

Contact Melting of Metals Explained via the Theory of Quasi-Liquid Layer

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Abstract: It has been shown that the contact melting rate for metals is determined by the fact that at least one of them has a quasi-liquid layer on the surface. As a result, the diffusion of metal atoms occurs in the liquid phase, and not in the solid phase, which determines the characteristic contact melting time (seconds and minutes).

Keywords: premelting; mass transfer; diffusion

1. Introduction

The processes underlying the appearance and growth of the intermediate phases that occur during the alloying of various metals to obtain intermetallic compounds and heterogeneous mixtures have not yet been fully studied. Moreover, of particular theoretical and practical interest is the clarification of the conditions required for mass transfer to occur at the boundaries of coexisting phases.

Contact melting is a phenomenon in which two metals that are initially in a solid state begin to melt upon contact. The reason for this melting is that metal atoms diffuse into each other; as a result, the melting temperature of such a solution decreases. This phenomenon is characteristic of metals with a eutectic phase, in which the melting point of the mixture is lower than the melting point of the individual pure substances.

The contact melting rate has yet to be fully elucidated. According to experimental data [1–7], contact melting of samples occurs on a timescale of seconds. However, in explaining this characteristic time, a contradiction arises. Indeed, in order for metal atoms to diffuse into each other, both metals must already be liquid, since the diffusion rate in a solid is negligible.

2. Results and Discussion

The statement of this problem has the following form (Figure 1):

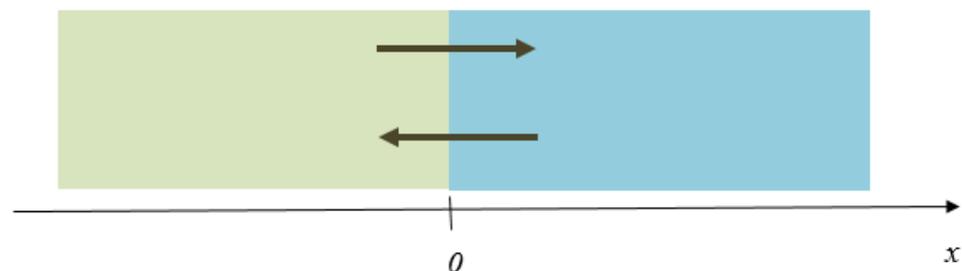


Figure 1. Mutual diffusion of atoms of two substances.

Diffusion equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad (1)$$



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Initial and boundary conditions for a homogeneous case (liquid or solid):

$$c|_{x \rightarrow \infty} = 1, \quad c|_{x \rightarrow -\infty} = 0, \quad c|_{t=0} = \eta(x), \tag{2}$$

where $\eta(x)$ is a Heaviside step function.

The solution of the equation, taking into account the initial and boundary conditions, has the form:

$$c(x, t) = \frac{1}{2} \left(1 + \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right) \tag{3}$$

where

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\zeta^2) d\zeta \tag{4}$$

The chemical potential of an atom in this case can be written as:

$$\mu = \mu_0 + kT \ln c, \tag{5}$$

where μ_0 does not depend on the concentration of substances. In this formulation of the problem, we neglect the chemical reactions between the components, as well as various cross effects.

However, until diffusion occurs, the metals cannot become liquid, because, being initially in a pure state, they are both solid. According to Einstein's formula, the mean square displacement can be written as:

$$\langle x^2 \rangle^{1/2} = \sqrt{2Dt} \tag{6}$$

where D is the coefficient of mutual diffusion for two metals, and t is the time. For liquid metals, diffusion coefficients are approximately $10^{-9} \text{ m}^2/\text{s}$; however, for solid metals, diffusion coefficients are approximately $10^{-20} \text{ m}^2/\text{s}$. It is easy to see that for typical experimental times of the order of a minute, solids will not have time to diffuse, and the root mean square displacement will be smaller than the size of an atom.

Thus, contact melting of metals should occur slowly, i.e., it should be determined by diffusion in a solid. Existing contact melting models (see, for example, refs. [8–10]) cannot explain this contradiction.

