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J. Mater. Sci. Technol., 2012, 28(12), 1169–1174.
JMST
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Investigation of the Heterogeneous Nucleation on Fractal Surfaces

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[Manuscript received November 2, 2011, in revised form December 6, 2011]

Classical theory of heterogeneous nucleation has been developed with an implied hypothesis of smooth substrate surfaces; however, morphologies of any real substrate surfaces are generally complicated and demonstrate fractal characteristics. In this paper, the wettability between the embryo and the fractal substrate surface was discussed, and heterogeneous nucleation behaviors were theoretically analyzed. The result shows that the roughness factor of a fractal surface varies with the scale of the embryo. As a result, the fractal character of the substrate surface has important effects on heterogeneous nucleation behaviors. It has been shown that the energy barrier for heterogeneous nucleation of a non-wetting phase on a fractal rough surface increases with increasing fractal dimensions, and both the critical nucleus radius and the nucleation energy barrier decrease with increasing fractal dimensions for heterogeneous nucleation of a wetting phase on the fractal rough surface. For a non-wetting system, the critical nucleus radius shows a slight shift with changes of the intrinsic wetting angle, but for a wetting system, the critical nucleus radius shows an obvious change with decreasing intrinsic wetting angle, thus imposes a stronger effect on the heterogeneous nucleation behaviors.

KEY WORDS: Solidification; Nucleation; Supersaturated solutions; Substrate; Surface structure

1. Introduction

As the first stage of liquid/solid phase transition, nucleation has strong effects on the formation of solidification microstructures[1]. Heterogeneous nucleation are commonly observed in practical process of solidification, as the energy barrier of heterogeneous nucleation is generally lower than that of homogeneous nucleation process[2]. Fletcher[3] has investigated the wetting angles between nucleus/substrate and dimension ratio of particles/nucleus during heterogeneous nucleation process, thus predicted the effects of substrate particle size on nucleation. It has been generally accepted that cracks and caves on the mould wall is benefit for the formation of nucleus[4]. Turnbull[5] has proposed that, nucleus may survive under superheating condition in the concave structures of certain geometry characteristics on the substrate surface, and thus further nucleation can be skipped when the system retains its supercooling conditions.

Although micro-morphologies of different scales exist on the factual material surfaces, the effects of the surface morphologies on nucleation has not been paid enough attentions in former researches. In our previous research, it has been found that the surface morphology characteristics imposed important effects on the heterogeneous nucleation on a rough surface, and a special selection behavior of the nucleation point, which is hard to be explained by classical nucleation theory, has been observed[6]. By considering the nucleation energy on a rough surface, a heterogeneous nucleation investigation based on Wenzel model was carried out. It has been shown that differences in the surface roughness contribute to different heterogeneous nucleation energy, thus changes the heterogeneous nucleation behaviors on rough surfaces[7]. It has been deduced that when the intrinsic wetting angle between the nucleus and the substrate is lower than 90°, the heterogeneous nucleation barrier de-

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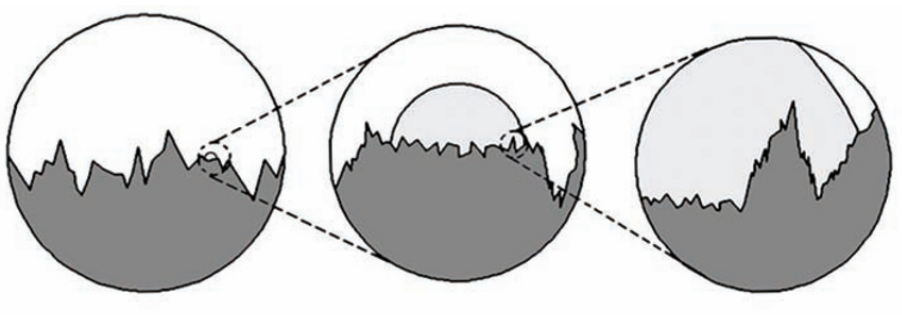

Fig. 1 A sphere-cap nucleus forming on a fractal surface

creases with increasing roughness of the substrate; however, when the intrinsic wetting angle is larger than 90 deg., the heterogeneous nucleation barrier increases with increasing roughness of the substrate.

