Journal of Engineering Physics and Thermophysics, Vol. 73, No. 4, 2000

ANALYSIS OF THE PROCESS OF ONSET AND GROWTH OF A LIQUID PHASE IN CONTACT OF DISSIMILAR CRYSTALS

A. A. Akhkubekov

UDC 548.0:053

Based on the concepts of percolation theory (leakage theory), an attempt is made to explain the initial stage of contact melting. Using the fluctuation-dissipation theorem, an equation is obtained for the kinetic and diffusion stages of the contact-melting process.

The first-order phase transition consisting in the formation of a liquid phase in contact of dissimilar solid substances is called contact melting. A necessary condition for the occurrence of contact melting is the presence of a minimum on the liquidus curve of the phase diagram of the contacting substances.

The process of contact melting has been studied in in a number of works [1-7] in which existing views on the process are analyzed in various classes of systems: metallic, organic, ionic, and cryohydratic. However, it must be noted that there is no unified and complete theory that can explain the onset and growth of a liquid volume in contact of dissimilar substances.

The number of theoretical and experimental investigations concerning the kinetics of the contact-melting process, especially in the initial stage, and the transition from a kinetic regime to a diffusion one is very limited [1, 2, 4, 7]. Use is made mainly of a diffusion approximation, which is incorrect in the initial stage. The works [8, 9] are devoted to investigations of the special features of this stage of growth of a new phase in interdiffusion; however the conclusions of these investigations are based only on a number of model assumptions.

In the present work we suggest a scheme of transition of the contact of two dissimilar crystals into a liquid that is based on leakage theory (percolation theory) and a derivation of the dependence of liquid-phase growth on time that is based on adoption of the Callen–Welton fluctuation-dissipation theorem [10, 11].

It is known that first-order phase transitions, which include contact melting, occur by fluctuation nucleation of a new phase in the volume of the initial phase, i.e., in the matrix. Here the process of formation and disappearance of these fluctuations is a dynamic process: at sites of the matrix where there is a sufficient concentration of foreign atoms, a new phase is formed locally that can disappear and appear at another site.

The contact-melting process is represented by us as follows. When two dissimilar metals come in contact, their interdiffusion occurs. "Foreign" atoms, penetrating into the lattice of the other metal, loosen it. When the concentration of "foreign" atoms near the contact zone reaches a certain threshold value (the so-called threshold of percolation or leakage [12-14]), a quasi-two-dimensional liquid interlayer with a thickness of the order of several interatomic distances first forms. Since there is a flow of foreign atoms into the solid phase, their concentration increases and correspondingly the number of heterophase fluctuation nuclei increases. The number of nuclei can become so large that they will begin to merge with each other, thus resulting in contact melting.

In contact melting diffusion occurs near the critical melting point. The regularities of this diffusion, as shown in [11], differ significantly from those of ordinary diffusion.

Let us consider this problem in more detail for a one-dimensional model of the process of contact melting.

Kabardino-Balkar State University, Nal'chik, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 73, No. 4, pp. 875-879, July–August, 2000. Original article submitted March 9, 2000.

1062-0125/00/7304-0863$25.00 ©2000 Kluwer Academic/Plenum Publishers

From the viewpoint of molecular-kinetic theory, diffusion of a "foreign" atom in a solvent lattice is a process of random movements. Let us select the origin of coordinates in the plane of initial contact of two cylindrical specimens and suppose that $x(t)$ is a random function of time that characterizes the position of a "foreign" atom relative to the origin of coordinates. We perform the spectral decomposition of this function:

$$x(t) = \int_{-\infty}^{\infty} x_{\omega} \exp(-i\omega t) \frac{d\omega}{2\pi}. \tag{1}$$

We find the average of the product of two functions taken at different instants of time:

$$K(t' - t) = \langle x(t)\, x(t') \rangle = \int\int \langle x_{\omega} x_{\omega'} \rangle \exp\left\{-i(\omega t + \omega' t')\right\} \frac{d\omega d\omega'}{4\pi^2}, \tag{2}$$

where the integrals are calculated, as in Eq. (1), between infinite limits. The angular brackets in Eq. (2) imply averaging over a Gibbs ensemble.

