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Interstitial Solute Trapping in Irradiated and Quenched Iron[1])

By

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The interaction of interstitial carbon and nitrogen solutes with defects produced by low temperature neutron irradiation and by quenching was studied in high purity and Ferrovac E iron. Magnetic disaccommodation techniques were applied to determine the interstitial solute content after irradiation and upon annealing. Doses of about 10^{17} neutrons/cm^2 caused the trapping of about 20 ppm (atomic) interstitial solutes at 65 (carbon) and 40 °C (nitrogen). Trapping of carbon in a Ferrovac E iron alloy occurred during a fast quench from 880 °C. After trapping, the interstitial solutes reappeared in solid solution at 300 (carbon, neutron irradiation), 200 (nitrogen, neutron irradiation), and 620 °C (carbon, quenching). Various possibilities for the defect traps were considered and it was concluded that trapping of the interstitial solutes occurred at iron interstitial clusters after neutron irradiation and at vacancy type defects after quenching.

Die Wechselwirkung von Kohlenstoff und Stickstoff auf Zwischengitterplätzen mit Defekten, durch Bestrahlung bei niedrigen Temperaturen und durch Abschrecken erzeugt, wurden in hochreinem und Ferrovac E-Eisen untersucht. Eine magnetische Desakkommodationstechnik wurde angewendet, um den Zwischengitterlösungsgehalt nach Bestrahlung und Tempern zu bestimmen. Dosen von ungefähr 10^{17} Neutronen cm^{-2} verursachten ein Trapping von ungefähr 20 ppm (atomarer) Zwischengitterplatzlösung bei 65 (Kohlenstoff) und 40 °C (Stickstoff). Das Trapping von Kohlenstoff in einer Ferrovac E-Eisenlegierung trat während eines schnellen Abschreckens von 880 °C auf. Nach dem Trapping bildet sich die Zwischengitterlösung in einen Mischkristall bei 300 (Kohlenstoff, Neutronenbestrahlung), 200 (Stickstoff, Neutronenbestrahlung) und 620 °C (Kohlenstoff, Abschrecken) um. Verschiedene Möglichkeiten für die Defekthaftstellen wurden in Betracht gezogen, und es wurde angenommen, daß das Trapping der Zwischengitterlösung an Eisen-Zwischengitteragglomeraten nach Neutronenbestrahlung und an Leerstellendefekten nach dem Abschrecken auftritt.

1. Introduction

Neutron irradiation of b.c.c. metals doped with interstitial solutes has been observed to affect the solute behavior in a remarkable manner. The first observations of these effects were made on supersaturated Fe–C alloys by Wagenblast and Damask [1] who used internal friction measurements to show that after neutron irradiation at low temperature most of the carbon disappeared from solution after two hours at 50 °C. While supersaturated solutions of carbon in iron decompose rapidly at slightly elevated temperatures, the composition

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used in the Wagenblast and Damask investigation would require several thousand hours at 50 °C for precipitation of all of the carbon in an unirradiated sample. Similar effects have been observed for supersaturated Fe–N alloys [2].

The mechanisms which have been proposed to account for the above observations fall into two categories: 1. The decomposition of the supersaturated solution after irradiation takes place by precipitation of the usual carbides or nitrides but at an accelerated rate because of the introduction of nucleation sites by the irradiation; 2. The carbon or nitrogen atoms are trapped at defects introduced by the irradiation and are thus bound up in a form which is not related to the carbide or nitride found in the unirradiated case. Damask et al. [3 to 5] proposed a mechanism in the latter category to account for their results; they suggested that carbon atoms are trapped at lattice vacancies [3] produced by the irradiation. Recently, trapping of interstitial oxygen in neutron irradiated niobium has been reported [6] and was shown to be consistent with trapping at dislocation loops formed by clustering of irradiation produced defects [7]. Thus, although it presently seems clear that interstitial solutes in b.c.c. metals are trapped at radiation produced defects the exact nature of the trapping defect is uncertain. The importance of further investigation to aid in identifying the trapping defect is apparent.

