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Interaction of solutes with irradiation-induced defects of electron-irradiated dilute iron alloys

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Abstract

Electrical resistivity recovery spectra were measured between 77 and 200 K on Fe and Fe dilute alloys (Fe–Mo, Fe–Cr, Fe–Si, Fe–P, Fe–Be) irradiated with 2.5 MeV electrons at 77 K in order to study the interaction of substitutional solutes with self-interstitials. Oversized Mo and undersized Si solutes annihilated the recovery stage I_E in pure Fe, whereas slightly oversized Cr, and undersized P and Be solutes yielded new recovery stages below I_E, the positions of which stages shifted toward lower temperatures with increasing solute concentration. These stages are most likely ascribed to the migration and annihilation of mixed-dumbbells formed for the most part in stage I_D. The characteristics of these recovery spectra have not been observed in FCC alloys, which leads to the indication that the mixed-dumbbell in these alloys has a higher mobility than the self-interstitial. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Radiation-induced segregation causes a change in the microstructure of alloys during irradiation. There is a close correlation between the radiation-induced segregation and the size-factor of solutes. Enrichment of solutes at defect sinks takes place below stage III because the mixed-dumbbells migrate, thereby transporting solutes. For this reason, to study the interaction of solutes with self-interstitials is essential to know the various properties of materials subject to irradiation.

From the studies on the interaction of solutes with self-interstitials in FCC metals, it has been generally accepted that there are two kinds of solute traps for freely migrating self-interstitials corresponding to the size-factor of solutes in the metals [1–4]. Oversized solutes, remaining at their lattice sites, trap self-interstitials. In contrast to this, undersized and some slightly oversized solutes combine with self-interstitials to form mixed-dumbbells, displacing themselves from their lattice sites [1–3].

For BCC metals experimental work has been concentrated on Fe alloys, using electrical resistivity and magnetic after-effect measurements [5–10]. Electrical resistivity recovery measurements were performed in some detail by Maury et al. on several kinds of Fe dilute alloys electron-irradiated at around 20 K [5–8]. They obtained the result that the recovery in such alloys as Fe–Cr [6] and Fe–Mn [8] (both solutes are slightly oversized) is enhanced compared to that in Fe between I_D and I_E. This demonstrates a marked difference from FCC metals.

With respect to the resistivity measurements by Maury et al., there still remain two experimental problems to be improved. One is the contamination of specimens by Si resulting from the quartz tube used for heat treatment in a hydrogen atmosphere. The other is the uncertainty of resistivity measurements stemming from ferromagnetic contribution of residual resistivity in the absence of a magnetic field. These problems become serious under the condition that the measurements must be carried out on dilute alloys containing only a small amount of Frenkel pairs (20–30 ppm).

Maury et al. attributed a distinct recovery stage at around 180 K in Fe–Si to the migration and annihilation of mixed-dumbbells formed between I_D and I_E [5]. This result hence raises the question whether or not any undersized solute stabilizes mixed-dumbbells thermally up to temperatures above stage I. This induced the authors to examine the resistivity recovery of Fe–P and Fe–Be,

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both P and Be being significantly less undersized than Si, and to study the dependence of solute size-factor on the recovery temperature, that is, the thermal stability of mixed-dumbbells.

2. Experimental

The high-purity Fe (RRR = 3000–3500) was obtained by zone refining ATOMIRON (99.999%, Showa Denko). The purities of solute elements were as follows: molybdenum (99.999%, JM) and chromium (MARZ grade, MRC) with subsequent zone-refining, silicon (99.9999%, Oki Electric Industry), Phosphorus (99.9999%, Kojundo Chemical Laboratory), and beryllium (99%, NGK Insulators). The five kinds of Fe dilute alloys (Fe–Mo, Fe–Cr, Fe–Si, Fe–P and Fe–Be) were fabricated by zone-leveling. All zone-refining and zone-leveling were carried out by floating technique in a palladium-purified hydrogen atmosphere. From these alloy rods thin wire specimens (0.3 mm in diameter) were prepared by cold-rolling, swaging and drawing. Furthermore heat treatment was followed in a purified hydrogen atmosphere. Special care was taken to remove surface layers of specimens contaminated by silicon during heat treatment at 1073 K in a quartz glass tube [11,12]. Final diameter of each specimen (0.16–0.18 mm) after chemical polishing was evaluated by gravimetry. Potential leads of thin Fe wire (0.08 mm in diameter) were then attached to the specimens by spot welding. Solute concentrations of alloys were determined by chemical analysis for Fe–Mo and Fe–Cr and estimated by using the specific resistivity of solutes in Fe presented in references for Fe–Si [13] and Fe–P [14].

