ISSN 0036-0295, Russian Metallurgy (Metally), Vol. 2013, No. 8, pp. 575–579. © Pleiades Publishing, Ltd., 2013.
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# Solidification Dynamics under Random External-Temperature Fluctuations

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Received April 27, 2012

**Abstract**—The nonlinear dynamic mechanisms of solid-phase formation with a phase transition region are studied under periodic and random fluctuations of the cooling-boundary temperature. It is theoretically shown that a mushy zone can form even at close liquid and cooling-boundary temperatures due to random temperature field fluctuations. The growth of a solid phase with the mushy zone is investigated as a function of the autocovariance characteristics of random noises.

**DOI:** 10.1134/S0036029513080028

## INTRODUCTION

The theory of phase transitions in solid–liquid systems originated in 1889 from pioneering Stefan's works dealing with a mathematical description of water solidification [1]. In those works, Stefan was the first to formulate a thermal problem with a boundary condition of heat balance at a moving phase transition boundary (solidification front), which is now known as Stefan's condition (or condition of the fourth kind). The disadvantage of this approach consists in the fact that it does not take into account the dependence of phase-transition temperature $T_p$ on the impurity dissolved in a liquid. For a melt with impurity concentration $C$, such a dependence is expressed as the liquidus equation $T_p = T_M - mC$, which takes into account the fact that the phase-transition temperature decreases as the impurity concentration increases ($T_M$ is the phase-transition temperature of the pure substance, $m$ is the liquidus slope). Moreover, the presence of a sharp boundary of the phase transition between solid and liquid phases in a system (solidification front) is an idealization of the real process of solidification.

The rejection of the impurity dissolved in a liquid that is caused by the growth of a solid phase leads to its accumulation before the interface, decreases the phase-transition temperature, and creates a concentration supercooling [2]. When the interface moves deep into the liquid, the modulus of concentration gradient $\nabla C$ in front of it increases, and temperature gradient $\nabla T$ coincides with the temperature gradient of the phase transition $-m\nabla C$ at a certain time. Then (when $-m\nabla C$ exceeds $\nabla T$), an extended region of concentration supercooling appears in front of the interface. This supercooled region favors the development of instability in the interface, which results in the formation of dendrite-like structures [3–13]. Thus, the region of a two-phase state of a substance, i.e., the mushy zone, appears in front of the interface.

## MODEL FOR THE PROCESS WITH RANDOM FLUCTUATIONS

The authors of [14–18] obtained the law of motion of the boundary of the mushy zone–melt (solution) phase transition $b(t)$, which actually represents the thickness of the region having formed by time $t$,

$$b(t) = \sqrt{\frac{2}{I}\left(T_L t - \int_0^t T_{ex}(\alpha)d\alpha\right)^+}, \qquad (1)$$

where

$$I = A\left[1 - \frac{D_L A}{T_L}\left(\frac{L_V D_L}{k_S T_L} + 1 - \frac{k_L}{k_S}\right)(\varphi_b - 1)\right].$$

Here, we introduced the following designations: $A = L_V\varphi_b/\Phi$; $\Phi = k_S\varphi_b + k_L(1 - \varphi_b)$; $L_V$ is the latent heat of solidification, $D_L$ is the diffusion coefficient of the impurity in the melt; $\varphi_b$ is the fraction of the solid phase at boundary $b$; $T_L$ is the melt temperature near boundary $b$; $k_S$ and $k_L$ are the thermal conductivities of the solid and liquid phases, respectively; and $T_{ex}(t)$ is the time-dependent temperature of the cooling boundary. Sign "+" is determined as follows: $a^+ = a$ at $a \geq 0$ and $a^+ = 0$ at $a < 0$; moreover, it reflects the fact that a solid phase does not form at $T_L t < \int_0^t T_{ex}(\alpha)d\alpha$ in Eq. (1). Note that Eq. (1) describes the frontal solution to the problem at $\varphi_b \to 1$. Equation (1) is the solution to the thermodiffusion Stefan problem with an extended phase-transition region in the case of an isothermal melt.

