

01 Jan 1982

Anomalous Diffusion Of Carbon In A 70/30 Iron-nickel Alloy

L. R. Chapman

D. A. Powers

Manfred Wuttig

Missouri University of Science and Technology

Follow this and additional works at: https://scholarsmine.mst.edu/matsci_eng_facwork



Part of the [Metallurgy Commons](#)

Recommended Citation

L. R. Chapman et al., "Anomalous Diffusion Of Carbon In A 70/30 Iron-nickel Alloy," *Scripta Metallurgica*, vol. 16, no. 4, pp. 437 - 440, Elsevier, Jan 1982.

The definitive version is available at [https://doi.org/10.1016/0036-9748\(82\)90168-5](https://doi.org/10.1016/0036-9748(82)90168-5)

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Materials Science and Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

ANOMALOUS DIFFUSION OF CARBON IN A 70/30 IRON-NICKEL ALLOY†

L.R. Chapman,* D.A. Powers,** and Manfred Wuttig
 Department of Metallurgical Engineering
 University of Missouri-Rolla
 Rolla, Missouri 65401

(Received January 29, 1982)

(Revised February 11, 1982)

Diffusion is called anomalous if the Arrhenius plot is strongly curved, the apparent pre-exponential factor D_0 falls outside the limits $5 \text{ mm}^2\text{s}^{-1} \leq D_0 \leq 500 \text{ mm}^2\text{s}^{-1}$ and if the apparent activation energy of diffusion Q differs substantially from the empirical rule $Q \approx 140 T_m \text{ Jmol}^{-1}$ where T_m is the temperature of melting in degrees Kelvin (1). The latter two criteria apply to anomalous self- or substitutional diffusion. Many theories have been suggested to explain the anomalies (2). Currently, there exists evidence that the diffusion anomaly in bcc metals and alloys displaying a low-temperature phase transformation is connected with this phase transformation. This is particularly true for the ω -transformation occurring in Ti and Ti base alloys (3). Here, the close similarity of the atomic displacements in the activated state and the transformation displacements suggest that the apparent decrease of the activation energy of diffusion upon approaching the ω -transformation from above is caused by the increasing "softness" of the parent phase (4,5). A like, albeit less pronounced, similarity occurs for the case of interstitial diffusion in fcc alloys which transform martensitically. Therefore, we measured the carbon diffusivity in an fcc Fe-Ni alloy over a wide temperature range. The pronounced anomaly which has been found is reported in this letter.

The Fe-Ni alloy was prepared from 99.9% pure starting materials by induction melting under argon. The resulting alloy contained 29.9 wt% Ni, as determined by chemical analysis. Cylindrical samples were carburized as described previously (6). The carbon content of all samples was $0.2 \text{ wt}\% \pm 20\%$.

Low temperature diffusivities were determined by disaccommodation and anelastic techniques. All apparatus used has been previously described (7-9). Measuring diffusivities in this fashion requires that the defect and its reorientation mode giving rise to both effects are known. Magnetic studies of Fe-Ni-C alloys have shown that a [100] tetragonal substitutional-interstitial pair does contribute significantly to the defect-induced magnetic anisotropy (10). This suggests that the diffusivity and the most probable relaxation time τ_m are related as (11)

$$D = a^2/18\tau_m \quad [1]$$

where a is the lattice parameter. It has also been shown that other defect configurations should be considered as well (10). It must be remembered, though, that many of the reorientation modes of the defects of lesser symmetry are frozen in as only the carbon is mobile at the temperatures and times pertaining to this study. The carbon jumps are all of the $[110]a/(2)^{1/2}$ type and the maximum differences in the relaxation times of the possible modes are then a factor of three (11). The effect of this uncertainty on the conclusion to be made will be discussed below.

In Fig. 1, all data collected in this study, as well as decarburization data (12), are presented. The data points labeled "decarburization" have been linearly interpolated between those available for an Fe-23 wt% Ni and an Fe-40 wt% Ni alloy (12). Judging from the composition dependence of the carbon diffusivity in Fe-Ni alloys in this composition range (12), a linear interpolation yields data which are about as accurate as the original ones. The data points

†Work supported by the National Science Foundation

*Now with Union Carbide Corporation, Nuclear Division, Oak Ridge, Tennessee

**Now with U.S. Nuclear Regulatory Commission, Washington, D.C.

resulting from our experiments were evaluated according to relationship [1] where τ_m was evaluated using a Gaussian distribution of the relaxation times. The width of the Gaussian, β , was the same as that observed before, $\beta = 2.1$ (6).