The quantity $K(t' - t)$ is called a correlation (paired) function and, by virtue of the homogeneity of time, depends only on the time difference $t' - t$. In order that the right-hand side of Eq. (2) also depend on $t' - t$, it is necessary to introduce the delta-function $\delta(\omega' + \omega)$ under the integral.

Consequently, it is required that

$$\langle x_{\omega} x_{\omega'} \rangle = (x^2)_{\omega}\, 2\pi\delta(\omega + \omega'). \tag{3}$$

Actually, this formula is the definition of the spectral density of the correlation function $(x^2)_{\omega}$.

Substituting Eq. (3) into Eq. (2) and eliminating the integration with respect to the variable ω' by means of the δ-function, we obtain

$$K(t) = \langle x(0)\, x(t) \rangle = \int_{-\infty}^{\infty} (x^2)_{\omega} \exp\left\{-i\omega t\right\} \frac{d\omega}{2\pi}. \tag{4}$$

In particular, the mean square of the fluctuating quantity is expressed as follows:

$$K(0) = \langle x^2(0) \rangle = \int_{-\infty}^{\infty} (x^2)_{\omega} \frac{d\omega}{2\pi}. \tag{5}$$

We consider the mean square of the displacement of an individual particle $\langle (x(t) - x(0))^2 \rangle$. Squaring and averaging, we obtain

$$\langle (x(t) - x(0))^2 \rangle = \langle x^2(t) \rangle - 2\langle x(t)\, x(0) \rangle + \langle x^2(0) \rangle.$$

By virtue of the homogeneity of time, $\langle x^2(t) \rangle\rangle = \langle x^2(0) \rangle = K(0)$. Thus, we have

$$\langle (x(t) - x(0))^2 \rangle = 2\int_{-\infty}^{\infty} (x^2)_{\omega} (1 - \exp(-i\omega t)) \frac{d\omega}{2\pi} = 4\int_{0}^{\infty} (x^2)_{\omega} (1 - \cos\omega t) \frac{d\omega}{2\pi}. \tag{6}$$

In transforming the integral, we take into account that the quantity $(x^2)_{\omega}$ is real.

For further analysis we should relate the spectral density of the correlation function $(x^2)_{\omega}$, which characterizes the coordinate fluctuations of the diffusing atoms, to the dissipative properties of the medium under an external action on it. To do this, we use the Callen–Welton fluctuation-dissipation theorem. As the dissipative characteristic of the medium, we take the mobility b_ω of the particles in exposure of the medium to the harmonic force

$$u_\omega(t) = \mathrm{Re}\left\{b_\omega F_0 \exp(i\omega t)\right\}. \tag{7}$$

The mobility entering Eq. (7) is a complex quantity: $b_\infty = b'_\omega + ib''_\omega$. According to the fluctuation-dissipation theorem, the spectral density $(x^2)_\omega$ is expressed in terms of the real part of the mobility [10, 11]:

$$(x^2)_\omega = \frac{2T}{\omega^2} b'_\omega. \tag{8}$$

Substituting Eq. (8) into Eq. (6), we obtain a formula for the mean square of the displacement [10]:

$$\langle (x(t) - x(0))^2 \rangle = 8T \int_0^\infty \frac{b'_\omega}{\omega^2} (1 - \cos \omega t) \frac{d\omega}{2\pi}. \tag{9}$$

We apply formula (9) to the analysis of the initial stage of the contact melting. It should be recalled that the mean value of the square of the displacement of an individual particle can also be interpreted for cooperative phenomena, i.e., for phenomena associated with the behavior of all the "foreign" atoms dissolved in the matrix. Since, upon reaching the leakage threshold, near the contact zone a liquid film is formed, in the vicinity of the critical melting point the left-hand side of formula (6) can be interpreted as the liquid-phase width. In [11] it was shown that there are no limitations on the use of the Callen–Welton theorem in the immediate vicinity of the critical point. Consequently, formula (6) should describe rather correctly both the initial stage of contact melting and the subsequent one.

