Interrelationship between the Diffusion Behaviour and the Phase Transformation Characteristics

By G. P. Tiwari* and Ken-ichi Hirano**

It has been observed that the metals which exhibit anomalous diffusion behaviour are all allotropic in nature. A hypothesis to rationalise this interrelationship between the diffusion behaviour and the phase transformation characteristics is discussed here. This relationship arises from the correspondence between the saddle-point configuration of the diffusing atom and the structure of an allotrope of the matrix. Thus, in the embryonic form, the saddle-point configuration represents the structure of the matrix after the phase transformation. Several characteristics of the anomalous diffusion behaviour can be explained with the help of the present suggestion. Further, an estimate of the diffusion rates for several metals made on the basis yields satisfactory agreement with the experimental results.

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I. Introduction

Several transition\(^1\)\(^-\)\(^3\), lanthanide\(^4\)\(^-\)\(^5\) and actinide\(^6\)\(^-\)\(^8\) elements exhibit anomalies in their diffusion behaviour. These anomalies comprise the small values of the activation energies as well as the frequency factors\(^9\). In some cases, a curved Arrhenius plot for diffusivity is also seen\(^2\)\(^-\)\(^3\). The anomalous metals also have significantly higher diffusion rates at the corresponding fractions of the melting temperatures\(^9\). An important additional characteristic of the metals showing anomalous diffusion behaviour is that they are all allotropic in nature\(^10\)\(^-\)\(^12\). This relationship between the diffusion behaviour and the phase transition characteristics is underscored by the correlations of the entropy of fusion with either of these properties\(^13\)\(^-\)\(^15\). It has been shown that the metals having the entropy of fusion less than 6.7 J mol\(^-1\) K\(^-1\) are allotropic in nature\(^13\). Again, the metals having the entropy of fusion less than 6.7 J mol\(^-1\) K\(^-1\) are found to exhibit anomalous diffusion characteristics\(^14\). Through their identical dependence upon the entropy of fusion, the diffusion behaviour and the phase transformation characteristics are intimately related to each other.

The object of the present paper is to discuss a hypothesis to rationalise the interrelationship between the diffusion behaviour and the phase transformation characteristics. This rationalization is achieved by assuming that the configuration of the diffusing atom at the saddle-point corresponds to the structure of an allotrope of the matrix. On this basis, the diffusion characteristics such as the violation of the correlation between the diffusion and the melting parameters, small activation energies and relatively higher diffusion rates at the corresponding fractions of the melting-point can be explained. A calculation of the diffusion rates is also made on the basis of the present suggestion and a satisfactory agreement with the experimental data is obtained.

The model for diffusion discussed here is somewhat similar to the one proposed by Sanchez and DeFontaine\(^11\)\(^-\)\(^12\). It was suggested by these authors that in the case of anomalous diffusion, the saddle-point atoms form an embryo of some phase (\(\alpha\)-phase in the case of \(\beta\)-Zr and Ti–Mn alloys). The diffusion jump is postulated to occur through the atomic exchange within this embryo. A generalisation of the same viewpoint is presented here. Specifically, it is suggested that the saddle-point configuration for normal as well as anomalous metals adopts the configuration of the phase which the matrix acquires after phase transition. In this way, it is possible to discuss the diffusion process in normal as well as

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anomalous metals with the help of a single hypothesis.

II. Relationship between the Diffusion Behaviour and the Phase Transition Characteristics

The parameters of the diffusion process in metals follow the simple relationships with the melting parameters. The activation energy for vacancy diffusion, \( Q (J/mol^{-1}) \), is related to the melting-point and the latent heat of fusion\(^{(16)}\) as follows:

\[
Q = 159 T_m, \tag{1}
\]
\[
Q = 16.5 L_m, \tag{2}
\]

where \( T_m(K) \) and \( L_m(J/mol^{-1}) \) represent the melting temperature and the latent heat of fusion respectively. \( T_m \) and \( L_m \) are similarly related to the formation energy of the vacancy also\(^{(17)}(18)\). Further, the activation volume for diffusion bears the same relation to the activation energy as that exists between the volume change associated with melting and the latent heat of fusion\(^{(19)}\). However, these relationships embodying the correlations between the process of diffusion and melting breakdown for metals exhibiting the anomalies in their diffusion behaviour\(^{(1)(9)}\). As mentioned in the previous section, the anomalous metals are allotropic. Melting as well as the solid-state transformations occurring in metals belong to the category of the first order transformations. In either case, the transformation is accompanied by a fixed entropy change. In the case of metals showing normal diffusion behaviour and obeying the correlations between the diffusion parameters and melting mentioned above, it has been proposed that the region around the vacancy structurally resembles a liquid and the process of diffusion involves the atomic exchange or shuffling of atoms in this liquid-like region\(^{(16)}(20)\). An analogous statement for the anomalous metals can be made by stating that the region around the vacancy, during the process of diffusion, acquires the structure adopted by the matrix after the phase transformation and the process of diffusion is equivalent to the atomic exchange in this region. Thus during the diffusion in an anomalous metal, the saddle-point configuration is structurally related to an allotrope of the matrix. In case there are several allotropic modifications of the matrix, the saddle-point configuration will be based on the phase requiring the least amount of excess free energy.