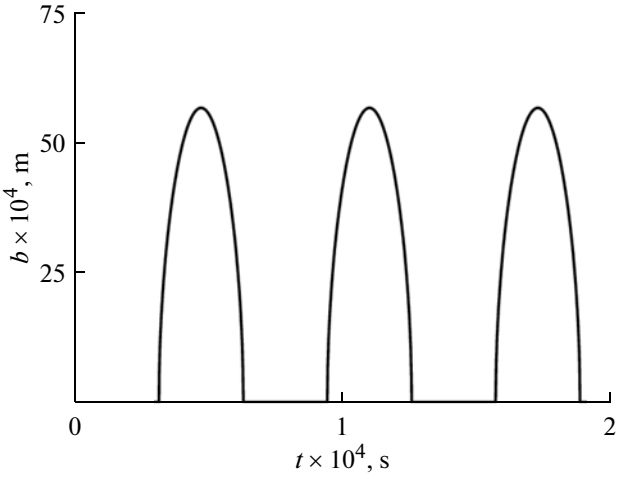


**Fig. 1.** Mushy zone thickness for a periodic change in the external temperature at $\delta = 2$ and $\omega = 0.001$. The thermophysical parameters of the system were taken from [14–16].

If external temperature $T_{ex}(t)$ is lower than liquid-phase temperature $T_L$ by constant $\delta > 0$, i.e., $T_{ex}(t) = T_L - \delta$, the law of variation of the mushy zone thickness has the form $b(t) = \sqrt{2\delta t/I}$. Here, the phase-transition region thickness increases with time as the root square of the process time, $b(t) \sim \sqrt{t}$, which is the self-similarity of solidification [19–23].

We now consider how cooling-boundary temperature fluctuations affect the mushy zone thickness. We first analyze the case where these fluctuations have a periodic deterministic character, $T_{ex}(t) = T_L + \delta\cos\omega t$, where the average cooling-boundary temperature coincides with the melt temperature. In this case, it follows from Eq. (1) that the mushy zone thickness also changes periodically, $b(t) = \sqrt{2\delta(-\sin\omega t)^+/\omega I}$. (Fig. 1). Hereafter, the thermophysical parameters of the system are taken from [14–18].

Note that the maximum values of $b(t)$ depend on both the cooling-boundary temperature oscillation amplitude and frequency $\omega$. An increase in the frequency leads to a decrease in the maximum values of the mushy zone thickness because of system inertness.

As a rule, the temperature fluctuations are random due to the action of various factors (turbulent melt, nonuniformity blowing of the cooling boundary, etc.) (see, e.g., [24]). Even small random perturbations can result in substantial changes in the dynamics of a nonlinear system [25–29]. The following wide spectrum of phenomena related to the action of random disturbances is well known: stochastic resonance [30, 31], noise-induced transitions [26], noise-induced stochastic bifurcations [32, 33], and noise-assisted order [34, 35] and chaos [36]. The role of noises in the generation of the magnetic field of a galaxy, the transition from a laminar to a turbulent flow, and the excitation of a neutron was studied in [37–39].

Therefore, we suggest a model that takes into account the effect of random temperature fluctuations on the cooling-boundary temperature. Let $T_{ex}(t) = T_L + \varepsilon\xi(t)$. Here, $\xi(t)$ is the Ornstein–Uhlenbeck process [40] set by the Langevin equation

$$\dot{\xi} = -p\xi + \sqrt{2p}\dot{w}, \qquad (2)$$

where $w(t)$ is the Wiener random process with parameters $E(w(t) - w(s)) = 0$ and $E(w(t) - w(s))^2 = |t - s|$. Stationary solution $\xi(t)$ to Eq. (2) has the following probabilistic characteristics: zero mean $E(\xi(t)) = 0$, unity dispersion $E(\xi(t))^2 = 1$, and autocovariance function $\mathrm{cov}(\xi(t), \xi(t + \tau)) = \exp(-p\tau)$. With parameter $p$, we can change the covariance characteristics; with scalar quantity $\varepsilon$, we can change the intensity of random cooling temperature fluctuations.

Figure 2 shows $T_{ex}(t)$ trajectories for $T_L = -2°C$, $\varepsilon = 1$, and three values of parameter $p$. The random values of $T_{ex}(t)$ belong to confidence interval ($T_L - 2°C$, $T_L + 2°C$) at a probability of 0.95, according to the theory (the two-sigma rule). A specific $b(t)$ function corresponds to each random $T_{ex}(t)$ process (see Eq. (1)). Here, the only deterministic characteristic is the ensemble mean $\bar{b}(t) = \langle b(t)\rangle$. Note that $\langle T_{ex}(t)\rangle = T_L$ is independent of parameters $p$ and $\varepsilon$, whereas the $\bar{b}(t)$ curves change substantially when these parameters change (see Fig. 3). These results demonstrate that, even if the mean value of cooling (external) temperature $T_{ex}(t)$ coincides with liquid temperature $T_L$, a mushy zone layer can form and grow in time owing to only random external-temperature fluctuations. This finding is explained by the interaction of the processes of solidification and impurity diffusion. For example, the solid phase grows when the instantaneous cooling-boundary temperature is below the phase-transition temperature at a given concentration. In this case, the entire impurity is rejected deep into the melt. From a theoretical viewpoint, melting can occur when the external temperature becomes higher than the phase-transition temperature. However, the concentration profile has no time to adapt to temperature field changes within the fluctuation times, and phase-transition temperature $T_p$ does not change. Figure 3 also shows that the $b(t)$ time dependence is close to the square root law $b(t) \sim \sqrt{t}$ and that the rate of increase of the mushy zone thickness increases with decreasing $p$ and increasing $\varepsilon$.

