Pattern formation in metallic glasses induced by helium-ion implantation. II. Model

I. Lovas
Central Research Institute for Physics, P.O. Box 49, H-1525 Budapest, Hungary

T. Tél
Institute for Theoretical Physics, Eötvös Loránd University, P.O. Box 327, H-1445 Budapest, Hungary

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A model is constructed to explain pattern formation in metallic glasses induced by helium-ion implantation. The migration of helium atoms is considered. The helium atoms are assumed to be in quasifree, in trapped, or captured, states. The density of the quasifree atoms and the energy density are governed by nonlinearly coupled diffusion-type equations. The critical value of the control parameter and the critical wave number characterizing the soft-mode instability of the system are determined. Their order of magnitude agree with that of the experimental data. Formally, the model can be reduced to the well-known Brusselator but the control parameter differs from that of the standard case.

Observations of the phenomena induced by helium-ion implantation in metallic glasses are reported in the preceding paper.[1] These observations can be summarized as follows: (i) On the surface of metallic glass samples irradiated by energetic helium ions a flaking process takes place at a critical dose. (ii) The thickness of the flaked-off layer is equal to the range of the helium ions. (iii) On the surface left behind the flaked layer a fairly regular pattern, viz., a wavelike structure can be observed. (iv) Pattern formation takes place only in the amorphous state and appears to be independent of chemical composition, manufacturing technology, and the energy of the helium ions.

In seeking the fundamental mechanism of pattern formation the transition from the undercooled, metastable, amorphous state to the stable, polycrystalline state seems to be the most natural candidate. During the experiments, however, the temperature of the samples was kept well below the crystallization temperature. Therefore, this process can be responsible for pattern formation only if the crystallization temperature decreases with the increasing pressure produced by the accumulating helium. Since, on the one hand, we have no compelling experimental evidence in favor of crystallization; on the other hand, the required unusual pressure dependence seems to be improbable, we look for other possibilities. Chemical ordering is out of the question since the pattern formation seems to be insensitive to the chemical composition. A further reason may be the mechanical deformation induced by the high pressure of the helium gas accumulated in a thin layer defined by the range and the straggling of the helium ions. Leaving open this possibility, another mechanism will be discussed here in detail.

We present a simple model based on the assumption that pattern formation is connected with the migration of the helium atoms in the metallic glass.[2] We will assume that during migration the helium accumulates into gas bubbles, and the pattern observable on the surface represents the density distribution of the gas bubbles.[3,4] The helium atoms inside the metallic glass can be classified roughly as follows: (i) quasifree atoms which are able to take part in a diffusion type motion; (ii) quasibound atoms which are trapped in the amorphous structure; (ii) precipitated atoms, which are captured in gas bubbles. In a polycrystalline sample the traps are associated with the sites of crystal defects where the potential energy of a helium atom is much lower than the average value. In an amorphous sample the number of traps is expected to be orders of magnitude higher since it is "full" of crystal defects.

The distribution of the implanted helium atoms among the possible states enumerated above is governed by nonlinearly coupled differential equations expressing the laws of conservation of matter and energy. These equations may have a steady-state solution which is constant both in space and time. Such a steady-state solution, however, might become unstable at some values of the parameters characterizing the system. Beyond the instability point, the solution of the nonlinear system of equations is not necessarily homogeneous; it may exhibit a characteristic pattern.

Since the traps and the bubbles are more or less localized, the migration of the helium can be followed by considering the continuity equation only for the quasifree helium density $H(\vec{r},t)$:

$$\frac{\partial H}{\partial t}+\vec{\nabla}\cdot\vec{\mathcal{J}}_H=S_H\ , \tag{1}$$

where the current density and the quasifree helium source density are denoted by $\vec{\mathcal{J}}_H$ and S_H, respectively. When the density of the implanted atoms is already approaching the density of the atoms constituting the metallic glass the energy density of the sample will depend also on the distribution of the helium. In other words, after a given time of irradiation one must explicitly take into account the variation of the energy density $E(\vec{r},t)$ governed by the equation:

$$\frac{\partial E}{\partial t}+\vec{\nabla}\vec{\mathcal{J}}_E=S_E\ . \tag{2}$$

The source densities S_H and S_E contain loss and gain terms:

$$S_H=-a(H,E)H+b(H,E)E-C(H,E)H+h\ , \tag{3}$$

$$S_E=+a(H,E)H-b(H,E)E+d(H,E)H+e\ . \tag{4}$$

In both equations the first, second, and third terms correspond to the rate of trapping, detrapping, and capture, respectively. The implantation rate is given by h and e stands for the power density released by the implanted helium. It should be noted that the energy density E is measured in units of the binding energy of a helium atom in an average trap. The coefficients of the first term is assumed to have the following form:

$$a(H,E)=\alpha-\sigma HE\ , \tag{5}$$

where the effect of the saturation of the traps is expressed approximately by the second term. All the other coefficients are expected to be nonzero in the vicinity of the instability point, thus they can be represented by constants in this region:

$$b(H,E)=\beta\ , \tag{6}$$

$$c(H,E)=\gamma\ , \tag{7}$$

$$d(H,E)=\delta\ . \tag{8}$$

As the helium atoms rapidly slow down in the bulk of the material we may set $e=0$.

Equations (1) and (2) thus can be rewritten in the follownig forms:

$$\frac{\partial H}{\partial t}-D_H\Delta H=-\alpha H+\beta E+\sigma H^2E-\gamma H+h\ , \tag{9}$$

$$\frac{\partial E}{\partial t}-D_E\Delta E=+\alpha H-\beta E-\sigma H^2E+\delta H\ . \tag{10}$$

Here the current densities are expressed in terms of the densities with the help of Fick's law and the diffusion constants of the helium atoms and the energy are denoted by D_H and D_E, respectively. These nonlinearly coupled differential equations are expected to describe the migration of helium in metallic glasses.

It should be noted that this set of equations can be reduced to the well-known Brusselator introduced by Prigogine and others[5–7] for the study of self-organizing processes taking place in chemical reactions. If we drop some terms, namely if $\beta=0$, $\delta=0$ and if we choose α as the control parameter then system (9),(10) is identical with the Brusselator. The only real difference between our case and the Brusselator is the choice of the control parameter. There is only a single parameter in the experiment which is really under our control and this is the inplantation rate h, which may be varied freely by the particle intensity of the beam.

It can be checked that the extra terms $\beta E,\delta H$ if they are small, do not change the behavior qualitatively; therefore, we shall study the case with vanishing β and δ.

The steady-state solution is then given by

$$H_0=\frac{h}{\gamma},\quad E_0=\frac{\alpha\gamma}{\sigma h}\ . \tag{11}$$

The stability of this solution against infinitesimal perturbations can be studied by applying the standard method.[8,9] The characteristic frequency ω_k of the Fourier component of the deviations from the steady-state values associated with wave number $\vec{k}$ must fulfill the secular equation:

$$\omega_k^2+b_k\omega_k+c_k=0\ , \tag{12}$$

where

$$b_k=\gamma-\alpha+\sigma h^2/\gamma^2+k^2(D_H+D_E)\ , \tag{13}$$

$$C_k=\sigma h^2/\gamma+k^2[D_H\sigma h^2/\gamma^2+D_E(\gamma-\alpha)]+k^4D_HD_E\ . \tag{14}$$

The steady-state solution is stable if $\mathrm{Re}\omega_k$ for all values of k^2, because in this case the deviations decrease exponentially in time. At large values of the control parameter h both b_k and c_k are positive and, therefore, $\mathrm{Re}\omega_k$ is negative. Instability points, defined by $\mathrm{Re}\omega_{k_c}=0$, can be reached, in our case, by decreasing the control parameter, contrasted with the standard model. The instability may occur in two different ways.

(1) Hard-model instability. In this case $\mathrm{Im}\omega_k\neq 0$ and a limit cycle, a homogeneous time periodic solution becomes stable below the critical point. The instability is realized if $c_{k_c}>0$ and $b_{k_c}=0$. The relation between control parameter values and wave numbers satisfying $\mathrm{Re}\omega_k=0$ is

$$h_h(k^2)=\gamma\left[\frac{\alpha-\gamma-(D_H+D_E)k^2}{\sigma}\right]^{1/2}\ . \tag{15}$$

This function has its maximum at $k^2=0$ and its value is

$$\max h_h=\gamma\left[\frac{\alpha-\gamma}{\sigma}\right]^{1/2}\ . \tag{16}$$

(2) Soft-mode instability. In this case $\mathrm{Im}\omega_h=0$ and a steady state is reached with a spatial periodicity. The condition is met for $c_{k_c}=0$ and $b_{k_c}>0$. From the relation $\mathrm{Re}\omega_k=0$ one obtains

$$h_s(k^2)=\gamma\left[\frac{(\alpha-\gamma)D_Ek^2-D_HD_Ek^4}{\sigma(\gamma+D_Hk^2)}\right]^{1/2}\ . \tag{17}$$