The experiments reported in this article had the following objectives: 1. to investigate the trapping reaction in much more dilute solutions of carbon and nitrogen than had previously been used in order to avoid precipitation during the solute trapping, 2. to obtain information about the temperature at which the interstitial solutes are released from the traps, 3. to investigate the trapping effects of defects introduced by quenching, 4. to determine the effects of the impurities present in the iron used in these investigations on the trapping mechanism. In order to accomplish these objectives most effectively, magnetic permeability measurements were used for the main investigative tool. Magnetic relaxation effects due to interstitial reorientation are well documented and include; a) a disaccommodation, i.e., the magnitude of the time-dependent change of reluctivities measured at very small fields, b) the stabilization field, and c) the magnetic loss. The magnitude of these effects have been shown to be dependent on the interstitial solute content [8, 9]. In particular, the disaccommodation amplitude, $(r_\infty - r_0) = 1/\mu \, (t = \infty) - 1/\mu \, (t = 0)$, is linearly proportional to the amount of interstitial solute in solution [8]. The kinetics of the disaccommodation are given by $(r_\infty - r_t) = (r_\infty - r_0) \exp(-t/\tau)$ where the time constant τ for the disaccommodation is characteristic of the particular interstitial solute giving rise to the effect. It is important to emphasize that the disaccommodation is specific to a particular interstitial solute in the same sense that internal friction peaks are specific to a particular solute. The value of the initial permeability μ_0 immediately after demagnetization is also sensitive to the formation of small precipitates. Unter condition where the stress field of the precipitates is of the order of the magnetostrictive stresses, the presence of precipitates will decrease the initial permeability [10 to 12]. Thus, removal of interstitial solutes from solution can be distinguished from precipitation by measurements of both the initial permeability and the disaccommodation amplitude.

2. Experimental Procedure

The specimens used in this study were prepared from Ferrovac E vacuum melted iron containing about 400 ppm substitutional impurities, principally

Ni and Co, and from a special pure iron kindly supplied by Oliver [13], which contained less than 7 ppm substitutional impurities.

Specimens were initially annealed for three days in pure, dry hydrogen at 800 °C, which reduced the carbon and nitrogen content to the limits of detection of the magnetic disaccommodation measurement ($\approx$ 20 ppb atomic). The specimens were then annealed for 30 min at 1000 °C and slow cooled (50 °C/h) to 600 °C to produce a random orientation of large grains. After these initial treatments, specimens were doped with carbon (20 ppm atomic) or nitrogen (15 ppm atomic) using mixtures of methane and hydrogen at 619 °C and ammonia and hydrogen at 590 °C respectively, followed by rapid cooling from the annealing temperature to retain the carbon and nitrogen in solution. The carbon and nitrogen contents determined by magnetic disaccommodation measurements agreed satisfactorily with those expected from thermodynamic data [14, 15].

The permeability measuring techniques have been described elsewhere [16]. A precision of 2 parts in 10^5 was achieved using a measuring field of 3.5 mOe. The initial permeability μ_t (reluctivity, $r_t = 1/\mu_t$) was determined as a function of time at -28 ± 0.1 °C for the Fe–C specimens and at -43 ± 0.1 °C for the Fe–N specimens. The reluctivity difference $(r_{t_2} - r_{t_1})$ is given by the relation

$$r_{t_2} - r_{t_1} = (r_\infty - r_0)\left[e^{-t_1/\tau} - e^{-t_2/\tau}\right]$$

and therefore the measured reluctivity difference $(r_{15} - r_0)_{\text{Snoek}}$ or $(r_{15} - r_{0.5})_{\text{Snoek}}$ is proportional to the total disaccommodation amplitude, $(r_\infty - r_0)_{\text{Snoek}}$ which is proportional to the amount of interstitial solute in solution [9].

3. Experimental Results

3.1 Neutron irradiated specimens

Specimens were irradiated in the Liquid Nitrogen Cryostat [17] at the Bulk Shielding Reactor (neutron flux 1.2×10^{12} neutrons/cm²s at $E > 1$ MeV) at temperatures of -160 °C or lower. The specimens were withdrawn from this facility while immersed in liquid nitrogen and stored in either liquid nitrogen or solid CO_2 until placed in the measuring apparatus.
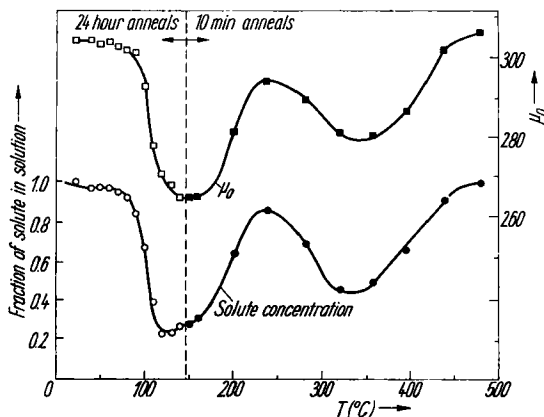