Now, let the randomly fluctuating temperature of the cooling boundary have an average value that is lower than the liquid phase temperature by constant $\delta$, $T_{ex}(t) = T_L - \delta + \varepsilon\xi(t)$. Figure 4 shows several random

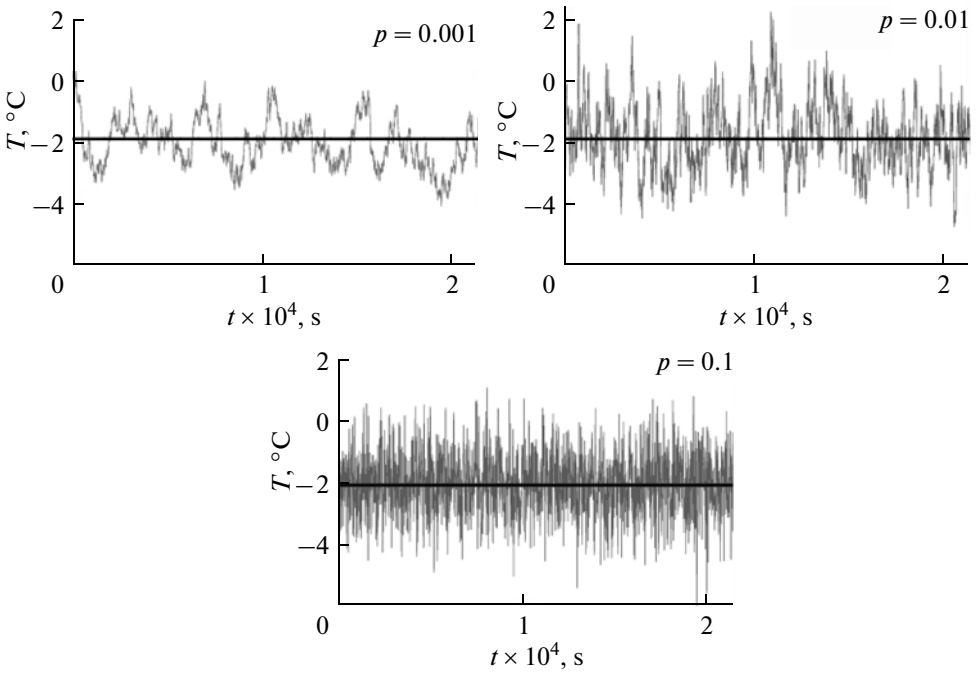


**Fig. 2.** Random external-temperature fluctuations.

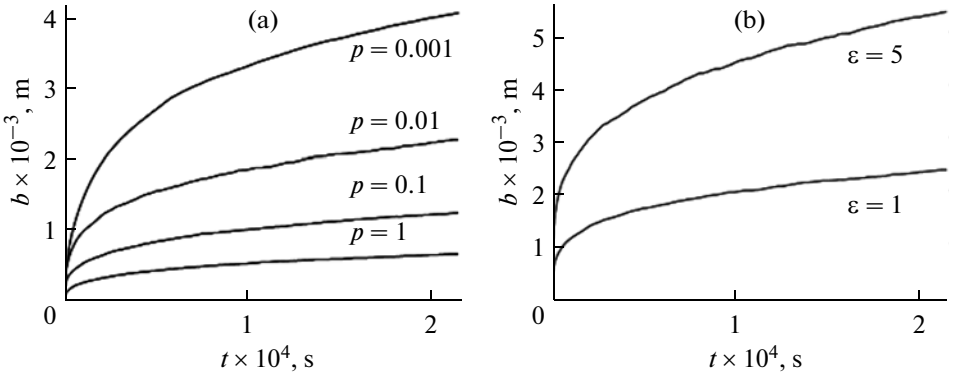


**Fig. 3.** Solidification dynamics under random external-temperature fluctuations at (a) $\varepsilon = 1$ and (b) $p = 0.01$.

