Oscillations of the Crystallization Front of Adsorbed Water

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Relaxation oscillations of the crystallization front in a gradient temperature field have been observed for water adsorbed on a metal film deposited on a glass substrate. The metal film plays an important role in heat removal from the crystallization front and determines the existence of oscillations. A possible mechanism is proposed for the development of oscillations. It is shown that the oscillations observed are similar to the oscillations of the front of self-propagating high-temperature synthesis. © *2000 MAIK "Nauka/Interperiodica".*

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In recent years, stable interest has been expressed to studying the development of morphological instabilities and dendritic growth in crystallization [1–3]. An analysis of linear stability made in [4] has become classical. However, it does not consider the periodic variation of the crystallization front velocity v_f, which can explain the appearance of the banded structure. This structure is often observed in metal alloys at high cooling rates [5, 6]. It consists of two successively alternating subbands that differ in microstructure and are aligned parallel to the crystallization front (CF). A typical period of the banded structure is of the order of 1 μm. The theory of CF stability was extended in [7] under the assumption that the distribution coefficient k_E depends on the velocity v_f. When the function $k_E(v_f)$ strongly depends on the value of v_f, the theory predicts the appearance of oscillatory instabilities of the CF for large values of v_f. Further development of the theory explaining the existence of oscillatory instabilities of the CF was obtained in [8, 9]. In [9], the diffusion of the latent heat liberated at the CF was taken into account. The main result of [9] was the conclusion that the development of the banded structure has its origin in CF oscillations, which arise when the velocity v_f decreases below the critical velocity v_c. For the values of the velocity v_f close to v_c, the oscillation amplitude λ grows as $\lambda \sim \sqrt{v_c - v_f}$; then, with decreasing v_f, the CF oscillations develop into relaxation oscillations. A further decrease in the velocity v_f leads to the Feigenbaum cascade of successive period-doubling bifurcations and further to chaotic oscillations. In this case, the oscillation wavelength is comparable to the temperature wavelength

$$\lambda \sim \sqrt{K_T \tau_{osc}}, \qquad (1)$$

where τ_{osc} is the oscillation period, and K_T is the thermal diffusivity.

In [10], oscillatory instabilities were predicted within the phase-field model for the rapid directional solidification of a binary alloy.

Only a few of the general class of phenomena with moving boundaries known as the Stefan problem are characterized by oscillatory front instabilities. Among these are the existence of self-oscillating modes of an explosive crystallization front [11] and the existence of the front of self-propagating high-temperature synthesis (SHS) [12]. A linear analysis of the thermal stability of stationary modes made in [13, 14] determined the existence domains of self-oscillating modes of the explosive crystallization front. In [14], the oscillation wavelength λ of the explosive crystallization front was determined as

$$\lambda = 6.1 K_T / v_f. \qquad (2)$$

Previously, similar problems were solved for the SHS front. In [15], the oscillation wavelength was estimated as

$$\lambda \cong 10 K_T / v_f. \qquad (3)$$

A similar value of λ was obtained in [16]:

$$\lambda = 2\pi K_T / v_f. \qquad (4)$$

For the SHS front and the explosive crystallization front, the numerical solutions found in [14–16] showed that, as the sample temperature T_S decreases and approaches the initiation temperature T_0, oscillations also exhibit a sequence of period doubling. Because the average velocity v_f of the CF may be defined as $v_f = \lambda/\tau_{osc}$, Eqs. (1)–(4) coincide to a constant factor and reflect the thermal mechanism of the propagation of oscillatory instabilities common to all the phenomena considered above.

It is known that water at normal pressure crystallizes into the hexagonal phase ($1h$). Depending on pressure and temperature, 12 polymorphous modifications, and at least 2 amorphous modifications, of ice exist (see,

e.g., [16, 17]). Investigations into the phase composition of water condensed onto cooled substrates indicate that the amorphous phase is formed at normal pressure at temperatures below 113 K [18].