Fig. 1. Fraction of carbon in solution (circles) and initial permeability immediately after demagnetization μ_0 (squares) of unirradiated Ferrovac E plus 20 ppm (atomic) carbon as a function of annealing temperature. Open symbols refer to 24 h and closed symbols to 10 min anneals

A solution-treated unirradiated specimen of Ferrovac E iron containing 20 ppm (atomic) carbon was annealed isochronally between room temperature and 500 °C to serve as a reference for the subsequent experiments (Fig. 1). From the simultaneous decrease of the initial permeability measured immediately after demagnetization, μ_0 and the values of the carbon concentration in solution (which was determined from $r_{15} - r_0$), it can be seen that precipitation occurred in two stages in the dilute Fe–C alloys.[3]) The first precipitate which formed during the isochronal anneals (24 h) in the temperature range around 90 °C is presumably the metastable ε carbide [17, 18]. The increase of μ_0 and interstitial carbon concentration between 110 and 230 °C indicates that the ε carbide tended to redissolve in the course of the isochronal anneals before the carbide Fe$_3$C was formed at 300 °C. Continued isochronal annealing (10 min) beyond this temperature led to resolution of the Fe$_3$C. The data indicate that the solubility of Fe$_3$C is about 20 ppm (atomic) at 400 °C in fair agreement with previously published data [17, 18]. Ten minute isochronal anneals in the temperature range 20 to 500 °C did not lead to any indication of precipitation in contrast to the results of the 24 h isochronal anneals.

Fig. 2, 3, and 4 show the variation of μ_0 and the interstitial carbon concentration of neutron irradiated Fe–C alloys containing 20 ppm (atomic) carbon upon isochronal annealing (10 min anneals). No removal of carbon from solution was observed on warming the specimen from the irradiation temperature to 20 °C. It was observed that carbon disappeared from solid solution [($r_{15} - r_0$) decreased] around 60 °C and reappeared between 280 and 350 °C. The specimen given the neutron dose of 1.8×10^{16} neutrons/cm^2 showed a decrease of carbon of about 4 ppm (atomic) during the trapping stage while the specimen given a dose of 1.8×10^{17} neutrons/cm^2 showed a decrease of about 20 ppm during the trapping stage. The removal and reappearance of the carbon were both accompanied by slight increases of μ_0 which contrast with the marked decrease of μ_0 during precipitation in the unirradiated specimen. These data are consistent with the idea that carbon is trapped at a radiation-produced defect. The traps appeared to anneal out as the carbon was released from the traps;
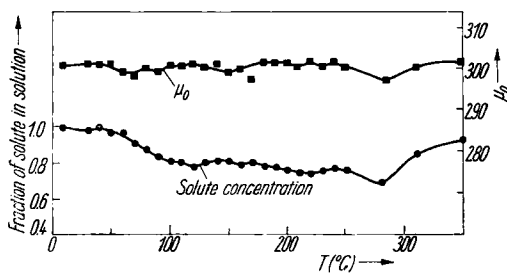

Fig. 2. Fraction of carbon in solution (circles) and initial permeability immediately after demagnetization μ_0 (squares) of a Ferrovac E plus 20 ppm (atomic) carbon irradiated with 1.8×10^{16} neutrons/cm^2 at ≤ -160 °C as a function of annealing temperature. 10 min isochronal anneals

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[3]) The precipitation of carbide in unirradiated high purity iron has been studied by Vigier et al. [29] who observed a single stage corresponding to the second stage of precipitation in this paper. Their carbon concentration can be estimated to be about 200 ppm (atomic) from the temperature of carbide resolution which they observed. While there may be an effect of purity on the precipitation stage in unirradiated iron, it will be shown that the interstitial trapping occurs in neutron irradiated Ferrovac E and high purity iron in about the same temperature range.

Fig. 3. Fraction of carbon in solution (circles) and initial permeability immediately after demagnetization μ_0 (squares) of a Ferrovac E plus 20 ppm (atomic) carbon irradiated with 1.8×10^{17} neutrons/cm² at ≤ -160 °C as a function of annealing temperature. 10 min isochronal anneals. See text for arrows
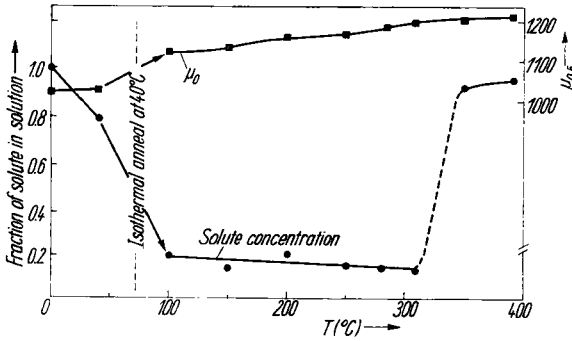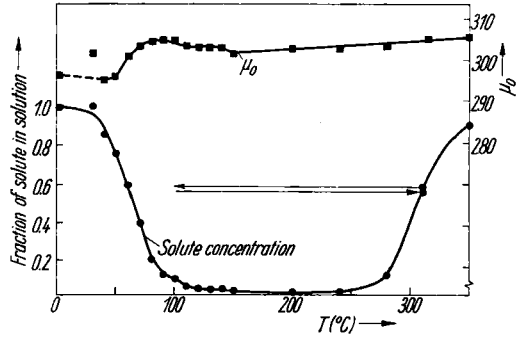

