

Nitrogen diffusion mechanism in the R_2Fe_{17} lattice

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In this report, a diffusion analysis has been extended to a lattice containing two interstitial sites, and the results obtained are used to understand: (1) the formation of a nitrated/un-nitrated N configuration for intermediate N content and (2) the abnormally small (apparent) diffusion frequency factor, both of which characterize the newly developed R_2Fe_{17} nitrides. It turns out that the diffusion mechanism for N atoms in the R_2Fe_{17} lattice is a chemical reaction diffusion rather than a free-diffusion process. © 1995 American Institute of Physics.

Nitrogen or carbon insertion into rare-earth intermetallics, such as R_2Fe_{17} (hereafter referred to as the 2:17 phase), has recently attracted considerable attention.¹⁻³ The understanding of the reaction mechanism is of importance as it is related to the homogeneity and stability of the magnetic properties for these materials. It was previously supposed that N atoms diffuse from the surface into the interior of a sample particle through a free-diffusion process, which results in a continuous solid solution distribution (CSSD) profile of N atoms in the particle during the process.⁴ However, recent experimental results have demonstrated that the N distribution does not follow the CSSD pattern; instead, a partially nitrated particle consists of a fully nitrated region and an un-nitrated region.^{5,6} Furthermore, the measured value of diffusion frequency factor, D_0 , for N diffusion in R_2Fe_{17} was of four orders of magnitude smaller than that for free-nitrogen diffusion in transition metals.^{4,7} The steplike nitrated/un-nitrated N distribution and the abnormally small diffusion frequency factor cannot be understood in the framework of the free N diffusion mechanism. In this letter, we present a description in which the N uptake is a chemical reaction diffusion process.

It was observed in studying the thermal stability of the 2:17 nitrides that only a small amount of the absorbed N atoms were released from the sample particles upon heating to temperatures above 400 °C, while most of the N atoms, which occupied the octahedral interstitial sites, were not.^{5,8} These experiments reveal that there are two types of N atoms in the lattice. The octahedral site N atoms which cannot be evacuated from the particle are either immobilized or are characterized by a very slow diffusion; while those N atoms which can be evacuated are in other sites and are characterized by rapid diffusion. (For a discussion of the possible sites, see Ref. 9.) The existence of gas atoms with different diffusion rates makes the diffusion problem more complicated than a free-diffusion process. Here, we consider the diffusion problem of gas atoms in a lattice containing two different interstitial sites in a general way and then apply the results to the nitrogenation process for the 2:17 phase.

Consider a spherical sample particle of radius R surrounded by a gas phase of atoms (i.e., H_2, N_2, C); and in the sample particle there are two different (f - and t -) types of interstitial sites which can accommodate these atoms. The gas atoms in the two types of sites are referred to as f - and t -type atoms, respectively. For generality, we assume that both the t - and f -type atoms are mobile but the t -type atoms have a smaller diffusion constant than that for the f -type atoms. Let $c_f(r, t)$ and $c_t(r, t)$ be the concentrations of the f - and t -type gas atoms, respectively, at a distance r from the center of the particle and at a time t . $c_{f0} = c_f(R, t)$ and $c_{t0} = c_t(R, t)$ are the corresponding concentrations at the surface of the particle whose radius is R . Also, these are the “equilibrium” values for $c_f(r, t)$ and $c_t(r, t)$, i.e., the concentrations that result throughout the particles after a very long time. It is assumed that the crystal structure and reaction kinetics are such that $c_{f0} \leq c_{t0}$. In the case where these two types of atoms diffuse independently, i.e., there is no exchange of atoms between the two types of sites, the diffusion of each type of atom is described by Fick’s laws

$$\mathbf{J}_f(r, t) = -D_f \nabla c_f(r, t), \quad \frac{\partial c_f(r, t)}{\partial t} = -\nabla \cdot \mathbf{J}_f(r, t), \quad (1)$$