This work is devoted to obtaining experimental evidence for the existence of oscillations of the adsorbed water CF. Samples were metal (nickel and tin) films about 30–50 nm thick deposited onto glass substrates 0.18 mm thick with linear sizes of ~5 × 15 mm. The samples were placed in a gradient temperature field at normal pressure and moisture. With decreasing sample temperature, a layer of water adsorbed from room air appeared on the substrate. On the side of the sample that had a low temperature, a CF that moved in the self-oscillating mode was formed (Fig. 1). Initially, when the cooling rate and the CF velocity were sufficiently large, the oscillation period and length were insignificant and the motion was of a chaotic character. As the CF approached a position with a temperature $T = 273$ K, its motion gained a pulsating mode and propagation was of a clearly defined relaxation character. In this case, the oscillation period was divided into rapid and slow parts. In the first part, the front jumped from one position to another at a velocity of ~ 0.1 m/s; next, in the second part, it stopped because of further cooling of the sample before the front. After that, the next jump occurred, and so forth (Fig. 1). The jump time τ_j was significantly shorter than the stop time τ_0 ($\tau_j \ll \tau_0$). Therefore, the oscillation period $\tau_{osc} = \tau_0 + \tau_j$ was determined by the stop time τ_0. As the CF approached a position with a temperature equal to the melting point $T_M = 273$ K, not only did the wavelength increase (Fig. 1), but the oscillation period increased as well. This behavior was likely determined by period doubling. These oscillations were observed visually or under low magnification.

Two scenarios are possible for the development of oscillatory instabilities of the CF on solidification of water adsorbed on a glass surface covered with a metal film. In the first one, oscillations appear in the motion of the CF from the liquid phase and the oscillation length is determined by Eq. (1). The front velocity during the jump is comparable to the front velocity observed in explosive crystallization [11]. Therefore, one may suggest the second mechanism of the development of oscillatory instabilities in the crystallization of an adsorbed water layer. The crystallization temperature is slightly lower than the melting point $T_M = 273$ K. At substrate temperatures T_S, explosive crystallization with a wavelength of λ is initiated that obeys Eq. (2). It is known that the explosive crystallization of ice has the initiation temperature $T_0 \sim 113$ K and a very low velocity of front motion $v_f \sim (0.2–1) \times 10^{-2}$ m/s. However, molecular dynamics studies of supercooled water [19] showed that a multitude of amorphous states can be formed. In [20], a transition to the solid state through an amorphous phase was substantiated. Theories explaining the appearance of a layered structure were devel-
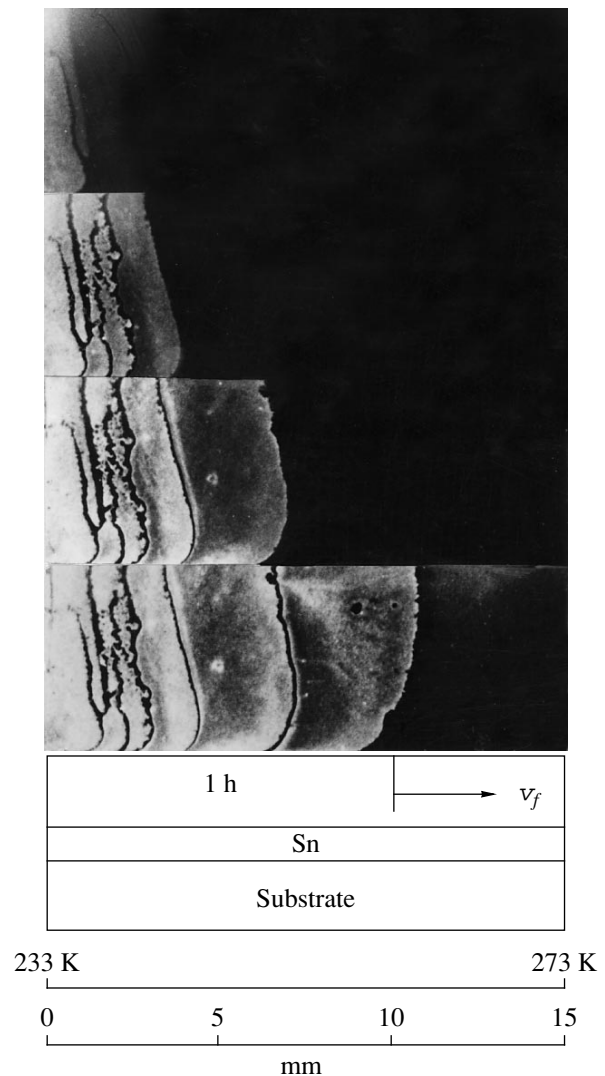

