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Abstract   Resistivity recovery experiments are performed on α-Fe and an Fe - 220 at. ppm C alloy after 5 MeV proton irradiation at cryogenic temperature of 50 K. By comparing the recovery spectra of pure Fe and the Fe-C alloy we are able to resolve the effect of carbon atoms on the point defect kinetics. It is observed that carbon interacts with both interstitial and vacancy type of defects and delays their annihilation. At temperatures above 500 K the formation of carbides reduces the resistivity of the alloy.

Keywords   proton irradiation, resistivity recovery, iron, carbon impurities

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INTRODUCTION

The presence of carbon in steels is one of the most important factors determining the microstructure and the mechanical properties. Carbon has also a major influence on the behavior of steels under irradiation due to its interaction with point defects. The effect of carbon impurities on the migration and annealing of point defects in iron has been investigated previously [1,2]. It has been shown that the formation of carbon-vacancy complexes is energetically favorable and, moreover, that these complexes exhibit reduced mobility and may serve as nucleation sites for larger vacancy clusters and nanovoids.

In the present work we investigate by electrical resistivity recovery measurements the interaction between carbon atoms and radiation defects produced in α-Fe by 5 MeV protons during low-temperature irradiation. The influence of carbon is revealed by comparing the resistivity recovery of pure and carbon-containing iron specimens.

EXPERIMENTAL DETAILS

High purity Fe and an Fe - 220 at. ppm C alloy were obtained by the European Fusion Development Agreement. They have been prepared by induction melting under high purity hydrogen and argon to reduce foreign impurities to ultra low levels. Foils of ~50 μm

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thickness were obtained from the starting material by cold rolling. Rectangular specimens 15 mm long and 2 mm wide were cut from the foils and annealed for 8 h at 700°C under a hydrocarbon-free vacuum of 10^{-6} mbar. Current and potential leads of pure Fe were spot-welded on the specimens for performing the electrical resistivity measurements according to the standard DC four-probe method.

Irradiations with 5 MeV protons were performed in the dedicated materials irradiation facility IR^2 at the TANDEM accelerator of NCSR "Demokritos" [3]. During irradiation the specimens were kept at cryogenic temperature (50 K) by means of a closed-cycle He refrigerator. At this low temperature most of the generated defects remain initially immobile. Simulations by the SRIM code [4] show that the protons penetrate through the 50 μm thick targets. The damage profile as a function of thickness is almost flat and thus defects are generated nearly homogeneously within the irradiated specimen volume. Data for the samples and irradiation conditions are given in Table 1.

The number of defects was quantified by *in-situ* measurement of the increase in electrical resistivity. After the total proton dose was delivered, the specimens were step-wise annealed at gradually increasing temperatures up to 700 K. The resistivity was measured after each annealing step and its recovery towards the pre-irradiation value was monitored as a function of annealing temperature.

Table 1. Sample data for 5 MeV proton irradiated Fe and Fe - 220 ppm C alloy.

	ρ_0 ($\mu\Omega$-cm)	Φ_0 (cm^{-2})	$\Delta\rho_0$ ($\mu\Omega$-cm)
Fe	0.066		0.79
Fe - 220 ppm C	0.251	2.2×10^{16}	0.71

ρ_0 - residual resistivity; Φ_0 - total proton dose; $\Delta\rho_0$ - total irradiation induced resistivity increase.