Assuming that the real part of the mobility is independent of the frequency over the entire frequency range, i.e., $b'_\omega = b$, and integrating Eq. (6), we obtain

$$\langle (x(t) - x(0))^2 \rangle = 2bTt = 2Dt, \tag{10}$$

i.e., the usual (parabolic) diffusion law.

Next we assume that the liquid phase is characterized by a certain maximum frequency ω_m of the Debye type. In this case in integral (9) the upper limit can be replaced by ω_m, or, which is the same, the function b'_m can be considered to be different from zero only for $\omega < \omega_m$. From the aforesaid it follows that there are the times t for which the condition $\omega_m t \ll 1$ or $t \ll \omega_m^{-1}$ is fulfilled. In this case it is possible to expand the cosine into a Taylor series and restrict oneself to the first two terms of this series:

$$\cos \omega t \approx 1 - \frac{(\omega t)^2}{2}.$$

Substitution of this expansion into integral (9) gives the dependence of the width of the liquid-phase layer in the vicinity of the critical point:

$$\langle (x(t) - x(0))^2 \rangle = \frac{4T\omega_m \bar{b}'}{\pi} t^2, \tag{11}$$

where $\bar{b}' = \frac{1}{\omega_m} \int_0^{\omega_m} b'_\omega \, d\omega$ is the mean value of the real part of the coefficient of mobility over the range of frequencies under consideration.

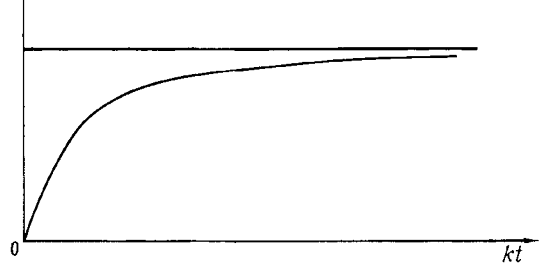

Fig. 1. Time dependence of the diffusion coefficient in contact melting.

Using the positive value of the square root of the right-hand side of Eq. (11), we obtain a linear law of growth of the liquid-phase width $y(t) = \sqrt{\langle (x(t) - x(0))^2 \rangle} = t\sqrt{4T\omega_m \bar{b}'/\pi}$ with a velocity $v = dy/dt = \sqrt{4T\omega_m \bar{b}'/\pi}$.

Thus, with rather natural assumptions formula (9) corresponds to the usual (parabolic) law of diffusion away from the critical point and a linear law of liquid-phase growth near the critical point (in the initial stage of contact melting).

Formula (9) can be written in the following form:

$$\langle (x(t) - x(0))^2 \rangle = 2D(t)\, t\,, \tag{12}$$

where the time-dependent diffusion coefficient has the form

$$D(t) = \frac{4T}{t} \int_0^\infty \frac{b'_\omega}{\omega^2} (1 - \cos \omega t) \frac{d\omega}{2\pi}\,. \tag{13}$$

To describe satisfactorily experimental data on the contact melting, the graph of the function $D(t)$ must be similar to that of the arctangent function (see Fig. 1), i.e.,

$$D(t) = D_0 \arctan (kt)\,, \tag{14}$$

where arctan (kt) implies that the principal branch of the multivalued function is considered.

A similar dependence of the width of the contact liquid interlayer on time for the Cu–Mg and Cu–Ag systems was established experimentally in [7].

Consequently, for small times the diffusion coefficient increases linearly with time, and for rather large times it tends to a certain asymptotic value D_0.