It is important to emphasize here that the presence of a vacancy itself does not lead to the formation of a saddle-point configuration related to either a liquid phase or an allotrope of the matrix. A definite amount of the thermal fluctuation is necessary before the region around the vacancy can acquire diffusive configuration.

On the basis of the preceding discussion, a diffusive jump is postulated to occur through the following steps:

(a) The formation of a vacancy in one of the nearest neighbour positions.
(b) The formation of a saddle-point configuration structurally related to either the liquid phase or an allotrope of the matrix.
(c) Vancancy migration within the saddle-point configuration to affect the positional change of the diffusing atom.
(d) The disintegration of the saddle-point complex through thermal fluctuation.

III. Estimation of the Diffusion Rates

According to the model outlined above, the diffusion rates will be controlled by the energy required to carry out the steps (a) through (c). The expression for the diffusion coefficient derived on the basis of the absolute reaction rate theory\(^{(21)}\) can be easily adopted here. The diffusion coefficient is expressed as

\[
D = f a^2 v \exp (-\Delta G/RT), \tag{3}
\]

where \( D \) is the diffusion coefficient, \( f \) the correlation factor, \( a \) the lattice parameter, \( v \) the Debye frequency, and \( \Delta G \) the energy required to carry out the steps (a) to (c).

Evaluation of \( \Delta G \)

\( G \) can be expressed as the sum of the three contributions mentioned above; namely the energy required for vacancy formation \( (\Delta G_f) \), the energy required for the formation of the saddle-point configuration \( (\Delta G_s) \) and the
energy required for the atomic exchange within the embryo formed at the saddle-point ($\Delta G_m$). Hence

$$\Delta G = \Delta G_f + \Delta G_v + \Delta G_m.$$  \hspace{1cm} (4)

(a) $\Delta G_f$ can be expressed as

$$\Delta G_f = \Delta H_f - T\Delta S_f,$$  \hspace{1cm} (5)

$\Delta H_f$ and $\Delta S_f$ being the enthalpy and the entropy of vacancy formation respectively. The experimental values of $\Delta S_f$ for a few fcc metals have been determined by Simmons and Balluffi\textsuperscript{22}\textsuperscript{25}. These values lie in the range of $\Delta S_f/R = 1 \sim 2.4$. Theoretical estimates of $\Delta S_f/R$ for fcc as well as bcc metals yield a value of nearly 1.5\textsuperscript{26}\textsuperscript{27}. Hence, for common fcc as well as bcc metals, $\Delta S_f/R = 1.5$ is taken here. In the case of anomalous metals, neither experimental nor theoretical values are available. However, in these cases, very low values of diffusional entropy—which are sometimes even negative—are obtained. Hence for these cases, it seems reasonable to take $\Delta S_f/R = 0$. The effect of $\Delta S_f/R$ on the calculated values of the diffusion coefficient is discussed later.

(b) The energy required for the formation of an embryo of the phase formed as a result of the transformation, $\Delta G_m$, is taken equal to the difference in the free energy of the matrix and the phase resulting after the transformation. This is schematically shown in Fig. 1 depicting a hypothetical two phase system ($\alpha$ and $\beta$). At any temperature $T$, the excess free energy for the formation of $\beta$-structure is obtained by extrapolation and is equal to $PQ$. Hence $\Delta G_v = PQ$ (Fig. 1). The values of this parameter have been graphically evaluated from the published data on the thermodynamic properties\textsuperscript{28}.

(c) With reference to the Fig. 1, if $\beta$ is a liquid phase, the diffusion jump will be affected by the atomic movement within a liquid-like region constituted by the saddle-point configuration. This step is equivalent to the process of diffusion in a liquid phase. According to Sherby and Simnad\textsuperscript{29} the energy required for this process is equal to $RKT_m$. $K$ is a constant equal to three for all metals. Hence, when the saddle-point configuration is structurally analogous to a liquid phase, we may write

$$\Delta G = \Delta H_f + \Delta G_v + RKT_m.$$  \hspace{1cm} (6)

Thus from (a), (b) and (c) above, $\Delta G$ can be written as

$$\Delta G = \Delta H_f + \Delta G_v + RKT_m.$$  \hspace{1cm} (7)

In case $\beta$ is not a liquid phase, such as will be the case for diffusion in $\alpha$-Zr, $\alpha$-Ti etc., the diffusive step will be accomplished within an embryo of $\beta$-Zr, $\beta$-Ti etc. A calculation of the energy required for atomic exchange within such a configuration has been made by Sanchez and DeFontaine\textsuperscript{12} for diffusion in $\beta$-Zr. This has not been attempted here. The quantitative estimate of the diffusion rates is, therefore, limited to the cases where the saddle-point configuration adopts the structure of a liquid phase.

