

Clustering of N and C in Fe*

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The clustering of N and C in solid solution in b.c.c. Fe has been deduced from anelastic measurements made in the vicinity of -25°C . For alloys of composition about .0005 atom fraction N or C, most interstitial atoms are singly dissolved in the lattice, but about 5% of the interstitial present is thought to be bound into pairs and triplets (combined). Pairs of N are estimated to have a binding energy of about 1,500 cal/mole, pairs of C about 1,900 cal/mole. (A positive binding energy means energy is required to dissociate the pair.) Triplets of N are estimated to have a binding energy of about 5,000 cal/mole, and triplets of C about 6,000 cal/mole. Large differences which exist between the characteristics of C pairs in b.c.c. Fe and those of C pairs in f.c.c. Ni are discussed.

Introduction

Ideal atom arrangement in solid solutions places atoms randomly on lattice sites; the chance of a site being occupied by an atom of a given type depends only on the stoichiometry of the alloy. Under such placement of atoms in dilute alloys, the chance of occurrence of pairs or other clusters of higher order is slight. If, however, a positive binding energy exists between the solute atoms, the fraction of atoms bound into clusters may be an appreciable fraction of the total, at least in certain temperature regions. This paper reports a study of such clustering in alloys of Fe with small amounts of either N or C. Besides the presence of single N or C atoms, the presence of pairs and triplets has been deduced from the data.

The method of investigation utilized the anelasticity of solid solutions of Fe with these impurities. The presence of single N or C atoms was detected as a result of the Snoek effect. Pairs (and apparently some clusters of higher order) also exhibit stress-induced ordering, so their presence could be detected as well. This detection is possible because the mean-time-of-stay of pairs in a given spatial configuration is different from that of single atoms, so their anelastic effects are separable from those of singles. Likewise, the effects of clusters of larger size

may be separated from both those of singles and pairs, so they too can be detected. Therefore, proper anelastic measurement on a solid solution containing clusters of several sizes yields a spectrum of discrete relaxation effects, from which the nature and relative number of clusters of various sizes can be deduced. The details of how this can be done will become clear in the discussion of the results.

Experimental Methods

The experiment was a measurement of the relaxation of stress at constant strain. The specimen, a helix of Fe wire containing small additions of N or C, was stretched to a given strain (elastic) and held fixed in that position. As the N or C atoms diffused about, the stress necessary to maintain the strain decreased. Measurement of the stress was made as a function of time. A typical measurement is given in Fig. 1 for a specimen of Fe containing about 0.18% N; the measurement was made with the specimen at -24.3°C . The details of the method are described by Tichelaar and Lazarus.¹⁾ Further details are described by Keefer.²⁾

Specimens were made from Fe from two sources. One lot of material was a zone-refined iron obtained from Battelle Memorial Institute; the other, a zone-refined iron obtained from the research laboratory of the General Motors Corporation. The specimens were helices of diameter about 1" made from about 1 meter of wire 0.020" in diameter. They were decarburized and strain annealed

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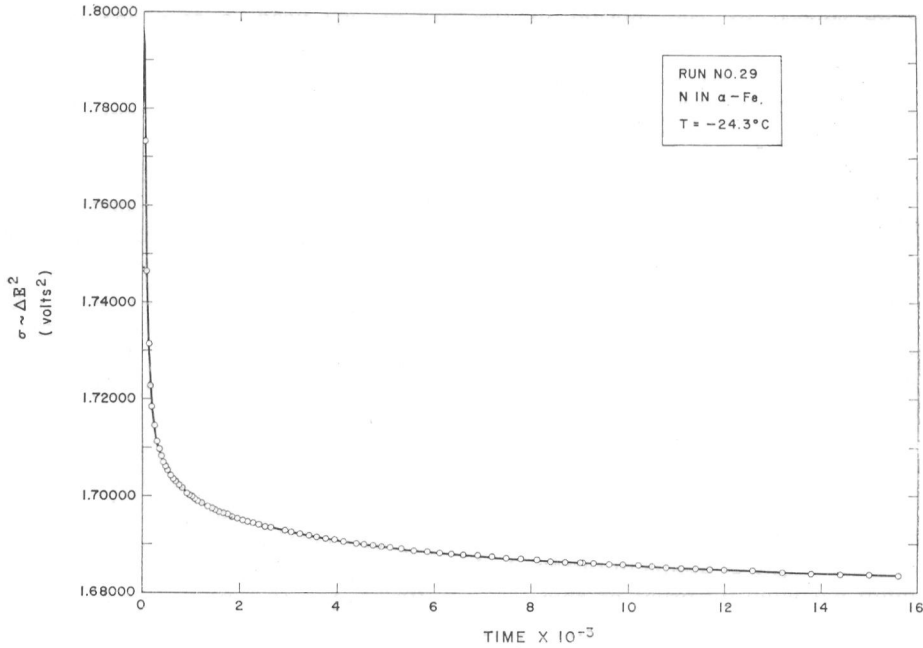