1 h $\quad\longrightarrow\ v_f$

Sn

Substrate

233 K $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ 273 K

| 0 | 5 | 10 | 15 |

mm

Fig. 1. Successive stages of the development of oscillations of the adsorbed water CF on the surface of a tin film (~40 nm in thickness) deposited on a glass substrate.

oped for binary alloys. These theories do not explain the existence of oscillations for pure substances. Therefore, the second scenario of the formation of oscillatory instabilities is more probable. This conclusion is confirmed by the existence of oscillations for directional crystallization in a given gradient temperature field. Similar oscillations are observed for explosive crystallization in the course of scanning over an amorphous semiconductor film with a laser beam [21].

The thermal mechanism for the appearance of oscillations is confirmed by experimental values of λ and τ_{osc}, which satisfactorily correspond to Eq. (1) with the coefficient $K_T = 5.0 \times 10^6$ m²/s (Fig. 2). The value of K_T obtained exceeds the thermal diffusivity of water (0.13×10^6 m²/s) by a factor of 40 and is smaller than the thermal diffusivity of the tin film (38×10^6 m²/s) by
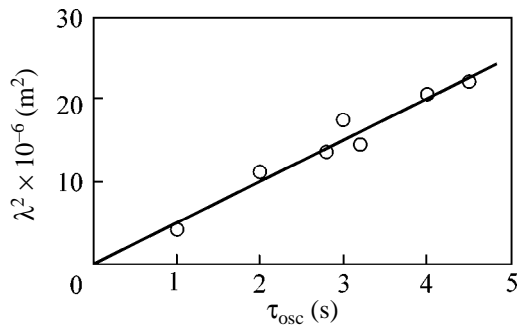
Fig. 2. Dependence of the wavelength λ on the oscillation period τ_{osc} of the adsorbed water CF on the sample surface depicted in Fig. 1.

almost an order of magnitude. This suggests that the metal film plays an important role in heat removal from the CF and determines the appearance threshold and the character of oscillations. Actually, oscillations of the adsorbed water CF were not observed in the absence of a metal film. Oscillations arise only on a freshly sputtered metal layer. The occurrence of oxides leads to degradation of the metal surface and to the termination of oscillations. If temperature noise with the average value $\langle \Delta T \rangle = 10$ K is superimposed on the constant temperature field under experimental conditions, then the CF exhibits spikes in the vicinity of an equilibrium position.

The propagation character of the oscillations of the adsorbed water CF described above is rather similar to the oscillations of the SHS front in thin films [22]. Multiple SHS (MSHS) [23] is a variety of SHS in thin films, which is different from SHS in powders. In [23], it is shown that MSHS is a reversible structural phase transition that corresponds to the eutectic crystallization of bulk samples. As distinct from eutectic solidification, MSHS in thin films occurs in the solid phase, and phase separation likely proceeds from the amorphous phase below the initiation temperature T_0. In this case, the eutectic temperature T_E of bulk samples is higher than the initiation temperature T_0 of MSHS. When temperature noise is superimposed, the MSHS front, as well as the adsorbed water CF, exhibits chaotic spikes in the vicinity of T_0. In [24], it is shown that low-energy excitations ($\epsilon \sim 100$ J/mol) are the basis of the structural instability that determines the mechanisms of chaotic spikes of the MSHS front and oscillations of the SHS front. This suggests a common mechanism of oscillatory instabilities for the CF of water adsorbed on a metal layer and for the SHS front in thin films. It follows from the above that the crystallization process in thin films significantly differs from the crystallization of bulk samples because of intense heat extraction into

the substrate and may exhibit instabilities in CF propagation.

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