Taking into account that for small t the function arctan $(kt) \cong kt$ and substituting formula (14) into Eq. (12), we obtain

$$\langle (x(t) - x(0))^2 \rangle = 2D_0 k t^2\,. \tag{15}$$

A comparison of the right-hand side of formula (15) with that of Eq. (11) gives

$$D_0 k = \frac{2T\omega_m \bar{b}'}{\pi}\,, \tag{16}$$

whence we have $D_0 = 2T\bar{b}'$ and $k = \omega_m/\pi$.

Thus, proceeding from fundamental concepts of the thermodynamic theory of fluctuations, it is possible to describe both the initial (kinetic) and subsequent stages of contact melting. To do this, one should select a spectrum of mobilities b'_ω such that the right-hand side of formula (13) would give the arctangent function (14) or a function that is similar in its properties to the arc tangent and reaches its asymptotic value rather rapidly.

Here a linear law of growth of the liquid-interlayer width is obtained within the framework of much more natural propositions of the thermodynamic theory of fluctuations and percolation theory than reasoning based on model assumptions.

NOTATION

t and t', different instants of time; $(x^2)_\omega$, spectral density of the correlation function $x(t)$; b_ω, particle mobility in exposure of the medium to a harmonic force; $u_\omega(t)$, particle velocity in exposure to the external force $F(t) = F_0 \exp(i\omega t)$; Re, real part of the complex number; ω_m, maximum frequency; b'_ω and b''_ω, coefficients of the real and imaginary parts of the complex number, respectively; ω, cyclic frequency; T, period of oscillations; i, imaginary part of the complex number $(\sqrt{-1})$; D, interdiffusion coefficient.

REFERENCES

1. P. A. Savintsev, V. E. Avericheva, V. Ya. Zlenko, and A. V. Vyatkina, *Izv. Tomsk. Politekh. Inst.*, **105**, 222-226 (1960).
2. N. N. Nilova, G. M. Bartenev, V. T. Borisov, and Yu. E. Matveev, *Dokl. Akad. Nauk SSSR*, **180**, No. 2, 394-397 (1968).
3. A. A. Akhkubekov, *Kinetics of Contact Melting of Low-Melting Metal Systems*, Candidate's Dissertation in Physical-Mathematical Sciences, Nal'chik (1976).
4. A. A. Shebzukhov, *Nature and Certain Regularities of Contact Melting*, Candidate's Dissertation in Physical-Mathematical Sciences, Nal'chik (1971).
5. S. P. Savintsev, *Kinetics of Liquid-Phase Growth in Contact Melting of Binary Systems,* Candidate's Dissertation in Physical-Mathematical Sciences, Nal'chik (1986).
6. P. F. Zil'berman, *Contact Melting of Ionic Crystals*, Doctoral's Dissertation in Physical-Mathematical Sciences, Tomsk (1993).
7. I. P. Dobrovol'skii, B. A. Kartashkin, A. I. Polyakov, and M. Kh. Shorshorov, *Fiz. Khim. Obrab. Mater.*, No. 2, 36-39 (1972).
8. Ya. E. Geguzin, *Diffusion Zone* [in Russian], Moscow (1979).
9. V. B. Sapozhnikov and M. G. Gol'diner, *Poverkhnost'. Fiz., Khim., Mekh.*, No. 10, 86-89 (1984).
10. L. D. Landau and E. M. Lifshits, *Statistical Physics* [in Russian], Pt. 1, Moscow (1976).
11. M. A. Leontovich, *Zh. Eksp. Teor. Fiz.*, **49**, Issue 5, 1624-1630 (1965).
12. B. I. Shklovskii and A. L. Efros, *Uspekhi Fiz. Nauk*, **117**, Issue 3, 401-435 (1975).
13. I. A. Chaban, *Fiz. Tverd. Tela*, **20**, Issue 5, 1497-1504 (1978).
14. B. I. Shklovskii and A. L. Efros, *Electronic Properties of Alloyed Semiconductors* [in Russian], Moscow (1979).