



A thermodynamic model for simultaneous growth of gas and solid phases from gas saturated melt



Ya Lu, Zhichun Wen, Qinglin Jin*, Yehua Jiang

Faculty of Materials Science and Engineering, Kunming University of Science and Technology, 650093 Kunming, China

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ABSTRACT

Production of ordered porosity materials by directional solidification is characterized by simultaneous growth of solid and gas phases from gas supersaturated melt. It is considered that the formation of ordered porosity is controlled by two independent processes: one is the hydrogen diffusion controlled growth of gas phase; and the other is the thermal diffusion controlled growth of solid phase. A simple thermodynamic model is developed to describe the relationship between the processing and the pore structure. The model is applied for the ordered porosity copper fabricated by directional solidification. The deviation between the calculated and experimental values is discussed with respect to the characteristics of hydrogen diffusion in liquid metal.

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1. Introduction

Ordered porosity material (also known as “gasar” or “lotus type material”) has received wide attention in the last two decades [1–5]. The production of such material usually involves gas saturation of a liquid melt in a chamber with high gas pressure, and subsequent directional solidification of the gas saturated melt [3,4]. The most important feature of the directional solidification is simultaneous growth of solid and gas phases from the gas saturated melt. The gas phase usually appears as rods of gas pores embedded in the solid matrix. A schematic illustration of the production technique by directional solidification [4,5], together with an example of ordered porosity, is shown in Fig. 1.

The first metal with ordered porosity was reportedly fabricated in 1979 by Shapovalov and his co-workers in Ukraine, and they named the new material “gasar”, which is a Russian abbreviation meaning “gas reinforced” [1–4]. Usually, the gas used for melt saturation is hydrogen, and most of the pioneering works were conducted in metal–hydrogen eutectic systems such as: Cu–H, Ni–H, Co–H, etc. For this reason, the solidification of gas saturated melt is often called “gas–metal eutectic reaction” [2].

The past decade has seen significant advances in the ability to obtain ordered porosity structures from a wide range of different materials. The works by Nakajima et al. are notable [4–10]. They have succeeded in obtaining ordered porosity in materials ranging from pure metals [5,6] and alloys [7,8] to semiconductors [9], and even ceramics [10]. However, it is not yet clear whether each of

these materials is necessary or able to form a eutectic system with hydrogen to give an ordered porosity. Nakajima et al. proposed that there are not enough evidences to support the eutectic nature of the solidification, and the formation of ordered porosity was attributed to the difference of hydrogen solubility in liquid and solid states, i.e. during the solidification, the hydrogen gas rejected by a growing solid will grow in length at the same rate that the solidification interface moves [4]. In addition, Nakajima and his co-workers used another name “lotus type material” in their studies [4–10], because the shape of the gas pores is quite similar to the holes in a lotus root.

The pore structure of ordered porosity material can be described by a set of parameters such as porosity, inter-pore spacing and pore diameter, and all these parameters are sensitive to the processing parameters (such as hydrogen pressure, melt temperature and solidification velocity) [11–15]. As the properties of ordered porosity materials are determined by the scale and regularity of the pore structure [4], it is practically important to develop a clear description for the essential relationship between the processing and the pore structure obtained [3,4]. However, the solidification of gas saturated melt is known as a complex process, which involves a series of concurrent physical phenomena such as gas diffusion, pore nucleation and growth, heat and mass transport, etc. [3]. This makes the mathematical modeling of the solidification difficult to some extent, and so far, there still lacks a clear and simple description for the solidification of gas saturated melt.

In this paper, we offer a thermodynamic model of simultaneous growth of solid and gas phase from gas saturated melts. From

* Corresponding author.