By comparing the broken and solid lines in Fig. 1, it can be seen that the diffusion of carbon in this Fe-29.9 wt% Ni alloy is distinctly anomalous. The anomaly remains if the uncertainty of the diffusivities mentioned above is considered. On the scale of Fig. 1, this uncertainty is slightly larger than the vertical size of the data points. The anomaly can also not be caused by the difference of the higher carbon content of the present samples, 0.2 wt%, as compared to the ones used in reference 12, 0.1 wt%. Assuming that the carbon diffusivity in this Fe-Ni alloy depends on the carbon concentration like it does in γ -Fe, the correction to be made would not be larger than 10% (13,14). This, again, is smaller than the size of the data points in Fig. 1.

In order to interpret the temperature dependence of the carbon diffusivity shown in Fig. 1, we refer to an expression derived for the case of anomalous substitutional diffusion in alloys (4), which eventually transform to the ω -phase at a low temperature,

$$D = D_0 \exp[-Q/RT(1 - \Delta H_m T_0 / QT)], \tag{2}$$

where ΔH_m is the enthalpy of motion of the vacancy. For interstitial diffusion, $\Delta H_m = Q$ and Eq. 2 reduces to

$$D = D_0 \exp[-Q/RT(1 - T_0/T)]. \tag{3}$$

Eq. 3 is strictly applicable to a transformation-controlled diffusion anomaly if the displacements of the atoms in the activated state are the same as the ones becoming "soft" as the transformation temperature is approached. Interstitial diffusion in fcc metals is a lattice-activated process (15). Two components of the displacements of the host metal ions which activate the diffusion process are shown in Fig. 2, left. They correspond to the antisymmetrical component of the

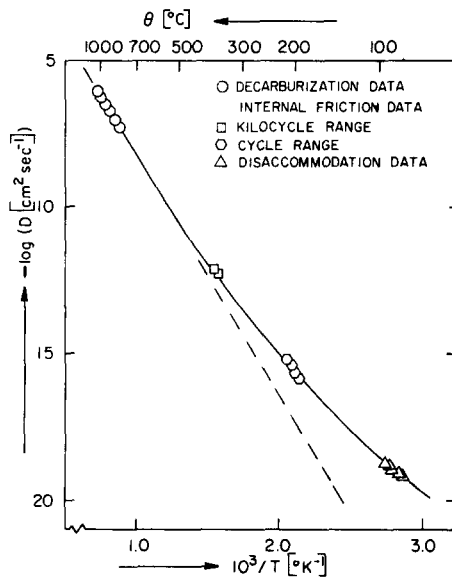
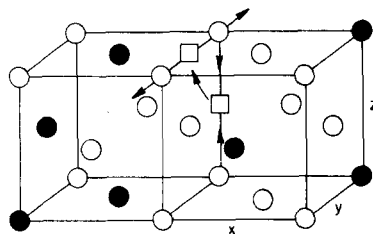
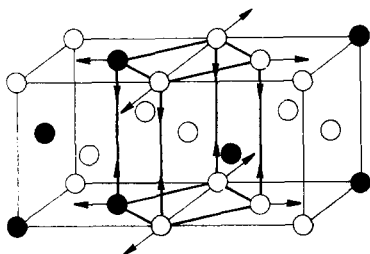


FIG. 1

The diffusivity of carbon in an Fe-29.9 wt% Ni alloy. The solid line represents Eq. 4. The dashed line demonstrates the anomaly.



- Fe-atom
- Ni-atom
- interstitial equilibrium site

FIG. 2

Left, directions of components of antisymmetric lattice displacement co-activating interstitial diffusion. Right, direction of lattice displacements leading to the martensitically transformed lattice.

isotropic self-trapping strain which controls a portion of the total activation energy of interstitial diffusion. In Fig. 2, right, the host ion displacements leading to the martensitic transformation are shown. A comparison of the two displacement patterns in Fig. 2, right and left, shows that they are identical. Eq. 3 may thus be used to formally interpret the present data.

An alternate explanation of the present diffusion anomaly might be sought in terms of the temperature dependence of the appropriate elastic constants (16). Such an explanation is, however, not possible here as the elastic constants $\frac{1}{2}(C_{11} - C_{12})$ and C_{44} go through a maximum at 350°C (17), whereas the anomaly develops in a monotonous fashion as the temperature is lowered.

It thus appears reasonable to fit Eq. 3 to the data. The result is that the carbon diffusivity in the fcc Fe-29.9 wt% Ni alloy is given by

$$D = 370 \exp[188 \text{ kJmol}^{-1}/RT(1 - 105 \text{ K}/T)] \text{mm}^2 \text{s}^{-1} \quad [4]$$

The preexponential factor, $370 \text{ mm}^2 \text{ s}^{-1}$, appears rather large. It might contain an appreciable entropy contribution. The activation energy of 188 kJmol^{-1} appears equally high, at least high compared to the values in the 120's commonly accepted for interstitial diffusion in fcc Fe-Ni alloys. The value of the characteristic temperature, $T_0 = 105 \text{ K}$, is interesting. The martensite start temperature of the alloy under investigation containing 0.2 wt% C is approximately 190 K (18). The difference of the two temperatures can be interpreted to reflect the "softening" of the antisymmetrical lattice mode only. In terms of the theory of lattice-activated interstitial diffusion, the activation energy of diffusion is given as the sum of the contributions stemming from the antisymmetrical and symmetrical modes,

$$Q = E_s + E_a. \quad [5]$$

If, in keeping with the correspondence shown in Fig. 2, it is assumed that only the antisymmetrical mode "softens" upon approaching the martensitic transformation temperature, T_0 , E_a may be written as

$$E_a(T) = E_a(T - T_0)/T \quad [6]$$

and the analogue to Eq. 3 becomes

$$D = D_0 \exp\{-(E_s + E_a)/RT[1 - E_a T_0/(E_a + E_s)T]\}. \quad [7]$$

The ratio of the two temperatures, 105 K/190 K, would then represent the ratio $E_a/(E_a + E_s)$. This would indicate that the contributions of the antisymmetrical and symmetrical contributions approximately equal each other in this alloy; not an unreasonable result.

The problem with the above interpretation is that no premartensitic softening has been observed to commence at temperatures as high as a few hundred degrees above T_0 (19). This dilemma can be resolved, however. It must be recalled that softening is not a prerequisite for the martensitic transformation to occur (20). Only amplitudes of vibration of the atoms in the parent phase just above a critical value and certain conditions concerning nn and nnn interactions are conceptually required. It may thus be argued that the observed diffusion anomaly occurs because the amplitude of vibration in the vicinity of the carbon interstitial exceeds this critical amplitude. Alternatively, the local amplitudes of vibration could be so large that heterofluctuations occur in the vicinity of the interstitial. Both arguments are really the same. They differ only in the assumption of the magnitude of the displacements occurring during diffusion.

In summary, the experimentally observed low temperature diffusion anomaly of carbon in Fe-29.9 wt% Ni is thought to represent the effect of local heterophase fluctuations on the antisymmetrical part of the activation energy of interstitial diffusion. This interpretation can be verified by investigating interstitial diffusion in Fe- X_1 - X_2 -C (X_1 and X_2 stand for substitutional elements like Ni or Mn) displaying a wealth of martensitic transformations.

The authors wish to thank the U.S. Bureau of Mines-Rolla for providing them with the Fe-Ni alloy. Thanks are also due Dr. D. Day who was kind enough to permit us to use his internal friction apparatus.

References

1. A.D. LeClaire, Diffusion in Body Centered Cubic Metals, ASM, Metals Park, Ohio, p. 3, 1965.
2. See, for instance, N.L. Peterson, Comments Solid State Physics 8, 93 (1978) for a more recent review.
3. J.M. Sanchez, Phil. Mag. 43, 1407 (1981).
4. J.M. Sanchez and D. de Fontaine, Phys. Rev. Letters 35, 227 (1977).

5. J.M. Sanches and D. de Fontaine, *Acta Met.* 26, 1083 (1978).
6. J. Keiser and M. Wuttig, *Phys. Rev.* B5, 985 (1972).
7. M. Wuttig and H.K. Birnbaum, *J. Phys. Chem. Solids* 27, 225 (1966).
8. J.E. Shelby, Jr. and D.E. Day, *J. Am. Cer. Soc.* 52, 169 (1969).
9. S.W. Taylor and D.E. Day, *Phys. Chem. Glasses* 11, 89 (1970).
10. E. Adler and C. Radloff, *J. Appl. Phys.* 40 1526 (1969).
11. A.S. Nowick and B.S. Berry, *Anelastic Relaxation in Crystalline Solids*, Academic Press, New York (1972).
12. R.P. Smith, *Trans. Met. Soc. AIME* 236 1224 (1966).
13. R.P. Smith, *Acta Met.* 1, 578 (1953).
14. D.C. Parris and Rex McLellan, *Acta Met.* 24, 523 (1976).
15. C.P. Flynn and A.M. Stoneham, *Phys. Rev.* B1, 3966 (1970).
16. H.I. Aaronson and P.G. Shewmon, *Acta Met.* 15, 358 (1967).
17. G. Hausch and H. Warlimont, *Acta Met.* 21, 401 (1973).
18. I. Ya. Georgieva and O.P. Maksimova, *Fiz. Met. Metalloved.* 32, 364 (1971).
19. R. Comstock and Cohen, personal communication.
20. T. Suzuki, *Met. Trans.* 12A, 709 (1981)