The maximum of this function is found at

$$k_c^2=\gamma^{1/2}(\alpha^{1/2}-\gamma^{1/2})/D_H\ , \tag{18}$$

and its value is

$$h_c-\max h_s=\gamma(\alpha^{1/2}-\gamma^{1/2})\left[\frac{D_E}{\sigma D_H}\right]^{1/2}\ . \tag{19}$$

The kind of instability realized depends on the maximum values given by expressions (16) and (19). By decreasing the control parameter the greater maximum is reached first. Comparing expressions (16) and (19) we may conclude that a soft-mode instability takes place if

$$\frac{D_E}{D_H}>\frac{\alpha^{1/2}+\gamma^{1/2}}{\alpha^{1/2}-\gamma^{1/2}}\ . \tag{20}$$

In our case $D_E\gg D_H$ and α differs significantly from γ,

consequently a soft-mode instability is expected occurring at $h_c = \max h_s$ and having a critical wave number k_c specified by (19). Furthermore, it is implied by the above formulas that α should be greater than γ; that is, the probability of trapping should be higher than that of capturing. In the case of metallic glasses, where the number of traps is extremely high, this condition seems to be satisfied.

When estimating h_c and k_c we use the fact that the heat diffusion coefficient in metallic glasses is[10] $D_E \sim 10^{-6}$ $m^2\,s^{-1}$, while the diffusion coefficient of the helium in such materials is expected to be[11] $D_H \sim 10^{-17}$ $m^2 s^{-1}$. As the quasifree atoms may spend some hours before being trapped we set $\alpha \sim 10^{-3}$ s^{-1}. The probability of capturing is estimated by $\gamma \sim 10^{-4}$ s^{-1}. In the critical situation the quasifree helium density, $H_{0c} = h_c/\gamma$ should be of the same order of magnitude as that of a helium gas in normal state, i.e., $H_{0c} \sim 10^{27}$ m^{-3}. From here, by means of (19), $\sigma \sim 10^{-46}$ $m^6 s^{-1}$ follows. Using these values of the parameters we obtain k_c in the order of magnitude of 10^6 m^{-1} and $h_c \sim 10^{23}$ $m^{-3} s^{-1}$. Since the dose rate of experiments[1] was approximately 10^{17} $m^{-2} s^{-1}$ which is to be distributed in a band of about 1 μm depth, and the electron microscope pictures show patterns with roughly 1 μm wavelength, the estimations above agree qualitatively with the observed data. The experiments, however, do not indicate how far they are from the critical point. Therefore, it would be highly desirable to perform measurements at different beam intensities and to investigate at which value of the control parameter the pattern disappears. Experiments with ions of other noble gases such as neon or argon might help in clarifying the open questions.

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[1]F. Pászti, M. Fried, L. Pogány, A. Manuaba, G. Mezey, E. Kótai, I. Lovas, T. Lohner, and L. Pócs, preceding paper, Phys. Rev. B 28, 5675 (1983).
[2]U. Littmark and W. O. Hofer, J. Mater. Sci. 13, 2577 (1978).
[3]W. D. Wilson *et al.*, J. Nucl. Mater. 53, 154 (1974).
[4]N. M. Ghoniem and M. L. Takata, J. Nucl. Mater. 105, 276 (1982).
[5]I. Prigogine and R. Lefever, J. Chem. Phys. 48, 1965 (1968).
[6]R. Lefever, J. Chem. Phys. 48, 4977 (1968).
[7]R. Leferer and G. Nicolis, J. Theor. Biol. 30, 267 (1971).
[8]G. Nicolis and I. Prigogine, *Self Organization in Nonequilibrium Systems* (Wiley, New York, 1977).
[9]H. Haken, *Synergetics: An Introduction,* 2nd ed. (Springer, Berlin, 1978).
[10]O. Kubaschewski, in *Landolt-Börnstein, Zahlenwerte und Funktionen für Physik, Chemie, und Astronomie, Geophysik, Technik* (Springer, Berlin, 1968) Vol. II, Part 5b.
[11]V. Phillips, Kernforschungsanlage, Jülich Report No. JÜL-1679 (unpublished).