

Microscopic model of porosity formation during solidification

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Abstract

The simple microscopic model on the microporosity formation during solidification is proposed. In this method is estimated the hydrostatic pressure arising in the residual liquid between the dendrite arms due to the shrinkage on solidification. The formation and the diffusion of the atomic vacancy is considered to describe the relaxation. Since the diffusion of the atomic vacancy can compensate the volume lack of due to the shrinkage on solidification, the maximum value of the hydrostatic pressure depends on the dimension of the residual liquid and the solidification time. The porosity formation in materials is estimated by getting the information on the microstructure from the macroscopic heat flow models.

1. Introduction

The alloy design supported by computers requires to estimate and predict the materials properties such as the mechanical, the electronic and the magnetic properties. The materials properties are determined not only by the composition or the structure but also by the process. The process is important to produce the materials which have sufficient properties. Computer-simulations have also been carried out to develop processings of materials. One of the examples is to predict casting defects and to determine countermeasures against them. Microporosity is one of the defects produced during solidification inside casting products.

Most of alloys show the dendrite solidification as shown in Fig. 1. The liquid phase are isolated between the secondary dendrite arms as solidification proceeds. The mechanism of the microporosity formation is closely related with this microstructure. The solubility of gas elements in solid state is usually much smaller than that in liquid state. Thus, gas elements are rejected to the residual liquid. For example, an amount of hydrogen gas is initially dissolved and it condenses in the residual liquid for Al alloys[1]. On the other hand, the resistance to the fluid flow into the residual liquid become great and the hydrostatic pressure occurs in this region[2]. The supersaturation of gas elements and the hydrostatic tension make a bubble in liquid phase. The stability condition of the bubble for mechanical equilibrium, or growth, of a bubble with radius r , internal pressure P_i and external pressure P_e is given by

$$P_i > 2\gamma/r + P_e \quad (1)$$

Here γ is the interface energy. The internal gas pressure is expected to be the result of gases in solution in metal which are approximately in equilibrium with the free volume of the porosity. The external pressure is mainly the hydrostatic pressure arising by the shrinkage on solidification. As shown in Eq(1), the estimation of not only the gas concentration but also the hydrostatic pressure are important to predict the porosity formation.

Some methods for predicting the porosity defect has been proposed[3]. There are two main methods to estimate the porosity defects: one is the thermal condition model which uses empirical parameters obtained by solidification analysis considering only the thermal conduction heat transfer. Although these methods are now in practical use, the empirical parameters are used. The other method is the direct simulation model in which the porosity formation is simulated by calculating pressure field and mass transfer[4]. In the method, the pressure are estimated to predict the porosity formation. Both methods are based on macroscopic heat or mass flow models. On the other hand, there are a few studies based on microscopic model on the porosity formation, which focus on the

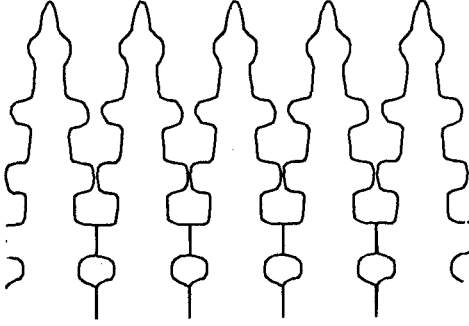


Figure 1. Morphology of the dendrite growth

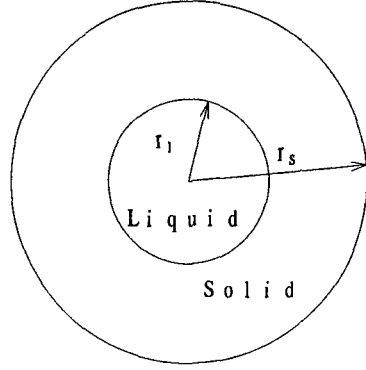


Figure 2. Solidification model. r_l is the initial radius of the residual liquid and r_s the radius of the solid shell.

residual liquid between the dendrite arms[2]. This paper presents a simple microscopic model of microporosity formation in which the atomic vacancy formation and diffusion is taken into account to the hydrostatic pressure due to the shrinkage.

2. Model

As solidification proceeds, the internal hydrostatic pressure builds up associated with the volume change on solidification. The hydrostatic tension should be depend on the microstructure and the condition of the solidification. If the solidification slowly proceeds, relaxation mechanism sufficiently operates and the pressure does not largely arise. The atomic vacancies are created near the solid-liquid interface and they form the dislocations[5]. The formation and the diffusion of the atomic vacancies are considered to compensate the volume lack of the solidification shrinkage in this model.