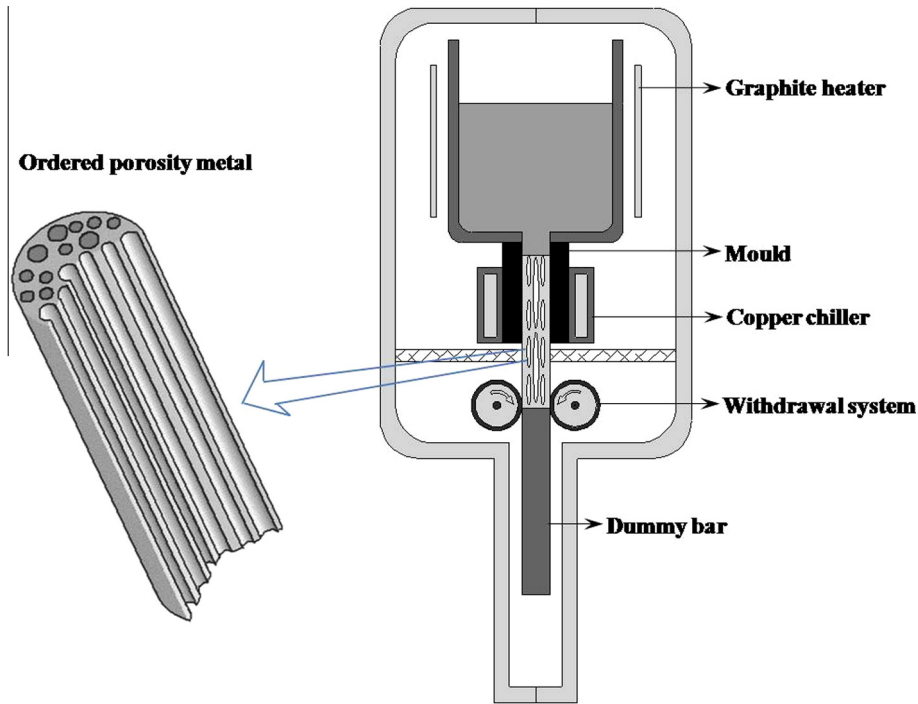


Fig. 1. Schematic illustrations of directional solidification (Bridgman-type) of gas saturated melt, and pore structure of ordered porosity metal.

thermodynamic point of view, a state with higher free energy is less stable with respect to a state with lower free energy in the same system. Because of this, all transformations are directed to formation of structures with lower energy. This is for instance what happens in the formation of ordered porosity. When a gas saturated melt is cooled, a melt temperature is reached, at which point a solid with ordered porosity structure forms from the melt. The formation of ordered porosity could be considered as a “self organized process” of the pore structure in order to minimize the system free energy. In all possible relations between the free energy change and the pore structure, it is to be expected that the optimum gas pore structure will correspond to the minimum system free energy.

The present paper discusses, in Section 2, the mechanism of the solidification of gas saturated melt with emphasis on the similarity and differences in the current understanding of the mechanism. Section 3 presents the basic thermodynamics that describes the driving force for diffusion of hydrogen and the free energy increase due to driving force for creation of solid–gas interface. A thermodynamic model is then developed by application of Gibbs energy minimization of the system considered. Section 4 discusses the accuracy of the model by comparing the calculated values with the experimental results. Special attention is paid to the influence of processing parameters on the diffusion rate of hydrogen in liquid metal.

2. Mechanism of the solidification of gas saturated melt

At a moderate pressure and temperature, the solubility of hydrogen gas in a metal could be described by the Sievert's law [16]:

$$X_L = k_1 P^{\frac{1}{2}} \quad (1)$$

$$X_S = k_2 P^{\frac{1}{2}} \quad (2)$$

for the liquid and solid, respectively. The X_L and X_S are the hydrogen solubility in liquid and solid respectively (mole fraction).

P is the hydrogen pressure over the liquid metal (Pa); k_1 and k_2 are parameters depending on temperature.

The Sievert's law is shown in Fig. 2 schematically. As seen, the hydrogen solubility increases with increasing temperature, and there is a large “solubility gap”, $X_L(T_m) - X_S(T_m)$, when the metal transforms from a liquid to a solid at the melting temperature T_m .

In directional solidification of gas saturated melt, the solidification interface is growing with essentially isothermal interface T_m into a melt of higher temperature $T(T > T_m)$, i.e. into a melt with positive temperature gradient. There should exist at the interface an excess amount of hydrogen, which is proportional to $X_L(T) - X_L(T_m)$. Theoretically this excess hydrogen would escape upwards from the interface in the form of gas bubbles.¹ Thus, the hydrogen gas that is able to diffuse into gas pores, n_g (mole), can be evaluated by the “solubility gap”:

$$n_g = n_{tot}[X_L(T_m) - X_S(T_m)] \quad (3)$$

where n_{tot} (mole) is the total amount of the hydrogen and metal in the melt. Eq. (3) gives, theoretically, the amount of hydrogen gas originated from the difference of the hydrogen solubility in the solid and liquid.

If the solidification of gas saturated melt is treated as a metal–gas eutectic transformation, the amount of hydrogen in gas pores can be calculated by using the lever rule, according to the phase diagram (Fig. 3):

$$\frac{n_g}{n_M} = \frac{x_E - x_S}{1 - x_E} \quad (4)$$

where x_E (mole fraction) is the eutectic composition; x_S (mole fraction) is the maximum hydrogen solubility in solid phase; n_M (mole) is the amount of solidified metal. Eq. (4) states that the amount of the hydrogen gas generated from a gas–metal eutectic reaction should be proportional to the amount of solidified metal, according to the values of the x_E and x_S .

¹ This is not the case in practice, because the growing interface would at least partially incorporate the excess hydrogen into the gas pores.

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