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Vacancy-Carbon Interaction in Iron

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Electron-irradiated high-purity α-iron doped with various amounts of interstitial carbon impurities has been studied by positron-lifetime measurements. It is shown that during vacancy migration at 220 K an asymmetric vacancy-carbon pair is formed, where the carbon atom is located off the center of the vacancy.

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The properties of atomic defects as well as their interactions, especially in bcc metals, are not well known in spite of their great technological importance.[1,2] The most important example in this respect is carbon in iron, where the characteristics of vacancies and interstitials have been difficult to extract. Recent experiments,[3] utilizing positron-annihilation technique,[4] revealed that vacancy migration occurs already around 220 K. At this temperature the interstitial carbon atoms are still immobile.[5] A contradictory view of vacancy migration, based mainly on the vacancy migration energy derived from high-temperature data, has also been presented.[6]

In this Letter we report positron-lifetime measurements of the interaction of monovancies and interstitial carbon impurities in electron-irradiated α-iron. Positrons are sensitive to vacancy-type defects, whereas interstitials and their agglomerates do not affect the annihilation characteristics. Positron localization at defect sites gives information on both the concentration and the internal structure of the defects.[4] Our results show that the migration of vacancies at 220 K leads to the formation of asymmetric carbon-vacancy pairs.

The high-purity α-iron samples were prepared by zone-refining methods described earlier.[3] The interstitial impurity concentration (carbon and nitrogen) was below 5 ppm. Carbon doping was made in the liquid phase followed by solution annealing at 750 °C. The specimens were then quenched into icy water, electrolytically polished, and stored at liquid nitrogen temperature. Two sets of samples were prepared with carbon concentrations of 50 and 750 ppm. Two identical samples ($6\times8\times0.3$ mm^3) from both sets were electron irradiated at 20 K with 3-MeV electrons to a total dose of about 3×10^{19} e^-/cm^2. Positron-lifetime measurements (resolution 290 psec full width at half maximum were performed after isochronal (30 min) annealing treatment of the samples. The lifetime spectra were measured at 77 K up to 340-K annealing, whereafter measurements were made at room temperature. After source-background corrections, the lifetime spectra were analyzed with use of one or two exponential components.

Figure 1 gives the shorter positron lifetime values τ_1 as a function of the isochronal annealing temperature for both carbon-doped, electron-irradiated Fe specimens. For comparison, we also give the τ_1 values for an undoped (< 5 ppm C) Fe sample with an irradiation dose of only 6×10^{18} e^-/cm^2 (refered to as the high-dose sample in Ref. 3). The longer lifetime values τ_2 as well as the relative intensities I_2 of the longer component are shown in Fig. 2. The corresponding data for pure iron are given in Ref. 3.

At annealing temperatures below 200 K all life-

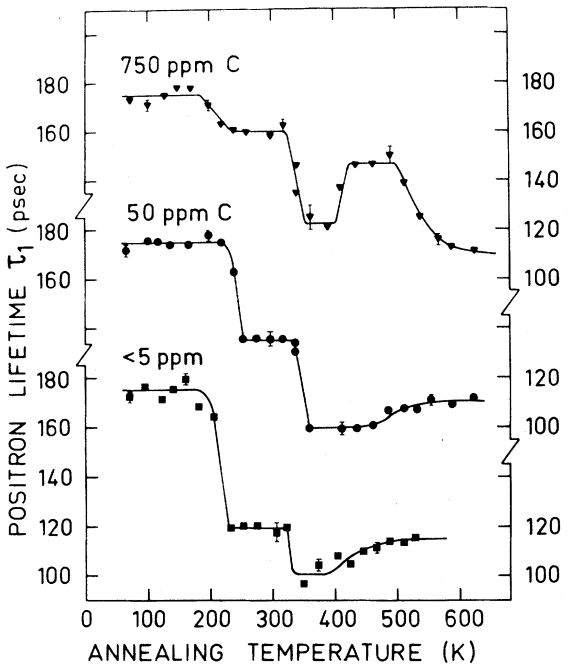

FIG. 1. The shorter positron lifetime τ_1 as a function of isochronal annealing temperature in electron-irradiated (3 MeV, 20 K) α-iron doped with 50 and 750 ppm C. The electron dose is about $3\times10^{19}\,e^-/\mathrm{cm}^2$. The data for undoped iron (<5 ppm C) from Ref. 3 correspond to a dose of about $6\times10^{18}\,e^-/\mathrm{cm}^2$. The error bars are statistical from the lifetime fit. Note a shift of scale in each curve.