Fig. 1. Relaxation of stress at constant strain for a specimen containing 0.18% N at -24.3°C . The stress, plotted as the ordinate, was measured electrically and is the square of an appropriate voltage in the circuit used. The abscissa is the time measured after the stress was first applied. Further data not shown were obtained out to about 30,000 seconds.

to produce large grains, after which they were either carburized or nitrided before measurements.

Results and Discussion

Many measurements of the type displayed in Fig. 1 were made for relaxation of N in Fe. Analysis of all these data showed that more than one relaxation process was present, since no experimental curve could be fit with a single exponential. Resolution of the data into its constituent relaxations (assumed to be discrete) was made by graphical methods. The several relaxation times are far enough apart so that the method of analysis used in decomposing composite radioactive decay curves could be used. This "subtraction-of-tails" method showed that four separate relaxations were present in strengths sufficient to be detectable. The relaxation times and relaxation strengths for these four were determined for those sets of data for which the data were extensive enough to warrant use of the technique. The relaxation times fell into four distinct groups; the traces of the lines fitted to the relaxation times are presented in Fig. 2. The next paragraphs

describe the interpretation of these times in terms of models.

The relaxation process labeled 4 is pro-

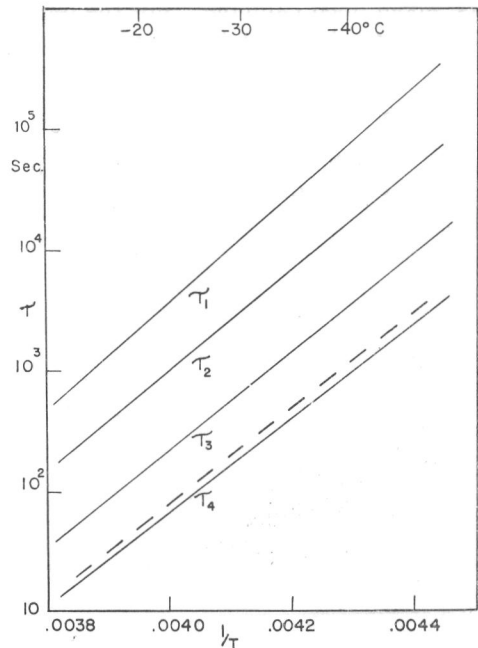


Fig. 2. Traces of lines fitted to the relaxation times determined for N in Fe.

posed to be caused by the motion in the lattice of single N atoms. It is therefore the Snoek relaxation. At the temperatures of measurement for the compositions 0.03 at. per cent to 0.18 at. per cent, three-quarters or more of the N present is dispersed singly. The dotted line in the figure is that for τ reported in the literature for diffusion of N in Fe.

Relaxation 3 has not been identified by us though it comprises from a few per cent of the total relaxation in some specimens to about 15% in some others. Its relaxation strength has the wrong temperature dependence for it to be associated with a positive binding energy; therefore, we do not believe it to be a result of a motion of a cluster. The possibility exists that this relaxation is associated with single N atoms in tetrahedral sites, though we have no proof of this.

The relaxation associated with time τ_2 we believe to be caused by the reorientation under stress of pairs of N atoms. The strength of the relaxation depends approximately on the square of the number of singles (at constant temperature) and decreases with increasing temperature (at constant composition). This is in accord with the thermodynamics of pairs bound by a positive binding energy. The binding energy is estimated to be about 1500 cal/mole. For the temperatures (about -25°C) and compositions (about

0.1 at. %) used, a few per cent of the N atoms are bound in pairs.

The reorientation under external stress of triplets of N atoms is believed to cause the relaxation designated by τ_1 in Fig. 2. Its strength varies as the cube of the N content and decreases with increasing temperature. The binding energy is about 5,000 cal/mole. For our experimental conditions, a few per cent of the N is bound in these triplets.

The measurement of stress relaxation of Fe containing C has been limited to a single determination to this time. It was a measurement for an alloy of about 0.08 at. % C at -24.3°C . This curve also decomposed into 4 measurable processes. The relaxation times for these 4 are indicated in Fig. 3 where they are labeled in order of decreasing relaxation times.

The relaxation 3 was strongest (about 70% of the total) and its relaxation time compares favorably with that calculated for τ from reported values for C diffusion (solid line). Therefore we believe that this relaxation is the Snoek effect of single C atoms in Fe.

By analogy with the assignments made above for N, we propose that relaxation 2 is a result of pair reorientation and that 1 is a result of triplet reorientation. They each account for from 5% to 10% of the C (precise calculation is not possible since we do not know the specific damping capacity of C or N in these clusters). The binding energies we estimate to be 1,900 cal/mole for pairs and 6,000 cal/mole for triplets. The approximate relaxation time given by Bosman, Brommer, Eykelenboom, Schinkel and Rathenau³⁾ for the relaxation of pairs is indicated by the open circle. Their measurement was made by magnetic methods. So far, we have been unable to establish a definite model to account for process number 4.

Carbon Pairs in b.c.c. and f.c.c. Lattices

If the above description of pairs of C atoms in b.c.c. Fe is correct, then the following things may be said about them:

1. The motional energy of a pair in Fe is probably about 22,000 to 23,000 cal/mole, slightly higher than that of motion of single C atoms. This motional energy may contain some of the energy of dissociation since any

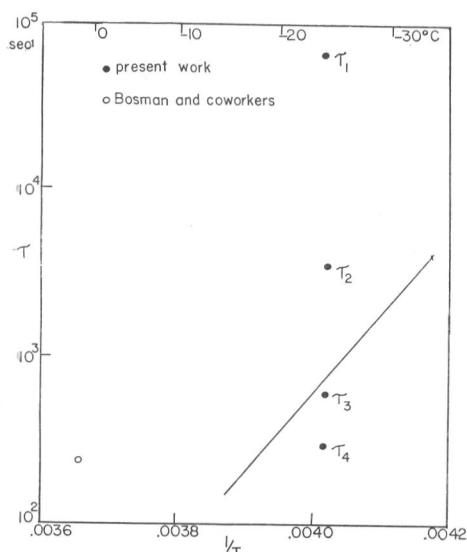


Fig. 3. Relaxation times calculated for C clusters in Fe.

single jump of either atom of the pair does not restore the pair. This is true since equivalent sites are not nearest neighbor sites.

2. Their binding energies are so low that for solutions of order 0.05 atomic per cent, only a few per cent of the atoms are associated into pairs at room temperature. At higher temperatures the pairs are even fewer, so perturbing effects of pairs on thermodynamic studies at high temperatures will only be seen with extreme care.

3. If the results of Powers and Doyle on oxygen pairs in Ta are valid for pairs of C (and N) in b.c.c. Fe, then the local strain about the pairs in the b.c.c. lattice is high. That this is true is seen by the fact that the specific damping capacity of the pairs is apparently high.

For C in pure γ -iron no similar measurements can be made since the temperature of existence of the γ -phase is too high. However, a damping peak in f.c.c. Ni containing C has been reported and assumed to be caused by motion of pairs of atoms.⁴⁾ The motional energy for these pairs is $37,000 \pm 5000$ cal/mole. This value is in the same range as that reported for C diffusion in Ni, which has been variously reported as 32,000 cal/mole (about that of C diffusion in γ -Fe) and 41,000 cal/mole. It is to be noted

that the closest pairs in the f.c.c. lattice can tumble through the lattice without dissociation.

Large alloy concentrations are needed to produce damping effects of sufficient size to be detected—concentrations of the order of several per cent. An alloy of 2 per cent C in Ni will produce a damping peak due to pairs (at 290°C) of the same order of size as that the pairs in an alloy of 0.1 per cent C in Fe will produce (at 60°C). Of course, the higher temperature needed for measurement of the peak in Ni results in more dissociation of pairs; nevertheless this is not the sole reason for the small effect in Ni. Clearly either the binding energy of C pairs in Ni must be small or the specific relaxation strength (and hence the elastic distortion about the pair) must be low. Perhaps both of these is true.

References

- 1 G. Tichelaar and D. Lazarus: *Phys. Rev.* **113** (1959) 438.
- 2 D. Keefer: Thesis, University of Illinois (1962).
- 3 A. Bosman, P. Brommer, L. Eykelboom, C. Schinkel and G. Rathenau: *Acta Met.* **8** (1960) 728.
- 4 C. Tsien: *Scientific Sinica* **10** (1961) 930; T. Kê, C. Tsien and K. Misek: *ibid.* **4** (1955) 519.

DISCUSSION

Ujjiye, N.: On behalf of those who are working on steel, those who deal with "iron" should make it a point to state the previous heat treatment as well as chemical composition.

Wert, C.: I agree that information about the chemical composition and heat treatment of the specimens is important. The basic material used for most of the investigation was zone-refined iron made by Dr. Rengstorff at Battelle. Its chemical composition was typical of data he has published about their iron. The specimens were heat treated before the nitriding treatment to produce a coarse grain bamboo-like structure.

Ujjiye, N.: In view of the range of nitrogen covered in the present experiments, would you think the upper limit could be extrapolated, say, ten-folds to 0.3%?

Wert, C.: Concentration of N as high as 0.3% could be used if they could be handled in such a way that precipitation could be prevented prior to measurement. Such precipitation begins in a few minutes at room temperature for such high concentrations.

Ujjiye, N.: What was the chemical composition of specimen with regard to carbon, manganese, silicon, sulphur and phosphorus?

Wert, C.: The total impurity content for all elements was not determined. The content of S and P is not known beyond what the data of Dr. Rengstorff has determined. Carbon should be low since the specimens were nitrided in moist hydrogen. Metallic elements and Si are relatively small, totalling not more than a few hundreds.

of ppm; not enough to appreciably trap nitrogen.

Vineyard, G. H.: The activation energies for relaxation of singlets, doublets, and triplets appear to be very closely alike. In view of the binding energies you report, isn't this rather curious?

Wert, C.: The activation energies which are calculated from the plot of $\log \tau$ versus $1/T$ are all just slightly less than 1 eV. Because of difficulties of determining the τ 's accurately we are unable to show positively a progressive increase in activation energy from singlets to triplets. We do believe that such increase does exist, however, since at a given temperature $\tau_1 > \tau_2 > \tau_4$.

Otte, H. M.: You stated that for your analysis, in terms of four relaxations, to be effective, you required the strengths A_i to be approximately equal, but in the Table of actual results I note that your A_i 's differ by a factor of 5 to 10. How seriously does this affect the resolution?

Wert, C.: The resolution of the data into a sum exponentials is a problem with many facets. My statement that the data are resolvable if $\tau_{i+1} > 2.5\tau_i$ for processes for which $A_{i+1} \approx A_i$ is a very general one. We are aided in our particular calculations by the fact that the τ 's differ by somewhat more than this so that we can tolerate some difference in the ratio of the A_i 's. To carry out their calculation properly in reasonable time, a machine program needs to be used. I am aware of no such general program at this time.