$b(t)$ curves for $T_L = -2°C$, $p = 0.01$, $\varepsilon = 2$, and $\delta = 1$. Here, the solid heavy line shows the $b_0(t)$ curve at $\varepsilon = 0$ and without fluctuations. Note that the random curves deviate from $b_0(t)$ rather nonuniformly: the scatter is maximal at the initial stage of mushy zone formation. In time, the scatter decreases substantially when the mushy zone thickness increases. Figure 4 shows that the initial stage of solidification is characterized by a high sensitivity to random external-temperature fluctuations, which result in the appearance of the mushy zone.

Now, let the external temperature of the cooling boundary have both periodic and random fluctuations, $T_{ex}(t) = T_L + \delta\cos\omega t + \varepsilon\xi(t)$. The solid heavy line in

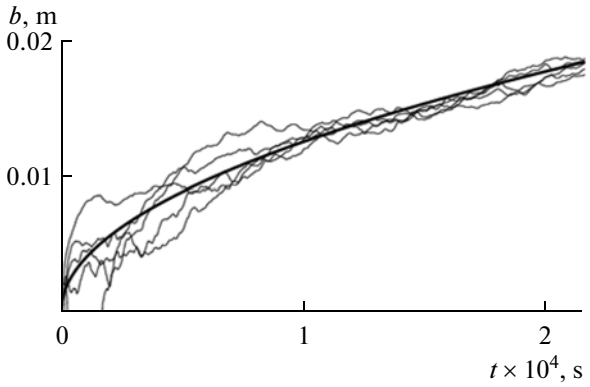


**Fig. 4.** Random $b(t)$ curves at $\delta = 1$ and $\varepsilon = 2$.

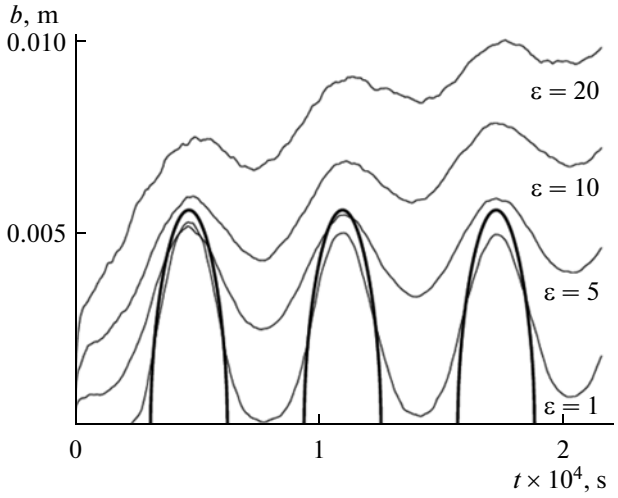


**Fig. 5.** Solidification dynamics under random external-temperature fluctuations at $\delta = 2$ and $\omega = 0.001$.

Fig. 5 shows the $b_0(t)$ curve for $\varepsilon = 0$ and the $\bar{b}(t) = \langle b(t) \rangle$ curves for $\varepsilon = 1$, 5, 10, and 20. In the absence of random fluctuations ($\varepsilon = 0$), there exist repetitive solidification and melting stages separated by time intervals without a solid phase. Note that the mushy zone does not disappear even for small noises and its minimum thickness tends to grow with time. As $\varepsilon$ increases, the effect of the deterministic periodic component weakens.

## CONCLUSIONS

The detected effects of random actions were found to be related to a high sensitivity of the system under study under conditions where the mean value of the fluctuating cooling-boundary temperature is close to the phase-transition temperature in a melt or a solution. The random external-temperature fluctuations caused by various natural noises lead to the formation of a mushy zone, and the rate of increase of the mushy zone thickness can reach several centimeters per day. The heat flow on the cooling boundary surface, which is inversely proportional to $b(t)$ [14–18], weakens as the mushy zone thickness increases. Due to the generality of the thermodiffusion Stefan model, this effect should also be characteristic of magma solidification models [41, 42] and the evaporation of metals with the formation of liquid films [43–47].

## ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 10-01–96022-ural, 11-01-00137, 12-01-97514-tsentr) and the federal program Scientific and Academic–Teaching Staff of Innovative Russia (2009–2013).

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*Translated by K. Shakhlevich*