Frenkel pairs were introduced by electron irradiation ($E = 2.5$ MeV, $T_{irr} = 77$ K) using the Dynamitron at the Takasaki Research Establishment of JAERI.

All the electrical resistivity measurements were performed in liquid He and in a longitudinal magnetic field of 53 KA/m in order to reduce residual resistivity originating from ferromagnetic material, which permits the reproducibility of resistivity measurements to be better than 3×10^{-14} Ω m. The heating rate of isochronal annealing between 77 and 200 K was 3 K/3 min.

3. Results and discussion

Fig. 1 shows the measured isochronal resistivity recovery spectra between 77 and 146 K of Fe and Fe–Mo alloys irradiated simultaneously. The irradiation-induced resistivity in Fe, $\Delta\rho_0 = 0.712$ nΩ m corresponds to a Frenkel pair concentration of 24 ppm [15]. From this figure, it is obvious that Mo solutes annihilate the stage I_E(≈135 K) and the recovery decreases with increasing

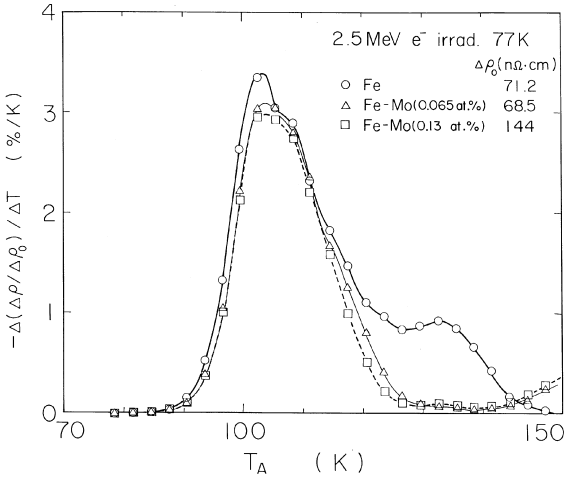

Fig. 1. Differential isochronal resistivity recovery spectra between 77 and 146 K of Fe and Fe–Mo alloys simultaneously irradiated with 2.5 MeV electrons at 77 K. $\Delta\rho_0$ indicates induced resistivity by irradiation.

solute concentration between 120 and 140 K. Similar recovery characteristics have been ordinarily observed in FCC alloys when a solute has an oversized size-factor, which led to the conclusion that solutes trap migrating self-interstitials and prevent them from annihilating with vacancies. Hence Mo solutes trap self-interstitials most likely owing to their oversized volume size-factor ($\Omega_{sf} = 27.5$) [16]. A recovery stage appearing at around 165 K as shown in Fig. 2, the position of which stage shifts scarcely with solute concentration, is accordingly considered as being due to detrapping of self-interstitials from Mo solutes.

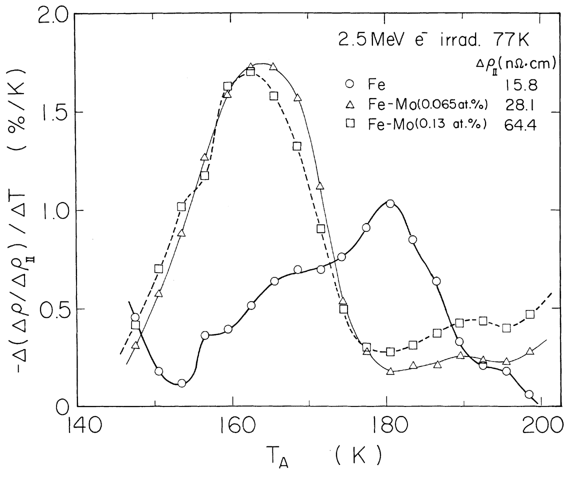

Fig. 2. Differential isochronal resistivity recovery spectra between 146 and 200 K of Fe and Fe–Mo alloys simultaneously irradiated with 2.5 MeV electrons. $\Delta\rho_{II}$ indicates retained resistivity at 146 K.