RESULTS AND DISCUSSION

Fig. 1 shows the increase of the electrical resistivity due to the proton irradiation as a function of dose for both pure Fe and the Fe - 220 ppm C alloy. The resistivity increases almost linearly with dose indicating that there is a constant accumulation of radiation defects. This is expected since at the irradiation temperature of 50 K defect mobility is significantly reduced and thus there is a low likelihood for annihilation to occur. By fitting a linear expression to the data, indicated by the dashed lines in fig. 1, we obtain the slope, which is 3.6 and 3.1×10^{-23} Ω-cm^3 for pure Fe and the Fe-C alloy, respectively. The difference between the slopes is within the experimental uncertainty, which is ~10% due to errors in the geometrical factors entering the evaluation of specimen resistivity and ion flux.
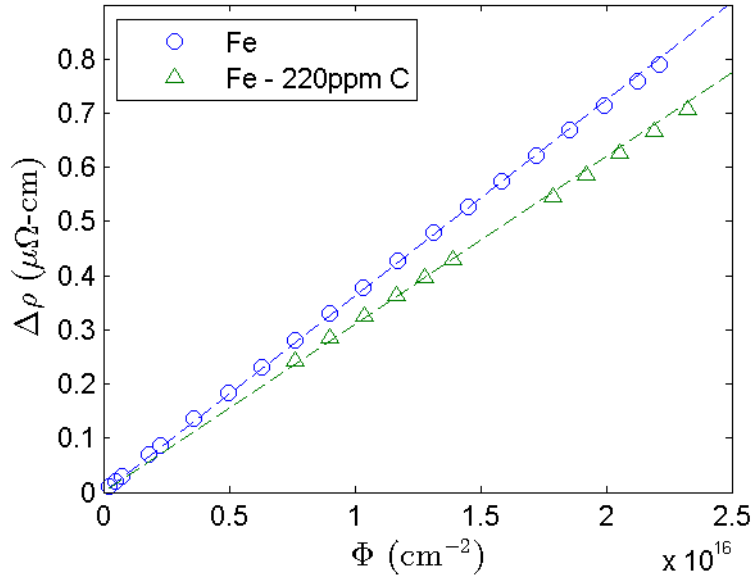
Fig. 1. Increase of the electrical resistivity as a function of dose during 5 MeV proton irradiation at 50 K of Fe and an Fe - 220 ppm C alloy.
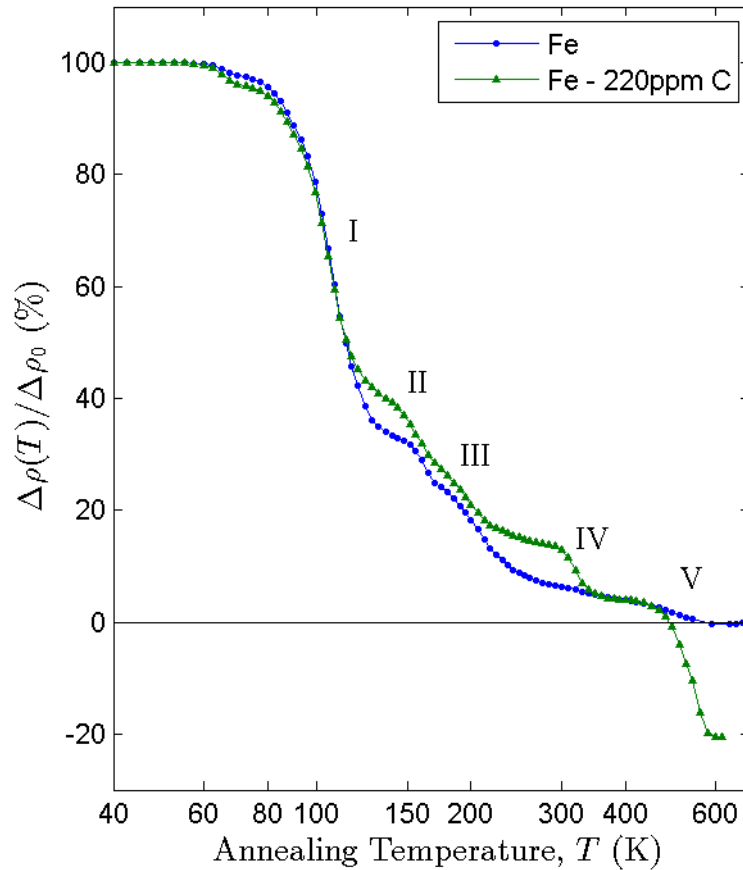
The resistivity increase as a function of dose Φ can be written as

$$\Delta\rho = \rho_F c_F = \rho_F \sigma_D \Phi ,\qquad(1)$$

where c_F is the concentration of generated Frenkel pair defects, ρ_F is the resistivity per unit concentration of Frenkel pairs and σ_D is the damage cross section. Thus the slope of the resistivity damage curve is equal to $\rho_F \sigma_D$. From the SRIM simulations it is obtained that the value of the damage cross-section is $\sigma_D \approx 1.4 \times 10^{-20}$ cm^2 and thus the defect concentration in the specimens at the end of the irradiation is estimated to be $c_F \approx 300$ ppm. Dividing the slope of the resistivity damage curves by σ_D we obtain the value of ρ_F, which is 2.6 and 2.2×10^{-3} Ω-cm for pure Fe and the Fe-C alloy, respectively. These values are in good agreement with previous measurements in iron, which found $\rho_F = 3.0 \times 10^{-3}$ Ω-cm [5] and $\rho_F = 2.0 \times 10^{-3}$ Ω-cm [6].