Fig. 4. Fraction of carbon in solution (circles) and initial permeability measured 0.5 min after demagnetization $\mu_{0.5}$ (squares) of a high purity iron plus 20 ppm (atomic) carbon irradiated with 1.3×10^{17} neutrons/cm² at ≤ -160 °C as a function of annealing temperature. 10 min isochronal anneals except at 40 °C

Fig. 5. Annealing kinetics at 40 °C for specimens irradiated with neutrons at ≤ -160 °C. Carbon disaccommodation measurements for Ferrovac E plus 20 ppm (atomic) carbon, 2.6×10^{17} neutrons/cm² $- \blacktriangle -$; and for high purity iron plus 20 ppm (atomic) carbon, 1.3×10^{17} neutron/cm² $- \blacksquare -$. Resistivity annealing at 38.5 °C for Ferrovac E plus 500 ppm (atomic) carbon, 4.2×10^{17} neutrons/cm² Fujita and Damask 1964, $- \bullet -$. Straight lines drawn with slope 3/5
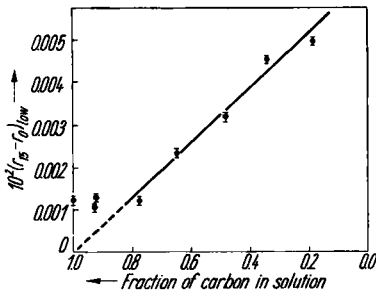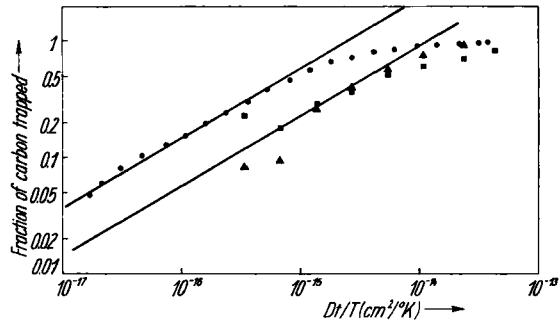

Fig. 6. Low temperature disaccommodation (measured at -123.7 °C) in a Ferrovac E plus 20 ppm (atomic) carbon alloy irradiated with 2.6×10^{17} neutrons/cm² at ≤ -160 °C as a function of the removal of the carbon from solid solution in the course of an isothermal anneal at 40 °C

it was not possible to retrap the carbon at 100 °C after the specimens were annealed at 310° and "air quenched" as indicated by the arrows in Fig. 3. It is further noted that the temperature range in which the carbon reappeared in solid solution is much narrower for the high purity iron than for the Ferrovac E iron (cf. Fig. 3 and 4), although the carbon trapping occurred in the same temperature range.

Isothermal annealing studies at 40 °C were carried out for the Ferrovac E and the high purity iron containing 20 ppm carbon. The results of these studies are plotted in Fig. 5 along with some resistivity data from Fujita and Damask for isothermal annealing at 38.5 °C [3]. In Fig. 5 the log of the fraction of carbon trapped versus the log $[D\,t/T]$ is plotted where D is the carbon diffusivity, t is the annealing time and T is the annealing temperature. The significance of the resulting curves will be discussed later.

