The basic idea of two phase zone theory consists in the following.

Volume fractions of liquid and solid phases in two-phase zone η_L and η_s connects by the relation

$$\eta_L + \eta_s = 1.$$

The correlation between the fractions depends on the temperatures of liquidus T_{liq} and solidus T_{sol} , which depend on the composition of the solution:

$$T_{sol} = \alpha_s + \beta_s \xi + \gamma_s \xi^2,$$

$$T_{liq} = \alpha_L + \beta_L \xi + \gamma_L \xi^2,$$

where ξ is the part of one of component; the constants $\alpha_i, \beta_i, \gamma_i$, $i = L, s$, could be found from corresponding state diagrams (Fig.2).

In this case, effective heat capacity should be calculated by formula

$$(c\rho)_{eff} = c\rho + Q_{ph}\rho_s \frac{\partial \eta_L}{\partial T}, \quad (15)$$

where

$$c\rho = (c\rho)_s (1 - \eta_L) + (c\rho)_L \eta_L.$$

In turn the capacities of solid and liquid phases depend on the composition. In the simplest case, one can use the approximation (the mixture rule)

$$(c\rho)_s = (c\rho)_{A,s}\xi + (1 - \xi)(c\rho)_{B,s},$$

$$(c\rho)_L = (c\rho)_{A,L}\xi + (1 - \xi)(c\rho)_{B,L}.$$

The heat capacities of individual substances can depend on temperature.

The volume part of liquid phase is calculated from the relation

$$\eta_L = 1 - \left(\frac{T_{liq} - T}{T_{liq} - T_{sol}} \right)^n, \quad (16)$$

where parameter n varies for different alloys.

The part of solid phase follows from $\eta_s = 1 - \eta_L$.

The examples of the simplest model of technology processes of thermal surface treatment are analyzed during the lecture with phase transition and without phase transition.