Fig. 2 shows the resistivity recovery of proton irradiated pure Fe and Fe - 220ppm C alloy as a function of annealing temperature. The ratio $\Delta\rho(T)/\Delta\rho_0$, where $\Delta\rho_0$ is the total resistivity increase at the maximum proton dose and $\Delta\rho(T)$ is the remaining resistivity after annealing at temperature T, reflects the fraction of radiation defects that survive after annealing. It is observed that the recovery proceeds step-wise in so-called annealing stages, which are enumerated with roman numerals. Stages I, II and III appear in both the pure Fe specimen and the Fe-C alloy at temperatures up to about 200 K. It is clear from fig. 1 that the presence of C significantly retards the recovery in stage I and also influences stages II and III. At higher temperatures two more stages, IV and V, are clearly observed in the recovery of the Fe-C alloy, whereas in pure Fe only a feature at the temperature of stage V is observed.

Notably, negative $\Delta\rho(T)$ is observed for temperatures above 500 K in the alloy specimen, which means that after irradiation and recovery annealing the residual resistivity of the specimen becomes lower that its pre-irradiation value. This indicates that the C solute atoms may have formed clusters or carbide precipitates that result in an overall reduced contribution to the sample resistivity.

Fig. 2. Recovery of the initial resistivity increase as a function of annealing temperature of proton irradiated Fe and an Fe - 220 ppm C alloy. Recovery stages are indicated by roman numerals.

In fig. 3 the recovery rate $-\Delta\rho_0^{-1}\left(d\Delta\rho/d\log T\right)$ is presented as a function of annealing temperature. The presence of annealing stages is most clearly seen in this plot, where the various stages are identified as sharp peaks. The fine structure of stage I recovery is revealed in fig. 3, where four distinct sub-stages are observed: I_B, I_C, I_D and I_E. The labeling is according to previous work [1]. I_B and I_C have been previously identified as due to the recombination of close Frenkel pairs. On the other hand, I_D and I_E are attributed to the correlated and uncorrelated recombination of Frenkel defects due to the migration of interstitial Fe atoms. Comparing the structure of I_D and I_E in pure Fe and the Fe-C alloy it is observed that presence of C suppresses almost entirely the sub-stage I_E. In this sub-stage interstitial defects perform long-range migration until either they recombine with another vacancy or they encounter other interstitials and form clusters. The suppression of I_E indicates that C hinders long-range interstitial migration. This is most probably due to trapping of interstitial defects at

C atoms. From the data of fig. 3 it is estimated that about 10% of the initially generated interstitials are trapped by C.
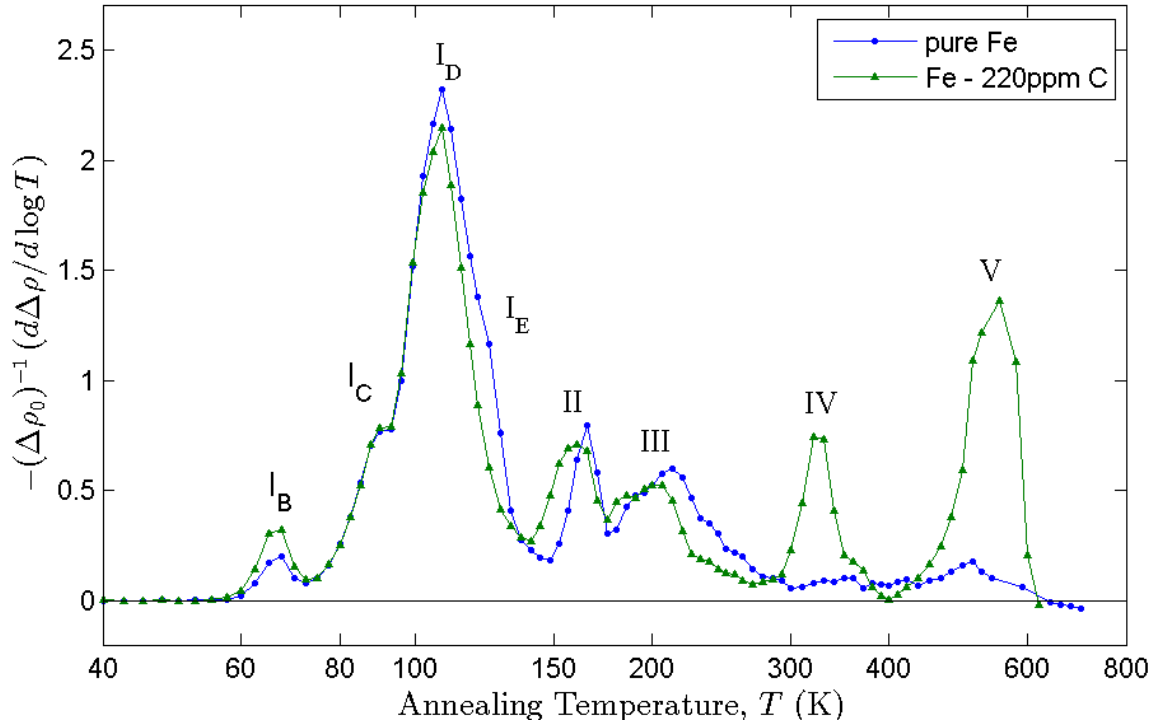
Fig. 3. Resistivity recovery rate as a function of annealing temperature in proton irradiated Fe and an Fe - 220 ppm C alloy.