To solve this problem, we will take into account that at temperatures close to the melting temperature a quasi-liquid layer (film) is located on the surface of a solid. Such quasi-liquid layers have been repeatedly recorded experimentally for different substances (see, for example, refs. [11–14]). When calculating the volumetric thermodynamic characteristics of a substance, such a layer can be neglected; however, for some cases in which the surface condition is important, its presence is crucial.

The temperature at which a quasi-liquid layer (premelting) is formed can be approximately estimated by taking into account the fact that an atom has a smaller number of neighbors on the surface of a solid compared with the atoms inside a sample (Figure 2).

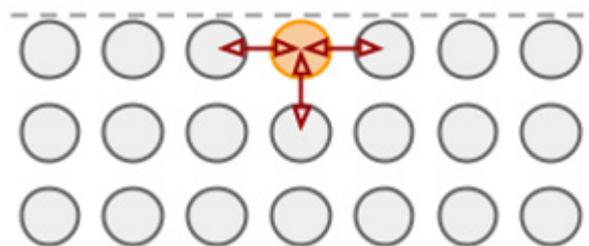


Figure 2. Atoms on the surface of a metal.

Let $V(x)$ be the potential energy of the interaction of the selected atom with one of its nearest neighbors. The potential energy for the interaction with N atoms is equal to $NV(x)$.

Each atom residing deep in the solid has six nearest neighbors, and an atom lying on the surface has five nearest neighbors. Therefore, the energies of this atom in such potential wells will be related by a 5/6 ratio. The energy required for melting should be proportional to the depth of the potential well; therefore, the temperature at which the quasi-liquid layer (premelting) appears in the first approximation is 5/6 of the melting temperature in the volume:

$$T_{ql} \approx \frac{5}{6} T_m. \quad (7)$$

In this regard, we consider contact melting experiments for some pairs of metals (Pb-Sn [6], Sn-In [7], Tl-Bi, Tl-Sn [2,7]), and show that when such metals contact each other, at least one of them has a quasi-liquid film on their surface. According to [2,7], contact melting was performed in a thermostat. The samples were cylinders with a diameter of ~3 mm and a length of ~2 cm. The contact surfaces of the samples were polished. From the moment of contact between the samples, the diffusion time begins. The growth of the liquid layer was observed visually using a microscope.

From Table 1 we can conclude that when the samples come into contact with each other, at least one of them (or both) has a quasi-liquid film on its surface. That is, upon contact between these metals, dissolution occurs of the solid metal in this quasi-liquid layer (the dissolution of solid metals in liquid is characteristic of most of the listed metals). As a result of the enrichment of the quasi-liquid layer with the second component, the melting temperature of the next metal layer decreases (for the same reasons as the decrease in the volume), i.e., it also becomes a liquid.

Table 1. Experimental contact melting temperature and quasi-liquid layer temperature for some metals.

Sample Materials Used in the Experiment and Their Melting Points, K [2,6,7]	Experimental Contact Melting Temperature, K	Maximum Pre-Melting Temperature (First Metal)	Minimum Pre-Melting Temperature (Second Metal)	Where is the Quasi-Liquid Film Located?
Pb (601)–Sn (505)	463	501	421	Sn
Sn (505)–In (430)	400	421	358	In
Tl (577)–Bi (545)	483	480	454	Tl, Bi
Tl (577)–Sn (505)	455	480	421	Sn

Note that the proposed model is simplified because it does not take into account the real structure of the crystal lattice of both contacting substances. An atom on a material's surface may have more or less than the usual 5 neighbors. However, the model is in qualitative agreement with the experiment and explains the rate of contact melting.

A similar phenomenon is observed upon contact between ice (snow) and salt. In this case, a quasi-liquid film is formed on the surface of the snow at temperatures above $-45\text{ }^{\circ}\text{C}$.

3. Conclusions

Thus, the reason for such rapid contact melting of metals is that a quasi-liquid layer is located on the surface of one of the metals. When the metals come into contact with each other, the atoms in the second metal dissolve sufficiently quickly, as a result of which the next layer becomes liquid (in the case of a phase diagram with a eutectic). Following the motion of the layer, diffusion also occurs. Thus, the contact melting rate is limited by the rate of mutual diffusion in liquid metals, although both metals are in a solid state before contact.

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