and

$$\mathbf{J}_t(r, t) = -D_t \nabla c_t(r, t), \quad \frac{\partial c_t(r, t)}{\partial t} = -\nabla \cdot \mathbf{J}_t(r, t), \quad (2)$$

where $\mathbf{J}_f(r, t)$ and $\mathbf{J}_t(r, t)$ are the radial atomic current fluxes across a unit area for the f - and t -type gas atoms, respectively, D_f and D_t are the corresponding diffusion constants. The solutions of Eqs. (1) and (2) result in a CSSD pattern of gas atoms radially throughout particle.¹⁰ Figure 1(a) illustrates the radial dependence of the concentrations in the two types of sites at a given time. For the situation illustrated, the time is such that the f -type sites can be almost completely occupied with the t -type sites remaining essentially empty. As shown in Fig. 1(b), the total gas atom distribution profile is basically a CSSD pattern of the f -type atoms except in the surface region.

In addition to the migration of gas atoms within each type of site, there can also exist an exchange between the f -

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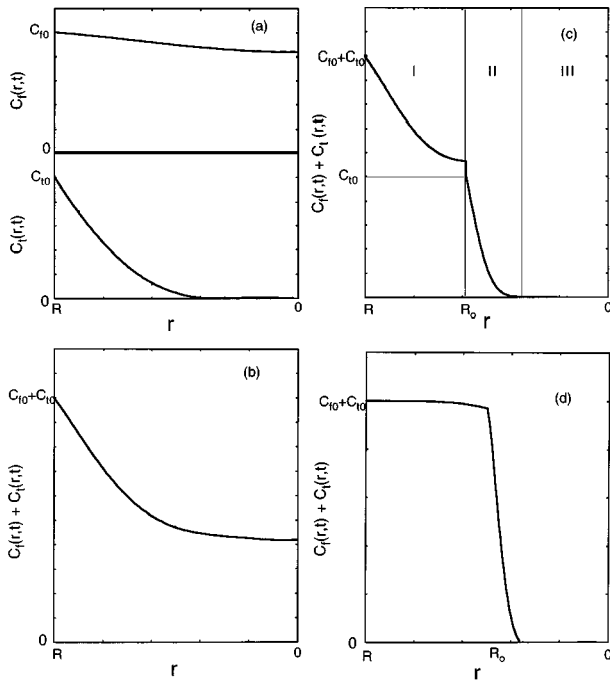


FIG. 1. Radial distribution profiles of the gas atom concentration $c(r, t)$, at a given time: (a) for f -type atoms and t -type atoms independently; (b) total atomic concentration distribution profile when there is no atomic transfer between the two sites; (c) total atomic concentration distribution profile when an atomic transfer is possible from the f -sites to t -sites. [It consists of three regions: in region I, the t -type sites are almost completely filled; in region II, the concentration distribution profile decreases very sharply to zero; in region III, the sites are essentially empty; in (a)–(c) it is assumed that $c_{t0} = c_{f0}$ and $D_t = (1/10)D_f$]; (d) total atomic concentration distribution profile under the assumption that $c_{t0} \gg c_{f0}$ and $D_t \rightarrow 0$.

and t -type sites for individual atoms. Because of the lower diffusivity for the t -type atoms, the probability for a gas atom to change from f - to t -type is greater than that from t - to f -type and thus, one observes for the most part only a transfer of gas atoms from f - to t -type sites. The modified diffusion equations for the two types of atoms in the particle can be written as

$$\mathbf{J}_f(r, t) = -D_f \nabla c_f(r, t), \quad (3)$$

$$\frac{\partial c_f(r, t)}{\partial t} = -\nabla \cdot \mathbf{J}_f(r, t) - \frac{\partial c_{ft}(r, t)}{\partial t}, \quad (4)$$