A new disaccommodation at about −130 °C was developed as carbon disappeared from solid solution during anneals of the irradiated Ferrovac E plus carbon alloys (20 ppm (atomic)) at temperatures less than 60 °C. No equivalent disaccommodation was found in the high purity iron alloys. As shown in Fig. 6, the low temperature disaccommodation amplitude increased as the carbon disappeared from solid solution. After an initial transient there appears to be a 1:1 correspondence between the amount of carbon removed from solid solution and the amplitude of the low temperature disaccommodation. The kinetics of this −130 °C disaccommodation can be well described by a single exponential using a lognormal distribution of the relaxation times [19]. The parameter β, characteristic of the half-width of the Gaussian relaxation time distribution, was found to be in the range between 1.05 and 1.3. The temperature dependence of the most probable relaxation time, τ_m, (Fig. 7) is described by $\tau_m = 5 \times 10^{-13}$ s exp $(+0.42 \text{ eV}/kT)$. The low temperature disaccommodation
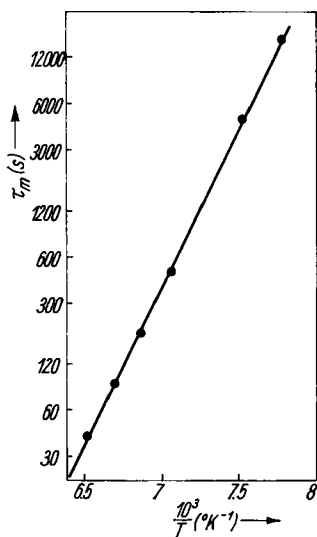

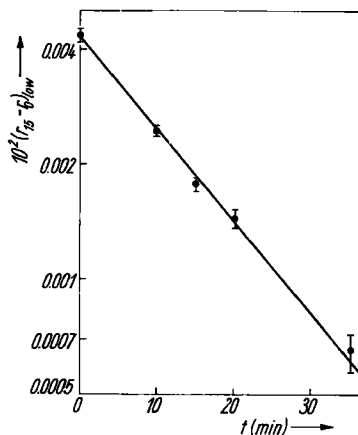Fig. 7. Arrhenius plot of the most probable relaxation time τ_m of the low temperature disaccommodation

Fig. 8. Annealing kinetics at 80 °C of the low temperature disaccommodation (measured at −123.7 °C) in a Ferrovac E plus 20 ppm (atomic) carbon alloy irradiated with 2.6×10^{17} neutrons/cm^2 at $\leq$ −160 °C and annealed 700 min at 40 °C

Fig. 9. Fraction of nitrogen in solution (circles) and initial permeability immediately after demagnetization μ_0 (squares) of unirradiated Ferrovac E plus 15 ppm (atomic) nitrogen as a function of annealing temperature. Open symbols refer to 24 h and closed symbols to 10 min anneals
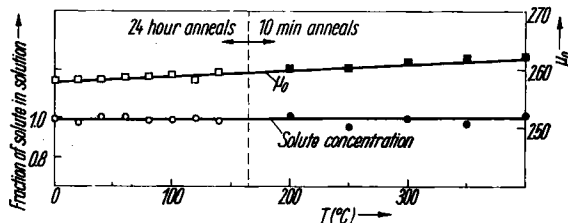
annealed out at 80 °C obeying first order kinetics (Fig. 8). It was observed that the carbon remained trapped during this anneal. No other disaccommodations were observed in the temperature range 77 to 373 °K.

Isochronal annealing of an unirradiated solution treated Ferrovac E iron plus 15 ppm (atomic) nitrogen showed that the initial permability μ_0 and the concentration of nitrogen in solid solution i.e., the amplitude of the nitrogen disaccommodation were not affected by 24 h anneals in the temperature range between zero and 140 °C and by 10 min anneals above this temperature (Fig. 9). After irradiation of the alloy with 1.3×10^{17} neutrons/cm^2 at low temperature, 12 ppm of the nitrogen was trapped around 50 °C (Fig. 10) and reappeared in solid solution in the temperature range between 100 and 300 °C. This temperature range is significantly lower and broader than that observed for the Ferrovac E iron plus carbon alloy (Fig. 3). No removal of nitrogen from solution occurred on heating the specimens from the irradiation temperature to 0 °C. The midtemperature of the trapping stage was shifted toward lower temperatures compared to that of the Ferrovac E iron plus carbon experiments as is expected from the higher mobility of the nitrogen interstitials. The initial permeability increased during the isochronal annealing. New disaccommodations were not observed in the temperature range 77 to 373 °K during the course of the annealing of the irradiated iron nitrogen alloy.