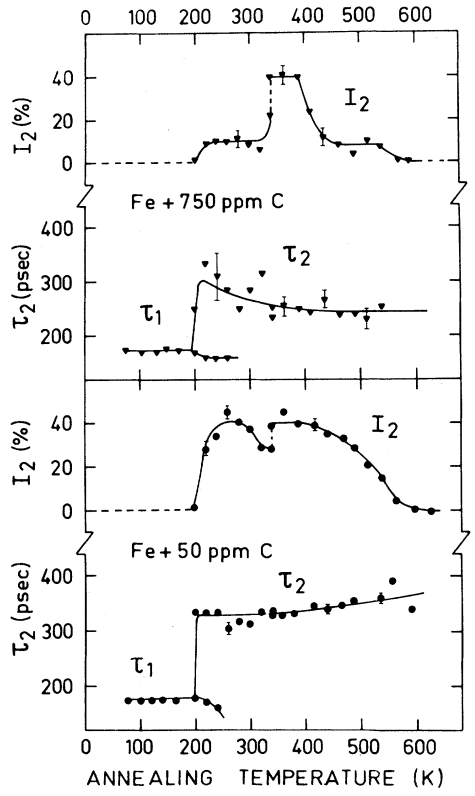

FIG. 2. The longer positron lifetime τ_2 and relative intensity I_2 as a function of isochronal annealing temperature in the electron-irradiated 50-ppm-C and 750-ppm-C specimens. For the data on undoped iron (<5 ppm C) see Ref. 3.

time spectra consist of a single exponential component with a lifetime $\tau_1 = 175$ psec, whereas the free positron lifetime in an annealed iron is 115 psec. Thus we have 100% positron trapping into monovacancies produced in electron irradiation. Annealing through 220 K (labeled as stage III in iron[6]) splits the lifetime spectra in all cases into two distinct components with the longer lifetime $\tau_2 \approx 300$ psec and its relative intensity I_2 varying from 10% to 40% (Fig. 2). The appearance of a long-lifetime component at 220 K is again strong evidence for vacancy migration which results in an agglomeration of small three-dimensional microvoids.[3,7-10]

Let us consider Fig. 1 in more detail. At 200 K, τ_1 decreases strongly in all samples, and it reaches a level which stays constant between 220 and 350 K. However, these levels are well above the free-positron lifetime of 115 psec. Moreover, the height of the levels strongly depends on the carbon concentration. This means that monovacancies are not completely annealed out during stage III, since positron trapping only into microvoids would give τ_1 values[4] well below 100 psec. In addition, the increased carbon concentration increases the number of monovacancies retained. We ascribe this behavior to the capture of migrating vacancies by immobile[5] carbon atoms resulting in bound vacancy-carbon pair formation.

In principle, the lifetime τ_1 between 220 and 350 K is a mixture of annihilations from free and trapped states at vacancy-carbon pairs. Here, however, we are not able to resolve these components by a three-component fit because of an additional trapping into microvoids. The estimated[3] vacancy concentrations in samples containing 50 and 750 ppm C just below 220 K are of the order of 10 to 50 ppm. Thus the carbon concentration in the 50-ppm-C specimen is comparable to that of vacancies whereas in the 750-ppm-C specimen, it is at least an order of magnitude higher. In the 50-ppm-C specimen, we already see considerable positron trapping into vacancy-carbon pairs. In the 750-ppm-C specimen, the pair concentration

is expected to be much higher, but the change of the plateau value from 135 to 160 psec is relatively small. Consequently, we take the value τ_1 = 160 psec for the 750-ppm-C specimen as the saturation value giving the trapped-positron lifetime in the vacancy-carbon pair. Yet it should be noted that even in the nominally "pure" iron (< 5 ppm C) there seems to remain a residual pair concentration since trapping only into microvoids would give[4] $\tau_1 \approx 75$ psec at 280 K.