Stage II recovery is observed at 164 K in pure Fe. According to previous work [1] this stage is due to the migration of di-interstitial clusters. As seen in fig. 3, stage II in the Fe-C alloy shifts to a lower temperature (158 K) and becomes also wider. There is ~7% more recovery in stage II of the Fe-C alloy with respect to pure Fe. This is attributed to the detrapping of interstitial defects, which occurs at a temperature slightly lower that the stage II temperature in pure Fe. That is why in the alloy the stage appears wider and centered at lower temperature. Most of the interstitial defects that are freed from traps annihilate with vacancies, contributing to the 7% increased recovery in stage II. The rest form interstitial clusters that are immobile at this temperature region.

Stage III in pure Fe is centered at 210 K and is attributed to the long-range migration of vacancies and their annihilation with interstitial clusters. From fig. 3 it is observed that stage III shifts to lower temperature in the Fe - 220ppm C alloy, while the recovery rate is reduced in the high temperature tail of the stage, between 210 and 260 K. This can be interpreted similarly to stage I by the trapping of vacancies at C atoms and the formation of vacancy-carbon clusters. The stability of such defects has been recently investigated theoretically and it has been found that they are energetically favorable [7,8]. Thus, the recovery reduction observed between 210 and 260 K in the Fe-C alloy can be attributed to the formation of vacancy-carbon clusters during the long-range vacancy migration.

At higher annealing temperatures the Fe - 220 ppm C alloy exhibits to strong stages, labeled IV and V, which do not appear so pronounced in pure Fe. Regarding stage IV, it is evident from fig. 2 that the defects that were trapped during stage III in Fe - 220ppm C and were not allowed to annihilate, are able to recover in stage IV so that $\Delta\rho(T)/\Delta\rho_0$ becomes identical in Fe and the Fe-

C alloy above about 370 K after stage IV is completed. Thus, stage IV is attributed to the de-trapping of vacancies from vacancy-C clusters and their annihilation with other remaining defects as, e.g., higher order interstitial clusters. Finally, stage V must be due to the migration of C and the formation of carbon clusters or carbides. Thus C atoms are removed from the Fe matrix and their contribution to the resistivity of the alloy is reduced. Thus, the final resistivity of the specimen after the recovery annealing is below the initial one. Further experiments on un-irradiated specimens are required in order to clarify the role of irradiation effects in carbon precipitation.

CONCLUSIONS

The resistivity recovery in pure Fe and an Fe - 220 at. ppm C alloy has been measured after 5 MeV proton irradiation at 50 K. The presence of carbon has significant effects on the Fe recovery stages and furthermore causes the appearance of two more higher temperature recovery stages. The results show that there is significant interaction between carbon atoms and interstitial and vacancy defects. At temperatures above 500 K the formation of carbon clusters and carbides results in the reduction of the alloy resistivity.

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