3.2 Quenched specimens

Wire specimens of 0.012 inch diameter (high purity iron) and 0.023 inch diameter (Ferrovac E iron) were used for the quenching experiments. The specimens were water quenched directly from a chamber filled with a helium-9%
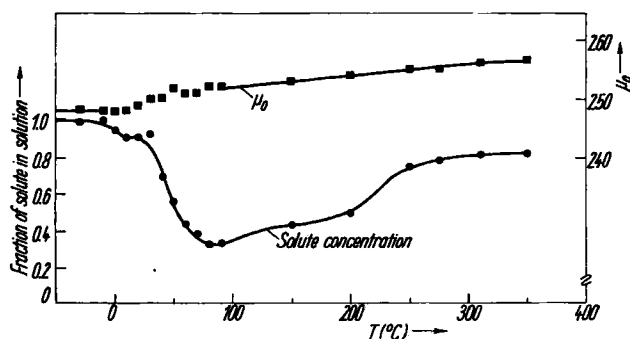

Fig. 10. Fraction of nitrogen in solution (circles) and initial permeability immediately after demagnetization μ_0 (squares) of a Ferrovac E plus 15 ppm (atomic) nitrogen alloy irradiated with 1.3×10^{17} neutrons/cm^2 at ≤ -160 °C as a function of annealing temperature. 10 min isochronal anneals

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hydrogen mixture or high purity argon (nominally 99.999% purity). The specimens were held for about 5 min at 1200 °C and then for 5 min at 880 °C from which temperature they were quenched at a rate of about 10^4 deg/s. All of the quenches were from the b.c.c. α phase as the Fe–C and Fe–N compositions used are equilibrium single phase structures below about 906 °C, and the holding time at 880 °C was sufficiently long to allow the f.c.c. to b.c.c. transformation to occur [20]. The values of the initial permability, μ_0, after the quenches were of the order of those obtained in the specimens after a solution treatment indicating that no phase transformation occurred during the quench.

The temperature independent logarithmic disaccommodation due to quenching strains [16] which was observed (Fig. 11) in the as quenched specimens was small and annealed out below 150 °C which accounts for a small decrease in the magnetic disaccommodation on isochronal annealing below 150 °C. Since the as quenched values of μ_0 are high and the logarithmic disaccommodation is small the quenching strains do not appear to be severe and anneal out below 150 °C. The carbon disaccommodation was not observed after the quench or after annealing at temperatures below 500 °C (Fig. 11) indicating that the carbon was removed from solution on quenching. The carbon returned to solution during isochronal anneals (10 min) in the temperature range 500 to 750 °C while the initial permeability increased slightly. The specimens were air cooled after each anneal. Similar results were obtained after quenches from He + H₂ and from high purity argon atmospheres. No additional disaccommodations were found in the range 77 to 373 °K after the specimens were quenched and annealed up to 100 °C.

Equivalent quenches performed with Ferrovac E iron nitrogen (15 ppm [atomic]) and high purity iron carbon (20 ppm [atomic]) alloys did not alter the magnitude of the disaccommodation due to the reorientation of the interstitial. Isochronal annealing after the quench did not lead to changes in the magnitude of the disaccommodation amplitude indicating that no trapping of the interstitial solutes occurred in these alloys after quenching from 880 °C. This negative result supports the conclusion that the carbon trapping after quenching the Ferrovac E specimens was *not* caused by lattice strains or transformation strains.
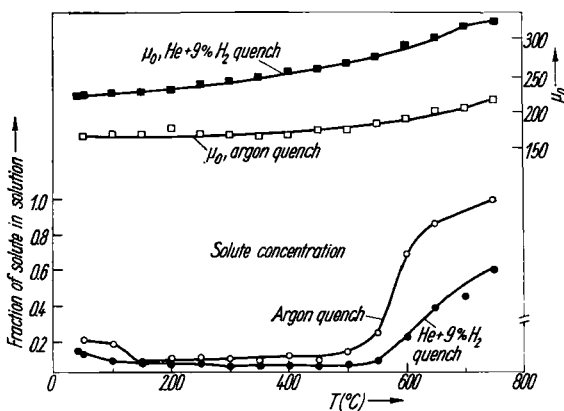

Fig. 11. Fraction of nitrogen in solution (circles) and initial permeability immediately after demagnetization μ_0 (squares) of a Ferrovac E plus 20 ppm (atomic) carbon quenched from 880 °C. Closed symbols refer to a quench from a helium plus 9% hydrogen atmosphere, open symbols to a quench from a high purity argon atmosphere