2-1. Vacancy concentration and hydrostatic pressure

The change of enthalpy and entropy of a solid with the atomic vacancies n_v and elastic strain ε under hydrostatic pressure are given by Eq.(2) and (3),

$$\Delta H = n_v E_f + \frac{9}{2} B V_0 \varepsilon^2 \quad (2)$$

$$\Delta S = -R[n_v \ln n_v + (1 - n_v) \ln(1 - n_v)] + n_v S_f \quad (3)$$

here, E_f , S_f are the formation enthalpy and entropy of a atomic vacancy, respectively. V_0 the mole volume, and B the bulk modulus. For convenience, the strain ε_0 is defined by the following equation,

$$\varepsilon_0 = \varepsilon + \frac{1}{3} n_v \quad (4)$$

In equilibrium condition, Eq.(5) is satisfied.

$$\frac{\partial \Delta G}{\partial n_v} = \frac{\partial}{\partial n_v} (\Delta H - T \Delta S) = 0 \quad (5)$$

Eq.(6) can be written by using Eq.(2)-(5).

$$\frac{n_v}{1 - n_v} = \exp\left(\frac{S_f}{R}\right) \exp\left[-\frac{E_f - 3B V_0 (\varepsilon_0 - \frac{1}{3} n_v)}{RT}\right] \quad (6)$$

Table 1. Physical properties of pure Al. The marked values are estimated values.

| T_m K | E_f kJmol ⁻¹ | S_f/R | B GPa | V_m m ³ mol ⁻¹ | D_v m ² s ⁻¹ | $\delta V/V$ % |
|------------|------------------------------|---------|------------|---|---|-------------------|
| 933 | 72.3 | 2.2 | 55* | 1.1×10 ⁻⁵ | 2.4×10 ^{-9*} | 6 |

As shown in Eq.(6), the formation energy could be regarded as $E_f - 3BV_0(\epsilon_0 - n_v/3)$, suggesting that the hydrostatic pressure decreases the formation energy, and the atomic vacancy concentration increases.

2-2. Solidification model

Figure 2 shows a simplified model to describe the residual liquid phase between the secondary dendrite arms. The solidification of the residual liquid with spherical shape inside the spherical solid are dealt as the porosity formation model. The spherical liquid and solid are divided into shells. It is assumed that the outer boundary of the solid is fixed and only the elastic deformation of liquid ($r = r_l$) and solid ($r = r_s$) occurs. The radius r_l correspond to the dendrite arm spacing and the relation between r_l and r_s indicates the solid fraction when the liquid is isolated between the dendrite arms.

The calculation was carried out by the following procedures,

- i. The solid-liquid interface is moved with a given rate.
- ii. Elastic strain ϵ_0 is determined by using the decrease of volume due to the shrinkage.
- iii. By using Eq.(4) and (6), n_v , ϵ and the hydrostatic pressure P are calculated with the Newton-Raphson method. The vacancy concentration of the solidified shells are determined to be the obtained value of n_v .
- iv. Volume flux of vacancy from j -th shell to $(j+1)$ -th shell, J_i , is calculated by Eq.(7).

$$J_i = -4\pi(r_i + \frac{dr_i}{2})^2 D_v \frac{dt}{dr_i} (n_v^{i+1} - n_v^i) \quad (7)$$

Here r_i is the radius of i -th shell and $dr_i = r_{i+1} - r_i$. The D_v is not self-diffusion coefficient (D_s) of constituent atoms but the diffusion coefficient of vacancy. The D_v was estimated from the relation $D_v n_v = D_s$. As n_v is usually the order of 10^{-4} at most, the vacancies diffuse much faster than the atoms do. The vacancy concentrations of the shells were calculated from the volume flux of the vacancies.

- v. The volume changes of the shell were calculated from the vacancy diffusion.

Above procedure were repeated until a given time came, and the value of the pressure were obtained at each time step.

3. Results and discussion

Figure 3 shows the atomic vacancy concentration n_v and the elastic strain ϵ_0 at the melting point. This calculation was made by using the values of pure Al listed in Table 1. Some of the values have not been reported and the estimated values were used for calculation. In the small ϵ region, n_v is almost constant and it is the equilibrium value (7.6×10^{-4}) at $\epsilon_0 = 0$. The n_v at $\epsilon_0 = 2 \times 10^{-2}$ corresponding to the solidification shrinkage is 23 times as large as that at $\epsilon_0 = 0$, although the value of ϵ is too large to consider the elastic deformation. Even at $\epsilon = 10^{-3}$, the value of the n_v increases in comparison with the equilibrium value. Therefore, the hydrostatic pressure due to the solidification shrinkage makes the excess vacancies in the solidified shells.