**IV. Comparison with the Experimental Results**

The data used in the calculation of the diffusion rates are listed in the Table 1. The comparison of the calculated and the experimental values is shown in the Figs. 2\textsuperscript{~}6. The
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(2) $\Delta H_f$=0.5×(Activation Energy for Self-Diffusion).
Fig. 2 Log $D$ vs $1/T$ plots for self-diffusion in aluminium and copper.

Fig. 3 Log $D$ vs $1/T$ plot for self-diffusion in $\delta$-iron.

Fig. 4 Log $D$ vs $1/T$ plot for self-diffusion in molybdenum.

Fig. 5 Log $D$ vs $1/T$ plot for self-diffusion in $\varepsilon$-plutonium.

Fig. 6 Log $D$ vs $1/T$ plots for self-diffusion in $\beta$-zirconium, $\gamma$-uranium and $\beta$-titanium.

Measured values are usually accurate to within 10–15% whereas the precision of the calculated values depends on the uncertainty in the knowledge of $\Delta G$. It is estimated that the uncertainty in $\Delta G$ does not exceed 20%. This will give rise to the uncertainty of nearly one order of magnitude in the calculated values of the diffusion coefficient. Except for copper, the discrepancies between the calculated and the experimental values lie within this limit. Hence we conclude that the degree of agreement obtained lends support to the model proposed here. It is particularly gratifying to note that satisfactory agreement exists for normal as well as anomalous metals.
The effect of the variation in $\Delta S_f$ on the calculated values of the diffusion coefficient is shown in Fig. 2-4 for Cu, Al, $\delta$-Fe and Mo. The diffusion coefficients are calculated for $\Delta S_f/R = 0$ and 1.5. In the case of Cu and Al, the agreement is worsened by taking $\Delta S_f/R = 1.5$ whereas it improves in the case of $\delta$-Fe and Mo. The statistical nature of agreement will, therefore, be perhaps not significantly influenced by the neglect of $\Delta S_f$ for anomalous metals.

V. Characteristics of the Anomalous Diffusion Behaviour

In the present section, the diffusion model discussed here will be used to explain certain observed characteristics of the diffusion behaviour in anomalous metals. Referring to the Fig. 1 and considering the diffusion in the $\alpha$-phase at any temperature, $T$, the saddle-point configuration will be akin to the structure of the $\beta$-phase. In the case of normal metals, $\beta$ is a liquid phase and the diffusion parameters will bear correlations to the parameters of the liquid phase. For an anomalous metal like $\alpha$-Zr or $\alpha$-Ti, $\beta$ is a crystalline phase. Hence the diffusion parameters will not be related to the parameters of the liquid phase and will show deviations from the correlations followed by the normal metals.

In Fig. 7, a free energy vs temperature plot similar to the Fig. 1 is shown. Here $\alpha$ and $\beta$ represent crystalline phases and $L$ is a liquid phase. Considering again diffusion in the $\alpha$-phase, the excess free energies required for the formation of the saddle-point configuration related structurally to either $\beta$ or $L$ are $PQ$ and $PR$ respectively. As $PQ < PR$, the structure of the $\beta$-phase will be adopted. Consequently, the free energy associated with the diffusion process ($PQ$) will be smaller than expected on the basis of melting-point correlations ($PR$).

The diffusion in the high temperature phase of a polymorphic metal is different from the low temperature phase in the sense that the saddle-point configuration is related to the liquid phase. However, even in this case, the deviations from the correlations referred to earlier are observed and the relative diffusion rates at the corresponding fractions of the melting-point are higher. This can be explained with the help of Fig. 8 where $\alpha$ and $\beta$ have the same meaning as in Fig. 7 and $\alpha'$ represents
a single phase system having the same melting-point as the system consisting of $\alpha$ and $\beta$. If we now consider diffusion at any temperature $T$, the saddle-point configuration will be based on the liquid phase for $\alpha'$ as well as $\beta$. The excess free energies for diffusion are $XZ$ and $YZ$ respectively. Since $YZ < XZ$, it follows that the free energy of diffusion in the $\beta$-phase will be smaller than that in the $\alpha'$-phase despite the fact that both have the identical melting-point. Thus the effect of phase transformation is to reduce the energy required for diffusion in the low- as well as the high temperature phases of a polymorphic system. Further, as the energy associated with the diffusion process is smaller than the value derived from the correlations with the liquid phase parameters, the allotropic metal will, therefore, exhibit higher diffusion rates at the corresponding fractions of the melting-point.

The diffusion in $\beta$-Zr and $\beta$-Ti presents a special case because the temperature range of diffusion measurements is rather large. It extends over nearly 1170 K. As a result, for diffusion in the low $\beta$-range, it perhaps energetically more favourable for saddle-point atoms to adopt a configuration similar to the $\alpha$-phase instead of the liquid phase. This is because the large extrapolation required in the latter case makes it energetically less favourable. In the high $\beta$-range, the saddle-point configuration will adopt the structure of the liquid phase as an atomic arrangement similar to the $\alpha$-phase will become less favourable for an identical reason (Fig. 8). Hence, in $\beta$-Zr and $\beta$-Ti, we have a situation where the nature of saddle-point configuration changes with the temperature. The origin of curvature in the Arrhenius plots for these cases may be attributed to this feature.

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