4. Discussion

In recent years electron microscope studies of neutron irradiated b.c.c. metals have revealed that defects are present in the form of small black spots and/or dislocation loops [21 to 23]. Since it is known that interstitial solutes in b.c.c. metals are strongly attracted to dislocations, it seems reasonable to assume that the dislocation loops observed in neutron irradiated metals would also act as traps for the interstitial solutes. Bullough *et al.* [7] have derived the kinetics appropriate to drift flow of interstitial solutes in the strain field of small dislocation loops. According to this work the fraction of available impurity, $F(t)$, trapped at dislocation loops in time, t, is given by

$$F(t) = B \left[\frac{D\,t}{T} \right]^{3/5}, \tag{1}$$

where D is the diffusion coefficient of the interstitial solute, T the absolute temperature, and B a constant which depends on the loop density and on the attractive force between the dislocation loop and the interstitial. The value of B is given by

$$B = 5.27 \, \varrho \left[2/3 \left(\frac{1+\nu}{1-\nu} \right) \mu \, r_0^3 \, b \, \varepsilon \, \pi \, \frac{a^2}{k} \right]^{3/5}, \tag{2}$$

where ϱ is the loop density, ν is Poisson's ratio, μ the shear modulus, b the Burger's vector of the loops, ε the misfit parameter of the interstitial impurities, a the loop radius, r_0 the radius of the interstitial hole, and k is Boltzmann's constant. The above equation (1) is only valid for the initial stages of the flow of interstitials to the loops since depletion effects and back diffusion were neglected in the derivation. Bullough *et al.* [7] showed that the kinetics of trapping of oxygen atoms in niobium obeyed equation (1) extremely well. In the niobium work dislocation loops had been observed in niobium irradiated to the same dose as the specimens used to study the kinetics of the trapping reaction [24]. In iron dislocation loops have been observed only after higher neutron doses than those used in the present experiments [21]. However, it seems reasonable that dislocation loops would also be present in iron at the doses used in our experiments, but they might be too small to be resolved in the electron microscope.

In order to see if the trapping of carbon in iron after neutron irradiation fits the kinetics appropriate to migration to loops, we have plotted isothermal measurements of the fraction of carbon trapped versus the parameter $D\,t/T$ on a log–log scale in Fig. 5 along with the resistivity data of Fujita and Damask for an isothermal anneal at 38.5 °C. The solid lines in Fig. 5 are drawn with a slope of $t^{3/5}$. It is seen that the resistivity data of Fujita and Damask obtained from specimens containing 500 ppm (atomic) carbon fit the form of the kinetics for drift to dislocation loops quite well. The disaccommodation measurements of the present experiments show considerable scatter in the early part of the process, but the data are not inconsistent with the $t^{3/5}$ law governing the early stages of the trapping reaction.

The value of the constant B must also be considered in judging whether the observed kinetics are appropriate for the proposed mechanism. For the trapping of oxygen in niobium B had a value of 1.2×10^8 °K/cm^2 [7]. This value of B was in excellent agreement with the theoretical value calculated using the observ-

ved loop density (5×10^{15} cm^{-3}) and size (100 Å diameter). For the data presented in Fig. 5 for trapping of carbon in iron the values of B are 6×10^8 °K/cm^2 for the Fujita and Damask data, and 2.3×10^8 for our data. These values are all in reasonable agreement, and the differences could be explained by differences in loop density and size.

It is apparent that the proposed mechanism of migration of interstitial solutes to dislocation loops may result in formation of precipitates on the loops under certain circumstances since electron microscrope studies have shown that both carbides and nitrides prefer to nucleate on dislocations. Calculations have shown that only a fraction of carbon in iron can be removed from solution by formation of a Maxwellian atmosphere around dislocations [25]. The results for oxygen in niobium are in agreement with this conclusion since only about half of the oxygen was removed from solution during the trapping reaction [7]. For the case of carbon in iron the almost complete removal of carbon from solution during the trapping reaction indicates precipitation on the dislocation loops. The size of the precipitates in specimens containing about 20 ppm of solute can be estimated using the isochronal annealing data after a neutron dose of about 2×10^{17} neutrons/cm^2. The trapping temperatures correspond to a mean number of jumps for the C and N which is of the order of 10^4. This corresponds to a trap density of about 3×10^{16} cm^{-3} and to about 200 interstitial solutes per trap. The precipitate size can be estimated to be about 50 Å diameter for a planar precipitate and about 20 Å for a spherical precipitate. If we postulate that precipitation occurs on the dislocation loops, we must have an explanation for the incomplete reactions observed after lower dose irradiations as in Fig. 2 and in the work of Wagenblast and Damask [1]. The mechanism for formation of interstitial loops proposed by Eyre and Bullough [26] may offer a solution for this problem. They proposed that after irradiation iron interstitial platelets grow on the (110) planes and after reaching a critical size, they shear to form dislocation loops with $a/2$ [111] Burger's vector. It may be that after the lower dose irradiations the platelets haven't reached the critical size for shear and although they still attract carbon atoms, conditions are not favorable for precipitate formation. Another explanation for the incomplete reaction after lower dose irradiations is that smaller loops have less attraction for carbon atoms than larger loops and so not enough carbon is pulled into the small loops to form critical nuclei for precipitation. The difficulty in nucleating carbides at these low concentrations is shown by the observation that ten minute isochronal annealing of unirradiated specimen did not lead to precipitation. A comparison of the data shown in Fig. 3 for the irradiated Fe–C specimen with that shown in Fig. 1 for the unirradiated Fe–C specimen suggests that the precipitate which forms on the dislocation loop is cementite, Fe_3C, rather than ε carbide. It will be seen that in the case of the irradiated specimen (see Fig. 3) the carbon in solution is below the solubility of ε carbide above about 100 °C (Fig. 1). However, the amount of carbon in solution above about 250 °C is slightly greater than the solubility of cementite (Fig. 1). Very small particles formed on dislocation loops might be expected to have a slightly greater solubility than larger particles formed on straight dislocation segments.