Complicated interface morphologies were frequently observed on factual materials surfaces, including the nucleation substrate surface. Fractal theory has been used to describe the complicity of the morphology[8], and it has been shown that fractal characteristic is very common on the surface of many natural or man-made materials[9], where the fractal dimensions of these surface range from 2 to 3, meaning that these surfaces lies between 2-dimension structures and 3-dimension structures. Lazaridis *et al.*[10] has indicated that the wettability of particles can be enhanced if the particle surface is rough and possesses some kind of self-similarity in its morphology, and thus change the nucleation behaviors on its surface. Based on the fractal surface wetting model by Halzett[11], Roldugin and Tikhonov[12] have developed a description for heterogeneous nucleation behaviors on fractal surface, however, as some definition in the thesis is not strictly given (for example with a droplet of radius R_0 attached to the fractal surface, the base area of the droplet were given as $S(R_0/d_0)^{2-d_\mathrm{f}}$, but not strictly deduced $S(2R_0\sin\theta/d_0)^{2-d_\mathrm{f}}$, deviations may exist in his results).

In present work, based on the rough surface heterogeneous nucleation model, which we have proposed in the previous work[7], the effects of the geometrical property of the fractal surface on heterogeneous nucleation behaviors were further discussed by considering the fractal characteristic in the substrate surface.

2. Theoretical Models

Heterogeneous nucleation was affected by the wetting property between the nucleus and the substrate. For a substrate surface with geometrical fluctuations, the contact behavior should be described by Wenzel model[13] instead of Young′s equation used in traditional heterogeneous nucleation model, where a concept of effective wetting angle θ^* is defined as

$$\cos\theta^* = f\cdot\cos\theta \qquad (1)$$

where f is the roughness factor for the interface between the substrate and the nucleus, and θ is the intrinsic wetting angle between the nuclei and the substrate.

For a fractal substrate surface with a factual surface area S_fractal and projection area, $S_\mathrm{projection}$, f is defined as

$$f = S_\mathrm{fractal}/S_\mathrm{projection} \qquad (2)$$

As illustrated in Fig. 1, assuming that the nucleation substrate surface has a fractal dimension of d_f between the length scale of l_min and l_max, where l_max corresponds to the upper length scale limit and l_min corresponds to the lower length scale limit of the fractal morphology, and the fractal dimension d_f lies between 2 and 3. According to the fractal theories, for any measurement scale of l, which lies between l_min and l_max, the area of the interface between the nucleus and the substrate can be given as

$$S_\mathrm{fractal} = S_0\cdot(l)^{2-d_\mathrm{f}} \qquad (3)$$

where S_0 is a constant for this fractal interface. Accordingly, for any measurement scale of l', which is less than l_min, the area of the interface between the nucleus and the substrate should be expressed as

$$S'_\mathrm{fractal} = S_0\cdot(l_\mathrm{min})^{2-d_\mathrm{f}} \qquad (4)$$

Define R as the radius of the embryo, then $2R\cdot\sin\theta^*$ is the diameter of the contact plane between the nucleus and the substrate. For a measurement scale of $2R\cdot\sin\theta^*$, the fractal interface can be simplified to a flat plane. Under this situation we have $S_\mathrm{projection}{=}S_\mathrm{fractal}|_{\mathrm{l=2R\cdot\sin\theta}}$, where $S_\mathrm{projection}$ is the projection area of the interface between the embryo and the substrate. For any value of $2R\cdot\sin\theta^*$ lies between l_min and l_max, the following formula can be obtained:

$$S_\mathrm{projection} = S_0\cdot(2R\cdot\sin\theta^*)^{2-d_\mathrm{f}} \qquad (5)$$

Refer to Eq. (2), the roughness factor of the substrate surface can be described as

$$f = (2R\cdot\sin\theta^*/l_\mathrm{min})^{\mathrm{d_f}-2} \qquad (6)$$

A reasonable value of l_min can be assumed as 1 nm as this value is generally larger than the lattice constant of any solid structure and less than the scale of an embryo. Then Eq. (1) can be transformed into: