Impurity mechanism for the excitation of short-wavelength periodic structures on the surface of a solidifying melt

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It has been established, for the first time, that short-wavelength periodic structures which arise on the surface of a cooling molten metal may be initiated by an instability of the solidification process if the melt contains a sufficiently high impurity concentration. Experiments were carried out on a titanium target (with an yttrium impurity) and a copper target (with a tin impurity), which were melted by an ion beam. The mechanism for this effect has been determined. It is an instability of the solidification front while a concentration cooling of the liquid phase is occurring, due to displacement of the impurity into this phase as the front moves. A dispersion relation is found for solidification waves at the interface in the case of a thin layer of melt. Solutions of this dispersion relation have been analyzed as a function of the impurity concentration and the heat-removal conditions. The theoretical values of the period of the structures and the theoretical condition for excitation agree with observations.

1. As the surface of a solid (a metal, a semiconductor, or an insulator) melts during ion bombardment, plasma bombardment, or laser bombardment, some short-wavelength periodic structures are observed on the surface after it has cooled.[1–3] Previous efforts to explain this effect have been based on the assumption that the structures arise as the energy flux is applied to the surface layer of liquid. Various versions of a thermocapillary instability[4–6] or of a parametric instability[1,7] have been proposed as the mechanism for the excitation of these structures. It has also been assumed that when the external agent is turned off these structures can become fixed on the cooled surface under appropriate "freezing conditions".[1] It has been assumed that the solidification process itself has no bearing on the excitation of the structures.

Several new experimental results which we have obtained on the ion melting of copper and titanium surfaces imply that when impurities are present these structures arise from an instability of the melt solidification front.

2. The experiments were carried out on two facilities. In the first, as in Ref. 1, a beam of ions (H^+, $^4H^+$, Y^+) was produced in the space-charge layer of plasma streaming out of a discharge along the magnetic field. For this purpose, a potential (of up to 500 V), negative with respect to the plasma, was applied to the molten plane electrode. In the second apparatus, the target was melted with a steady-state beam of positive ions ($^4He^+$) with a current $I_+ = 20$ mA and an energy up to 30 keV. This beam was focused onto the target by means of a magnetic lens. In each case, the specific power of the ion beam reached roughly 10^4 W/cm^2. The index of the current modulation due to the discharge noise in the first apparatus was $\eta = 0.1$–0.2, with a characteristic frequency $f = 1$ MHz; the index in the second apparatus was substantially lower ($\eta < 0.01$). Because of the low noise level in the second case, it was also possible to carry out experiments with external modulation of the beam current. This modulation was introduced by applying a voltage from an rf oscillator to the discharge gap of the ion source. The modulation frequency f could be varied over the range 0.04–5 MHz, and the amplitude η could be varied over the range 0.01–1. It turned out that the "frozen" structures did not depend strongly on either the frequency or the modulation index of the ion beam. In addition, these structures were observed even in the absence of a significant current modulation (Fig. 1). These facts rule out parametric instability as an explanation of these structures of the liquid surface.

A variation of the specific power of the ion beam also fails to alter the characteristics of the structures. The "thermocapillary" version of the origin of these structures is thus also discarded.

The structures are most obvious at the periphery of the melt, i.e., outside the zone in which the ion beam acts directly on the target. This circumstance would again be difficult to explain on the basis of the above mechanisms. The depth of the melt at the periphery is significantly smaller than the thickness of the solid phase.

Here are some pieces of experimental evidence which

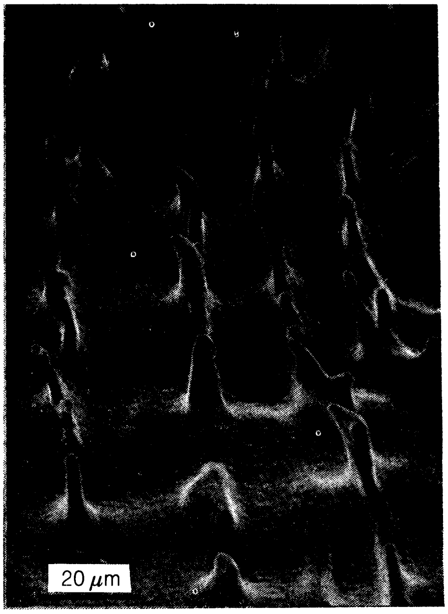

FIG. 1. Portion of a solidified surface of technical-purity copper (M2), which had been melted by an unmodulated beam of 30-keV $^4He^+$ ions at a current $I_+ = 15$ mA.

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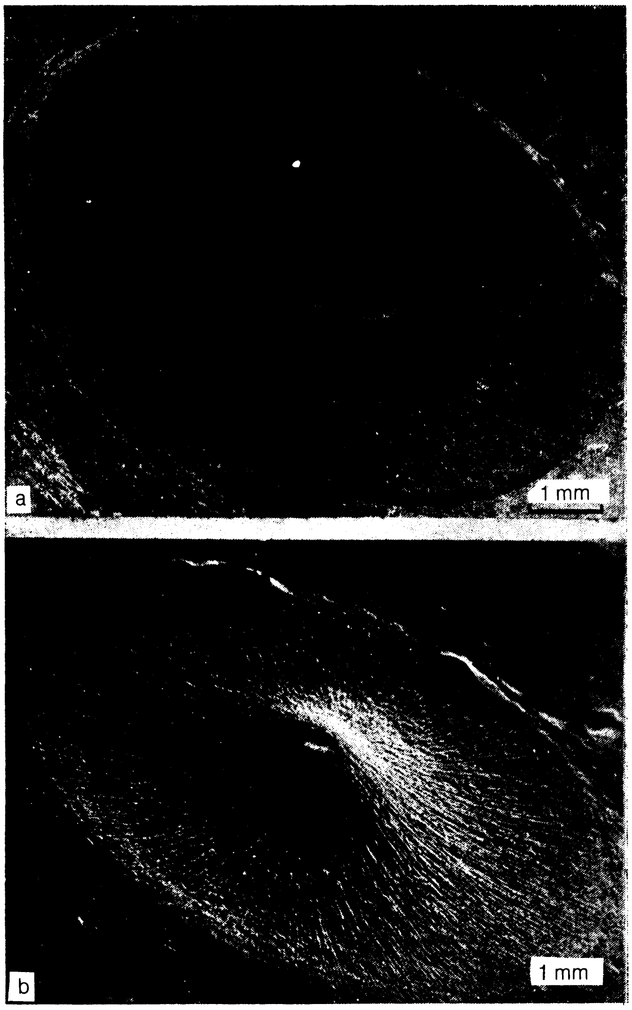

FIG. 2. General view of the solidified surface of a melt in the case of (a) pure titanium and (b) titanium with an yttrium dopant ($c_0 = 0.4\%$). The ion beam causing the melting had a current $I_+ = 0.5$ A and an ion energy of 500 eV.

point to a governing role of the solidification process in the mechanism for the formation of these structures.

1) When the beam is applied, the melt has a nearly mirror finish; only after the beam power is turned off, and the melt is solidifying, does the mirror finish eventually give way to a matte finish. This fact is evidence that the structures appear on the surface during the solidification process.

2) Structures were observed only when the target had had a significant impurity concentration. In the case of the copper target, for example, the structures appeared when the impurity concentration exceeded 0.1% (M1 and M2 technical-purity copper, with impurities of tin, nickel, etc.). When purer copper targets were used (with an impurity concentration less than 0.01%), there were no structures. The melt retained a mirror finish even after the solidification. Structures did not appear on the surface of pure titanium melted by ions ($^4He^+$) from a gas. The structures did appear during sufficiently prolonged bombardment of a target with a beam of yttrium ions. Figure 2 shows photographs of the surface of a solidified melt. These photographs demonstrate the nature of the surface finish in the case of (a) pure titanium and (b) titanium with a fairly high impurity concentration, in which case "frozen" periodic structures appear on the surface.

With these experimental results in mind, we carried out experiments with controlled doping of initially "pure" samples. The experiments were carried out in vacuum; the pressure in the working chamber was less than $5 \cdot 10^{-5}$ torr. These experiments revealed a critical impurity concentration, at which wave structures began to appear on the solidified surface. It turned out that this critical concentration increases with increasing heat removal and differs substantially for copper–tin and titanium–yttrium alloys. Near the critical concentration, the structures are rounded humps (Fig. 3a), and as the dopant concentration is raised the structures become sharp peaks (Fig. 3b). The wavelength in the copper–tin case (Fig. 3c) is noticeably larger than that in the titanium–yttrium case.

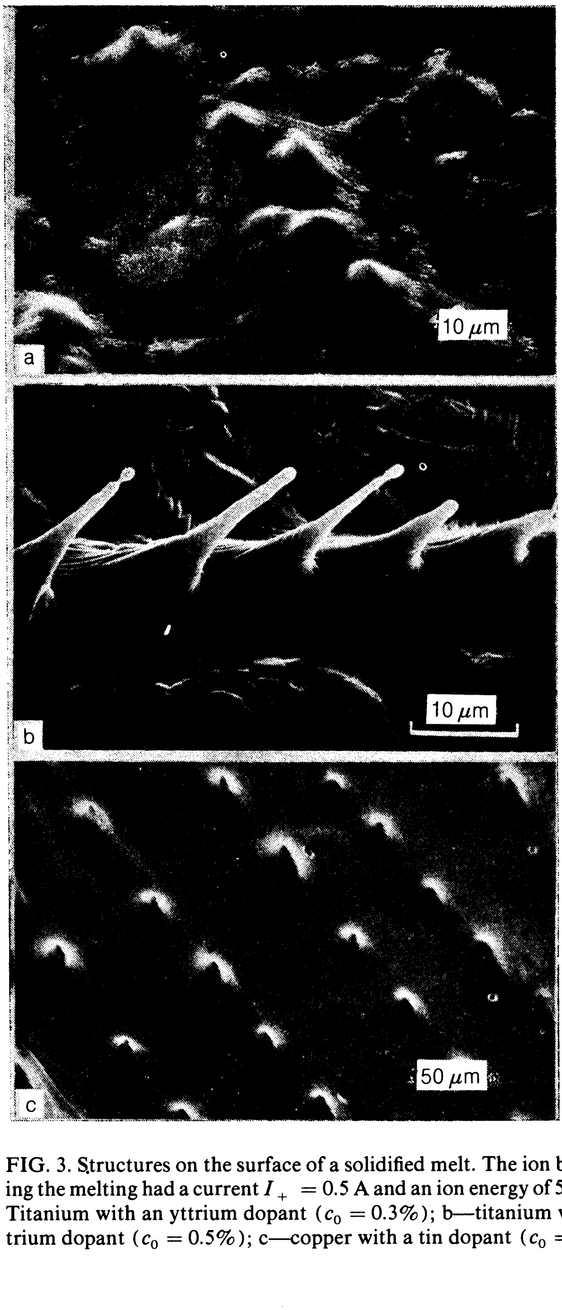

FIG. 3. Structures on the surface of a solidified melt. The ion beam causing the melting had a current $I_+ = 0.5$ A and an ion energy of 500 eV. a—Titanium with an yttrium dopant ($c_0 = 0.3\%$); b—titanium with an yttrium dopant ($c_0 = 0.5\%$); c—copper with a tin dopant ($c_0 = 0.2\%$).

We turn now to a discussion of the experimental data.

3. During zone melting, the solidification front is known[8] to be unstable if there is a sufficiently high impurity concentration (various structures arise at the solid–liquid interface). This instability stems from concentration supercooling of the liquid layer[8-10] which arises during the solidification because of a displacement of impurity into the liquid

phase (the segregation effect). A corresponding instability occurs in our experiments on the solidification of a plane surface layer of liquid phase. Because of the segregation and diffusion in the liquid layer, an impurity concentration profile falling off toward the surface of the melt is established.

The "liquidus" temperature T_L of the melt (i.e., below T_L the liquid solidifies) decreases with increasing dopant concentration. A positive gradient of the temperature T_L thus arises in the liquid phase near the interface, in the direction in which the solidification front moves (along the z axis). If this gradient

$$g_L = \frac{dT_L}{dz}\bigg|_{z=0}$$

($z = 0$ is the position of the interface in the coordinate system moving with the front) is higher than the temperature gradient in the melt (g_l), the liquid near the interface is supercooled. Accordingly, fluctuational protuberances at the interface will grow as the front moves toward the free surface; i.e., the interface will become unstable.[11,12] The surface tension at protuberances limits the instability region on the short-wavelength side. On the long-wavelength side, a limitation is imposed by the decrease in the diffusion flux along the perturbed solidification front. This decrease slows the expulsion of the dopant from the crest of a protuberance to the bottom of a depression. (This process accelerates the development of the depression and of the protuberance.)

The onset of a spatially periodic instability of the interface is also accompanied[11,12] by the growth of perturbations of the temperature and the dopant concentration in the interior of the liquid layer, with the same spatial period. Consequently, a periodic structure which has arisen at the interface will "emerge" at the free surface of the liquid phase and will be fixed at the end of the solidification process. The primary mechanism for this "emergence" is the Marangoni driving force,[13,14] which arises in the boundary condition on the tangential stresses at the surface of a liquid if the dependence of the surface tension on the temperature and the dopant concentration is taken into account. The words "driving force" are to be understood here in the sense that the temperature grating and the concentration grating at the free surface, which are responsible for the appearance of the Marangoni force, are determined by the structure of the instability of the interface.

We turn now to a calculation of the basic characteristics of the solidification waves at an interface in the case of a thin layer of melt. We then compare the results with experimental data.

4. We first determine and analyze the dispersion relation describing the time evolution of solidification waves in the linear stage, in which the initial interface is planar, and the melt is shallow. We choose the perturbations of the interface in the form

$$\xi = \bar{\xi} \exp\,(pt + i\mu x),$$

where $\bar{\xi}$ is the initial displacement amplitude, p is the growth rate, and μ is the wave number along the interface. We consider the case in which the depth of the liquid phase, h, is much smaller than the thickness d of the solid phase. Since the melt cools off rapidly, over a time h^2/χ_l, where χ_l is the thermal diffusivity of the liquid phase, g_l is small. It reaches a steady-state value determined by the radiated power:

$$\bar{g}_l = -\frac{\gamma}{\varkappa_l}\sigma_s T_l^4, \tag{1}$$

where γ is the emissivity of the melt, $\varkappa_l$ and T_l are the thermal conductivity and temperature of the liquid phase, and σ_s is the Stefan–Boltzmann constant. As will be shown below, the values of the temperature gradient in the solid phase, g_s, are in practice much larger than $|\bar{g}_l|$, and the velocity of the solidification front in the case $\xi = 0$ is determined by g_s:

$$v = \frac{\varkappa_s}{L}\frac{dT_s}{dz}\bigg|_{z=0} - \frac{\varkappa_l}{L}\bar{g}_l \approx \frac{\varkappa_s}{L} g_s, \tag{2}$$

where L is the latent heat of melting per unit volume, $g_s = (T_M - T_d)/d$, if $d^2/\chi_s < \tau$, τ is the duration of the ion bombardment, T_M is the temperature of the unperturbed interface, and T_d is the temperature of the lower part of the plate. The latter temperature depends on the heat-removal conditions. If $d \gg h$, then we have $g_s = \text{const}$ during the solidification process, at fixed values of T_M and T_d. At this point we set $\varkappa_{s,l} = \varkappa$ and $\chi_{s,l} = \chi$. Approximation (2) is valid if $h^2/\chi \ll h/v$ (or $h \ll L\chi/\varkappa g_s$; in this case, the time over which the liquid phase cools down is significantly shorter than the overall duration of the solidification: $\tau_{\text{sol}} = h/v$). In the case of a thin layer of melt, we thus have a situation characteristic of zone melting, in which a plane front is moving at a constant velocity.[8,9]

The temperature T_L of a binary melt on a curved interface ($z = \xi$) is given by[11,12]

$$T_L|_{z=\xi} = T_N - mc_l - \frac{\sigma T_N}{L}\mu^2\xi, \tag{3}$$

where T_N is the melting point of the pure metal (without the dopant), c_l is the dopant concentration in the liquid phase, and σ is the surface-tension coefficient. The quantity m is determined by the Van't Hoff relation[9]

$$m = \frac{k_B T_N^2(1-K)}{L},$$

where k_B is the Boltzmann constant, and $K = c_s/c_l|_{z=0}$ is the segregation coefficient, which determines the extent to which the dopant is displaced into the liquid phase during the solidification (c_s is the dopant concentration in the solid phase). In the steady state we have[15] $c_s|_{z=0} = c_0$ for $1 > K \gg D/vh$ (if the right-hand inequality holds, a steady state is established in a time considerably shorter than τ_{sol}), where c_0 is the initial dopant concentration in the melt, and D is the dopant diffusion coefficient in the liquid phase. Relation (3) holds under the condition $mc_0/K \ll T_N$ (in this case we have $T_M \approx T_N$). Using (3) and the conservation of the dopant flux at the interface (diffusion in the solid phase is being ignored), one can derive[9] an expression for g_L which determines the nature of the solutions of the dispersion relation. Using (2), we find

$$g_L = \frac{k_B T_N^2(1-K)^2 \varkappa g_s c_0}{L^2 DK}. \tag{4}$$

Consequently, g_L is determined by the dopant concentration, the value of K, and the value of g_s, which determines the velocity of the front and which depends strongly on the conditions of the heat removal from the lower part of the plate.

For short-wavelength perturbations, $|\mu| h \gg 1$, the dispersion relation can be written in the following dimensionless form, where we are making use of the results of Refs. 11 and 12 and assuming that the melt is thin ($g_l = 0,\ v = \text{const}$):

$$y=|\bar{\mu}|\left\{\left[1-\frac{2(y+K)}{2K-1+(\bar{\mu}^2+4y+1)^{1/2}}\right]b-\frac{1}{2}-a\bar{\mu}^2\right\}, \quad (5)$$

where

$$\bar{\mu}=\frac{2D}{v}\mu, \quad y=\frac{Dp}{v^2}, \quad b=\frac{g_L}{g_s}=\frac{k_B T_N^2(1-K)^2\varkappa c_0}{L^2DK},$$

$$a=\frac{\sigma T_N\varkappa^2 g_s}{4L^3D^2}, \quad v=\frac{\varkappa g_s}{L}.$$

It can be seen from (5) that the nature of the solutions of the dispersion relation does not depend on the sign of μ. We thus set $\mu > 0$ at this point.

The dispersion relation (5) describes an aperiodic instability of the solidification waves ($\operatorname{Im} p = 0,\ p > 0$). This instability arises in a certain interval of wave numbers. If $b \gg 1/2, a$, holds then $p > 0$ if

$$\left(\frac{2K}{b}\right)^{1/2}<\bar{\mu}<\left(\frac{b}{a}\right)^{1/2}. \quad (6)$$

Near the maximum of the growth rate for the corresponding values of $\bar{\mu}$, the condition $\bar{\mu}_m^2 \gg 1 + 4y_m$ holds, and the dispersion relation (5) reduces to

$$y=\frac{\bar{\mu}}{2b}(b-a\bar{\mu}^2), \quad (7)$$

from which we find $\bar{\mu}_m = (b/3a)^{1/2}$, $y_m = \bar{\mu}_m/3$.

The wavelength of the structure corresponding to $\bar{\mu}_m$ (near the maximum of the growth rate) is determined from

$$\lambda_m=\frac{4\pi D}{\bar{\mu}_m v}=2\cdot 3^{1/2}\pi\left[\frac{\sigma LDK}{g_s\varkappa k_B T_N(1-K)^2 c_0}\right]^{1/2}. \quad (8)$$

Let us look at some numerical estimates of λ_m for our experimental conditions (Fig. 3). For titanium with an yttrium dopant we would have $T_l \approx T_N = 1.67\cdot 10^3$ °C, $\gamma = 0.25$, $L = 2\cdot 10^3$ J/cm^3, $\varkappa = 0.2$ J/(cm·s·deg), $\sigma = 1.4\cdot 10^3$ erg/cm^2, $\chi = 0.1$ cm^2/s, $K = 0.15$, $D = 100^{-4}$ cm^2/s, and $c_0 = 0.4\%$. The duration of the ion bombardment is $\tau = 1$ min, and we have $g_s \approx 5\cdot 10^2$ deg/cm ($h = 0.1$ cm, $d = 0.5$ cm). The front velocity is $v \approx 0.05$ cm/s, and we have $|\bar{g}_l| \approx 80$ deg/cm, $b = 25$, and $a = 0.02$. From (8) we find $\lambda_m \approx 11$ μm and $p_m = 1.75\cdot 10^2$ s^{-1}.

For copper with a tin dopant we have $T_l \approx T_N = 1.08\cdot 10^3$ °C, $\gamma = 0.15$, $L = 1.5\cdot 10^3$ J/cm^3, $\chi = 0.4$ cm^2/s, $\varkappa = 1.65$ J/(cm·s·deg), $\sigma = 1.3\cdot 10^3$ erg/cm^2, $K = 0.5$, $D = 10^{-4}$ cm^2/s, $c_0 = 0.2\%$, and $g_s \approx 50$ deg/cm ($h \approx 0.02$–0.03 cm, $d = 0.5$ cm). In this case the front velocity is $v \approx 0.055$ cm/s, and we have $|\bar{g}_l| \approx 2$ deg/cm, $b = 10$, and $a = 0.18$. Calculations yield $\lambda_m \approx 43$ μm and $p_m \approx 50$ s^{-1}.

The calculated values of λ_m agree with the observed values (Fig. 3). From these estimates we conclude $g_s \approx |\bar{g}_l|$.

Let us use (5) to determine how the critical dopant concentration for the onset of an instability of the interface depends on the heat-removal conditions (on the parameter g_s). It can be seen from (5) that a necessary condition for the excitation is $b > 1/2$, and this condition does not depend on g_s. This condition is the same as that found previously[11,12] [$g_L > (g_s + g_s/2)$] if we use (2) and (4) and set $g_l = 0$. This is essentially a more rigorous condition for concentration supercooling of a liquid. When would this be a sufficient condition? From the conditions $y = 0$, $dy/d\bar{\mu} = 0$, which hold at the excitation threshold, we can find the excitation condition and the wave number at the threshold $\bar{\mu}_t$. These conditions reduce to

$$b_t=a\theta_t(\theta_t+2K-1)^2/K, \quad (\theta_t-1)^2(K+\theta_t)=K/2a, \quad (9)$$

where $\theta_t = (1+\bar{\mu}_t^2)^{1/2}$.

If $K/2a \gg 1$ holds (poor heat removal; g_s is small), then $\theta_t \approx \bar{\mu}_t \approx (K/2a)^{1/3}$, and under the condition $\theta_t \gg 1$ we have $b_t = 1/2$. Consequently, only at very small values of a (or g_s), such that the condition $(K/2a)^{1/3} \gg 1$ holds, is the condition $b > 1/2$ a sufficient condition. In this case the wavelength at the excitation threshold,

$$\lambda_t=2\pi\left(\frac{4D\sigma T_N}{\varkappa K g_s^2}\right)^{1/3} \quad (10)$$

decreases with increasing g_s, in proportion to $g_s^{-2/3}$.

At large values of g_s (good heat removal), with $K/2a \ll 1$, we find

$$\theta_t \approx 1+\left[\frac{K}{2a(K+1)}\right]^{1/2}, \quad \bar{\mu}_t \approx \left[\frac{2K}{a(K+1)}\right]^{1/4}$$

and $b_t \approx 4a$K. In this case the threshold dopant concentration increases in proportion to g_s, and we have

$$\lambda_t=2\pi\left[\frac{2(K+1)}{K}\frac{D^2L\sigma T_N}{\varkappa^2 g_s^3}\right]^{1/4} \propto g_s^{-3/4}. \quad (11)$$

Let us use (9) to estimate the threshold dopant concentrations under the conditions of our experiments. For titanium with an yttrium dopant, with $g_s = 5\cdot 10^2$ deg/cm, we find $b_t \approx 1$; for copper with a tin dopant (with $g_s = 50$ deg/cm), we find $b_t \approx 2$. In each case, the value of b_t corresponds to a dopant concentration $\approx 0.02\%$. Note that in order to observe an instability effect at the surface of the melt we would need a sufficiently high instability growth rate $p \gg v/h$ (the perturbations grow significantly over the total solidification time). This condition is satisfied, as is demonstrated by a numerical calculation of the dispersion characteristics, at dopant concentrations two or three times the threshold values found from (9). We can thus assume that the threshold characteristics for the interface instability also agree with the experimental data.

In summary, it has been shown in this study that short-wavelength periodic structures which arise on the surface of a melt which has cooled are a consequence of an instability of the interface during the solidification of a liquid phase containing a dopant. There has been no previous discussion of this mechanism for the excitation of surface structures. Just how this instability determines the shape of the observed structure of the frozen waves in the nonlinear stage requires further study.

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