In the present experiments the trapping of nitrogen after neutron irradiation may occur without precipitation since the total amount of nitrogen is below the solubility of Fe_4N at temperatures above 100 °C. As Fig. 10 shows, the nitrogen trapping reaction doesn't go to completion and only about 2/3 of

the total nitrogen is removed from solution by the trapping reaction. The gradual increase of nitrogen in solution, as the temperature is raised indicates a complex process. As the temperature is raised in the isochronal annealing process, the nitrogen atmospheres will start to dissolve and if the dislocation loops do not simultaneously disappear some of the nitrogen will return to the loops upon subsequent cooling. The amount of nitrogen in solution at the measuring temperature would then reflect not only the binding energy of the nitrogen atom to the dislocation but also the cooling rate from the isochronal annealing temperature. The gradual release of nitrogen from traps is in sharp contrast with the release of carbon in the high purity iron. This latter case might be a cooperative process in which the carbon trapped on the dislocation loop prevents annealing until the temperature is reached at which the carbon atmosphere begins to dissociate and then the dislocation loops anneal out very rapidly.

Damask and co-workers proposed that carbon is trapped at lattice vacancies in neutron irradiated iron, but we have suggested instead that the carbon atom is trapped at dislocation loops. However, the idea that carbon atoms would be strongly attracted to lattice vacancies is quite reasonable, and the main reason for rejecting the vacancy trap in the case of neutron irradiated iron is that present concepts of neutron radiation damage hold that the number of single vacancies would be a very small fraction of the lattice defects produced by the irradiation. Also, as we have shown, the kinetics of the trapping reaction seems to fit the kinetics derived for drift to dislocation loops. An interesting outgrowth of the work by Damask et al., was the calculations by Johnson [27] who used the supposed binding energy of a carbon-vacancy complex as determined by Arndt and Damask [4] to derive an equation for the interaction between an iron atom and a carbon atom. Johnson showed that the interaction equation so derived gave reasonable agreement with observed values when used to calculate a number of properties of iron–carbon alloys. Thus, even though we do not believe that the trapping reaction observed in neutron irradiated iron can be primarily trapping of single carbon atoms at individual vacancies, the calculations of Johnson do suggest that the binding energy of vacancies and carbon atoms must be fairly close to that determined by Arndt and Damask (0.4 eV/atom). The only reasonable explanation of our quenching experiments outlined above is that carbon atoms are strongly attracted to lattice vacancies. An explanation involving trapping of carbon atoms at dislocations produced by quenching strains cannot be valid since nitrogen was not trapped after a similar quench, and it is known that nitrogen is strongly attracted to dislocations [28]. Furthermore, no trapping was observed in high purity Fe-C alloys after identical quenches. The difference between the behavior of carbon and that of nitrogen in the quenching experiments may be explained by assuming that the binding energy of nitrogen to vacancies is somewhat less than the binding energy of carbon to vacancies. Thus, during a quench of the Fe–N alloy the vacancies may make more jumps before they become associate with the interstitial nitrogen solute and the temperature at which the vacancies are retained (or "frozen-in") is correspondingly lower leading to a smaller vacancy concentration after the quench. Even in the case of the iron–carbon alloys, conditions during the quench are close to favoring the vacancies reaching sinks other than carbon atoms since no trapping was observed in the high purity iron–carbon alloys. Apparently the substitutional

impurities in the Ferrovac E (400 ppm) help to slow down the decay of the excess vacancy concentration during the quench. The vacancy formation energy required to give a vacancy concentration equal to the carbon concentration (200 ppm [atomic]) at 880 °C is 1.1 eV, and since the self-diffusion energy of iron is 2.5 eV, the motion energy of vacancies would be about 1.4 eV.

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