$$\mathbf{J}_t(r, t) = -D_t \nabla c_t(r, t), \quad (5)$$

$$\frac{\partial c_t(r, t)}{\partial t} = -\nabla \cdot \mathbf{J}_t(r, t) + \frac{\partial c_{ft}(r, t)}{\partial t}, \quad (6)$$

where the term $[\partial c_{ft}(r, t)/\partial t]$ on the right-hand side of Eqs. (4) and (6) represents the rate for the gas atoms changing from f - to t -type, which is dependent on the strength of gas-lattice bonding. In this case, the fast migrating (f -type) atoms fill the slow activation (t -type) sites, resulting in the occupancy of the t -type sites near the surface of a particle to its equilibrium concentration c_{t0} . This makes the gas atom distribution deviate from the CSSD pattern. Figure 1(c) illustrates a typical distribution profile. The particle can be separated into three regions. In region I (ideally it is the outer shell of the particle with a radial thickness of $R - R_0$), the

t -type sites have been completely filled for $R_0 \leq r \leq R$, mostly through the transfer of f -type atoms. Region II is a transition region in which the filling of both types of sites is developing. In region III, there are no gas atoms in either site.

In region I, we have

$$\mathbf{J}_f(r, t) \approx 0, \quad \frac{\partial c_t(r, t)}{\partial t} \approx 0, \quad \frac{\partial c_{ft}(r, t)}{\partial t} \approx 0, \quad (7)$$

and

$$\frac{\partial c_f(r, t)}{\partial t} = D_f \nabla^2 c_f(r, t). \quad (8)$$

For region II, Eqs. (3)–(6) can be combined as

$$\frac{\partial c_f(r, t)}{\partial t} + \frac{\partial c_t(r, t)}{\partial t} = D_f \nabla^2 c_f(r, t) + D_t \nabla^2 c_t(r, t). \quad (9)$$

Although the term $[\partial c_{ft}(r, t)/\partial t]$ does not occur explicitly in Eq. (9), this equation is based on the existence of this term. The transfer of gas atoms between the two types of sites introduces a correlation between the concentration of the two types of atoms and Eq. (9) represents such a relationship. When the diffusivity of the t -type atoms is rather small compared with that of the f -type atoms and therefore the filling of the t -sites is mainly due to the transfer of the f -type atoms, the ratio of $c_t(r, t)$ to $c_f(r, t)$ can be approximately taken as a constant.¹¹ We then can write

$$c_f(r, t) \approx \frac{c_t(r, t)}{k}, \quad (10)$$

and, therefore

$$\frac{\partial c_t(r, t)}{\partial t} = \frac{D_t k + D_f}{1 + k} \nabla^2 c_t(r, t) = D \nabla^2 c_t(r, t). \quad (11)$$

The same equation is also obtained for $c_f(r, t)$. In Eq. (11),

$$D = \frac{D_t k + D_f}{1 + k}, \quad (12)$$

is the “effective” diffusion constant. At the boundary R_0 between regions I and II, the t -type sites in region II are completely filled. With the evolution of diffusion, R_0 varies from R to 0. For atomic diffusion which is dealt with in this letter, the diffusion rate is much smaller than the jump rate of individual atoms. At each step of the process, the gas atom distribution is well-established corresponding to the R_0 at that time. Therefore, when solving these equations for each region, R_0 can be approximately taken as a constant.

In region II, the solution of Eq. (11) for $c_t(r, t)$ [along with the solution of the same equation for $c_f(r, t)$] yields

$$c(r, t) = c_0 \left(1 - \frac{2R_0}{\pi r} \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m} \times \sin \frac{m \pi r}{R_0} e^{-m^2 \pi^2 D t / R_0^2} \right), \quad (13)$$

where $c(r, t) = c_t(r, t) + c_f(r, t)$ and c_0 is the concentration of the gas atoms at the boundary

$$c_0 = c_{t0} + c_f(R_0), \quad (14)$$

where $c_f(R_0)$ is the concentration of the f -type atoms at R_0 . Again, $c_f(R_0, t)$ has a "fixed" value as R_0 moves slowly toward the interior of the sample particle.