The next annealing stage in Fig. 1 occurs at 350 K. At this temperature, migration of carbon interstitials is known[5,11] to occur. In all specimens the τ_1 values decrease considerably and in the Fe specimen and the Fe specimen with ppm C, positron trapping into vacancy-carbon pairs ceases totally, since τ_1 goes below the bulk value (115 psec) and is consistent with trapping into microvoids only. We interpret this behavior as a further decoration of vacancy-carbon pairs with migrating carbon atoms, resulting in a nullification of positron trapping into the pairs. This is consistent with the earlier observations of Snead *et al.*[12] and Weller, Diehl, and Triftshäuser.[13]

Above 400 K there is a small increase in τ_1 in the 750-ppm-C specimen. It is connected with some rearrangement of the vacancy-carbon complexes resulting in an increased positron trapping. The possible trapping of positrons at carbon precipitates, which are formed at these temperatures, seems to be ruled out, since our measurements on an unirradiated 750-ppm-C sample as a function of isochronal annealing did not show any increase from the bulk lifetime τ = 115 psec up to 700 K. The final annealing of all defects including the microvoids formed at 220 K occurs in a broad temperature range of 400 to 600 K and the τ_1 values reach the bulk lifetime 115 psec in all specimens.

The vacancy-carbon pair formation is also clearly reflected in the behavior of τ_2 and I_2 in Fig. 2. The microvoid intensity I_2 above 220 K is significantly reduced in the 750-ppm-C sample, as compared with the 50-ppm-C sample, due to increased vacancy capture by carbon atoms. In the undoped iron (< 5 ppm C) the I_2 value is[3] about 40%, even though the irradiation dose was a factor of 5 smaller. The small discontinuity in the I_2 values at 340 K in Fig. 2 is due to a change in the temperature of lifetime measurements from 77 K to room temperature: Trapping of positrons into microvoids is known to be[14] temperature dependent. The abrupt rise of I_2 in the 750-ppm-C sample at 350 K is due to two competing positron trapping mechanisms below 350 K: The decrease of positron trapping into vacancy-carbon pairs increases the relative fraction of positrons at the already existing microvoids. The reverse phenomenon occurs in the 750-ppm-C specimen at 400 K as I_2 decreases from 40% to 10%. Finally, the microvoids anneal out in a wide temperature range up to 600 K where the lifetime spectra resume a one-exponential form.

The most significant feature in our annealing curves is the vacancy-carbon pair formation at 220 K. The migration sequence of the constituents is reversed from what has been assumed earlier: It is the migrating vacancy which is captured by a stable carbon atom. This result is in agreement with the calculations of Johnson[15]: He obtained a monovacancy migration energy of 0.68 eV for α-iron, lower than the value of 0.86 eV for carbon migration. A remarkable fact is the strong positron trapping into the pair. An opposite example is hydrogen in copper vacancies,[16] which prevents positron trapping. As a result of the strong positron trapping into vacancy-carbon pairs, we argue that the carbon atom is located off the center of the vacancy, e.g., the pair does not recombine into a substitutional carbon atom, as there would then be no positron trapping. The trapped positron lifetime τ_1 = 160 psec in the pair is only slightly smaller than that in a pure vacancy in iron (175 psec); this also indicates that carbon is located rather far from the center of the vacancy. Such a structure of the pair is consistent with the calculations of Johnson and Damask,[17] who reported that the carbon atom is positioned at 0.73 half-lattice constants from the vacancy center along a ⟨100⟩ line, not far from the neighboring octahedral position at the distance of one half-lattice constant.

No evidence of the stability of the vacancy-carbon pairs above 350 K can be found in our data, since at this temperature carbon migration stops positron trapping via further decoration of the pairs. This decoration can be easily visualized: There are six equivalent positions for the carbon around the vacancy, and additional occupied positions decrease the free space for positron localization thus preventing their trapping. Electron-microscope studies[18] would suggest a dissociation of vacancy-carbon complexes at 520 K.

The strong binding between vacancies and carbon atoms below room temperature is seen indirectly in many phenomena; it affects strongly the behavior of ferritic steels during neutron irradiation[19] and delays the precipitation of carbon in the

presence of vacancies.[18] The analysis of experimental data on point defects in iron-carbon system must be greatly modified in many cases.[19,20] The picure of an asymmetric vacancy-carbon pair is consistent with magnetic aftereffect results[21]: Stage-III annealing at 220 K gives rise to a new magnetic aftereffect band (reorientating[21] at 128 K), which vanishes above 300 K, where a second magnetic aftereffect band (reorientating at 160 K) arises. The latter evidently corresponds to the decorated pairs above the carbon-migration stage, and the band anneals out above 400 K.

In conclusion our positron-lifetime measurements on electron-irradiated carbon-doped α-iron show direct evidence of the formation of a binding between a vacancy and an interstitial carbon atom during the migration of vacancies at 220 K. The pair is highly asymmetric and stable to at least 350 K, where carbon migration changes its structure. Our results should strongly affect the analysis of the behavior of point defects in iron-carbon system.

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