Figure 4 shows the time-dependence of the hydrostatic pressure arising in the liquid phase ($r_l = 10\mu\text{m}$, $r_s = 20\mu\text{m}$) with several solidification times, t_0 . The value of the pressure of the liquid depends on the solidification time. In the rapidly solidified case ($t_0 = 0.01\text{s}$), the values of the pressure is about 450MPa. On the other hand, the value in $t_0 = 10\text{s}$ is less than 70MPa. This result suggests that the formation and diffusion of the atomic vacancy could compensate for the shrinkage on solidification. This model can

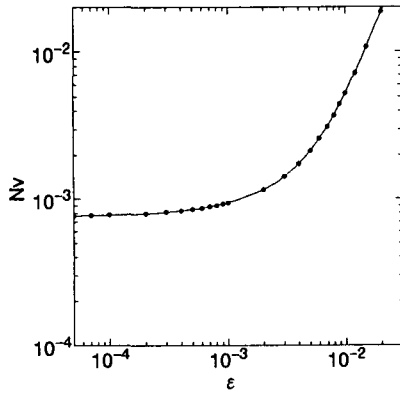


Figure 3. Atomic vacancy concentration n_v as a function of the strain ϵ_0 .

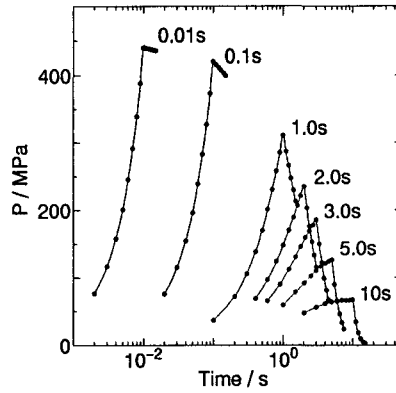


Figure 4. Hydrostatic pressure arising in the liquid during solidification.

estimate the solidification-time dependence of the hydrostatic pressure. Figure 5 shows the maximum pressures in the case of $r_s/r_l = 2$ as a function of the solidification time. The pressure depends the dimension of the residual liquid as well as the solidification time. The r_s/r_l dependence of the pressure is shown in Fig 6. The r_s/r_l dependence becomes larger with decreasing the solidification time. The value of r_s/r_l corresponds to the critical solid fraction at which the liquid is isolated between the dendrite arms. The critical solid fraction also affect the hydrostatic pressure.

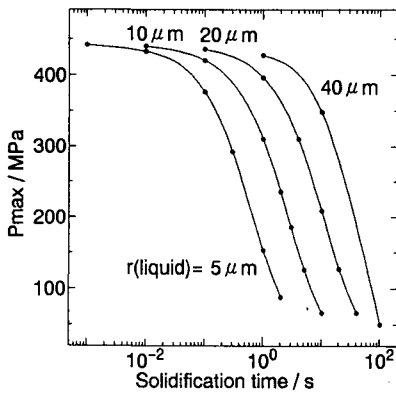


Figure 5. Maximum pressure P_{max} as a function of the solidification time t_0 . $r(\text{solid})/r(\text{liquid})=2$.

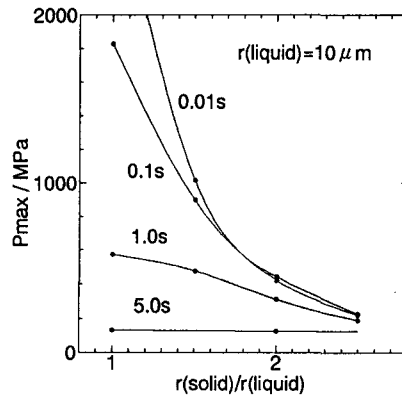


Figure 6. Maximum pressure P_{max} as a function of the $r(\text{solid})/r(\text{liquid})$.

The values of r_s , r_l and t_0 are needed to estimate the pressure arising during solidification of materials. These values in this model present the microstructure of the solidification. The parameters, r_l , r_s/r_l and t_0 , are not independent each other in the dendrite solidification. For example, the r_l decreases with decreasing t_0 . Thus, it is needed for predicting the porosity defect formation by this method to obtain the information on the microstructure. The microstructure can be determined by the macroscopic heat flow model and the experimental observation. The hydrostatic pressure arising during solidification can be estimated by the model in which the microstructure of solidification is considered.

References

- [1] J.Campbell: *Trans. TMS-AIME*, 242 (1968) 138.
- [2] C.E. Ransley and H. Neufeld: *J. Inst. Metals*, 74 (1948) 599.
- [3] I. Ohnaka: *Introduction to Analysis of Heat Transfer and Solidification by Computer*, Maruzen 1985 Tokyo.
- [4] J.D. Zhu and I. Ohnaka: *Modeling of Casting, Welding and Advanced Solidification Processes V*, The Mineral, Metals and Materials Society 1991 p.435.
- [5] T. Kobayashi, Y. Nishikawa and T. Imura: *J. Cryst. Growth*, 84 (1987)489.