The solution of Eq. (8) gives the distribution of the f -type atoms in region I, that is

$$c_f(r, t) = c_{f0} \left(1 - \frac{2(R-R_0)}{\pi(r-R_0)} \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{m} \times \sin \frac{m\pi(r-R_0)}{(R-R_0)} e^{-m^2\pi^2 D_f t / (R-R_0)^2} \right). \quad (15)$$

Because $D < D_f$, a more rapidly decreasing gas atom distribution profile is expected in region II than that in region I. The larger the differences in equilibrium concentration and in diffusion constant between the two types of gas atoms, the sharper the decline of the profile in the transition region. Such a sharp decline leaves region III empty of gas atoms. The principal feature for this case is that the gas atoms are concentrated in the surface region of the particle, leaving the interior region of the particle essentially empty. Therefore, it is concluded that as long as there are different interstitial sites corresponding to different activation energies for atomic migration and there is a transfer of gas atoms between these sites, the diffusion process is characterized by a steplike gas atom distribution profile.

In the extreme case where $c_{t0} \gg c_{f0}$ and $D_t \rightarrow 0$, the atomic concentration distribution profile in region I is actually flat. In the region II, Eqs. (3)–(6) become

$$\mathbf{J}_f(r, t) = -D_f \nabla c_f(r, t), \quad \mathbf{J}_t(r, t) \approx 0 \quad (16)$$

and

$$\frac{\partial c_f(r, t)}{\partial t} = -\nabla \cdot \mathbf{J}_f(r, t) - \frac{\partial c_t(r, t)}{\partial t}. \quad (17)$$

Thus, we obtain

$$\frac{\partial c_t(r, t)}{\partial t} = D \nabla^2 c_t(r, t), \quad \text{with } D = \frac{D_f}{1+k}. \quad (18)$$

This equation was previously derived by Crank.¹¹ The solution of Eq. (18) is similar to Eq. (13); however, due to a very large value of k in this case and, hence, a much reduced effective diffusion constant, a more pronounced steplike gas atom distribution profile exists through the transition region. This is shown in Fig. 1(d). The condition $D_t \rightarrow 0$ corresponds to a chemical reaction under which the diffusing atoms are trapped and remain immobilized or produce a new compound.

Nitrogen diffusion in the R_2Fe_{17} lattice is very much like the extreme case discussed above. The N atoms at the octa-

hedral interstitial sites correspond to the t -type atoms, and those N atoms occupying other sites to the f -type atoms. Since the diffusion constant is exponentially dependent on the activation energy, a slight difference in the gas-lattice bonding between these two sites will lead to a significant difference in their diffusion constants. Each individual N atom behaves as an f -type atom when it initially enters the lattice. It diffuses for a certain period of time and then, when occupying an octahedral site, becomes immobilized. The complete occupancy of the octahedral sites near the surface of a particle makes the mobile (f -type) N atoms which follow, migrate a longer distance before falling into available octahedral sites. This keeps the nitrogenation process continuing. This explains the formation of the two phase (nitrided/unnitrided) configuration of N distribution during the nitrogenation process.

The activation energy, E_a and frequency factor D_0 are determined by measuring the temperature dependence of diffusion constant. From the above discussion of the nitrogenation process

$$D = \frac{D_0}{1+k} e^{-E_a/k_B T}. \quad (19)$$

This result clearly shows that what is deduced from the D vs T curve for N diffusion in the R_2Fe_{17} lattice is not D_0 , but $D_0/(1+k)$. This explains why the previously obtained (apparent) frequency factor is much smaller than that for free N diffusion in metals. Thus, the two major aspects of N diffusion in the R_2Fe_{17} lattice can be well understood based on the diffusion mechanism proposed above. In this regard, nitrogenation of the 2:17 phase is more like a chemical reaction diffusion, rather than a free-N diffusion process.

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