In Fig. 3 are shown the recovery spectra of Fe–Si alloys together with Fe, which demonstrate a similarity in appearance to the spectra of Fe–Mo alloys in the temperature range of 120–150 K in spite of the fact that Si is an undersized solute in Fe ($\Omega_{sf} = -7.9$) [16]. Furthermore, as indicated in Fig. 4, the recovery spectra measured between 150 and 200 K reveal that a definite stage at around 180 K appearing in the most dilute alloy shifts toward lower temperatures with solute concentration. This induces us to ascribe the disappearance of stage I_E to formation of mixed-dumbbells and the appearance of 180 K stage to migration and annihilation of mixed-dumbbells as pointed out already by Maury et al. [5].

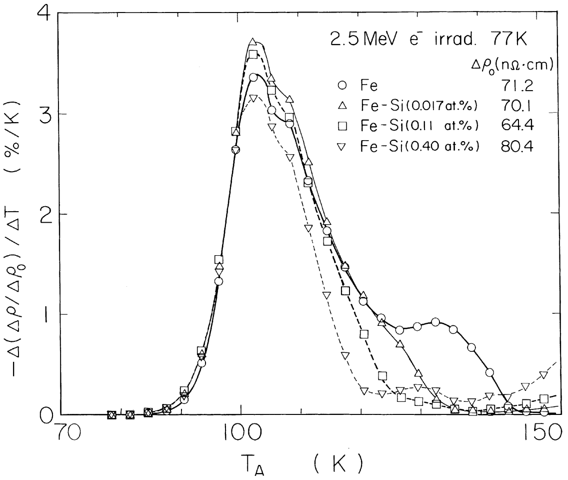

Fig. 3. Differential isochronal resistivity recovery spectra between 77 and 146 K of Fe and Fe–Si alloys simultaneously irradiated with 2.5 MeV electrons at 77 K. $\Delta\rho_0$ indicates induced resistivity by irradiation.

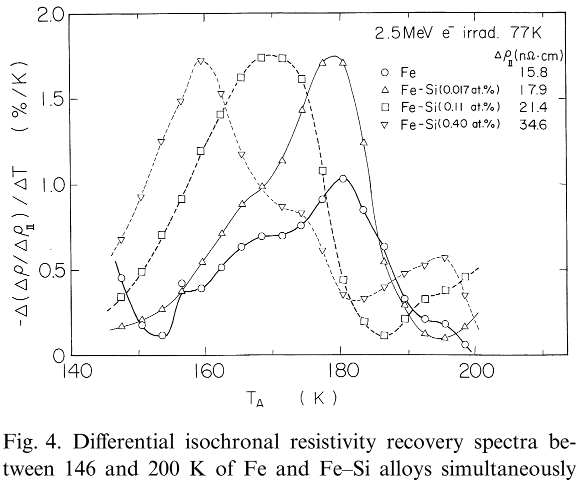

Fig. 4. Differential isochronal resistivity recovery spectra between 146 and 200 K of Fe and Fe–Si alloys simultaneously irradiated with 2.5 MeV electrons. $\Delta\rho_{II}$ indicates retained resistivity at 146 K.

Fig. 5 shows the recovery spectra of Fe and Fe–Cr alloys ($\Omega_{sf} = 4.4$) [16]. A new distinct recovery peak below I_E shifts its position toward lower temperatures and increases its amplitude with increasing solute concentration. On the other hand, another recovery stage was found at around 180 K as shown in Fig. 6, the position of which stage does not shift sensitively with solute concentration. The characteristics of the two stages suggest that mixed-dumbbells migrate and get trapped at solutes below I_E, and get released from them and thereby annihilate with vacancies above I_E.

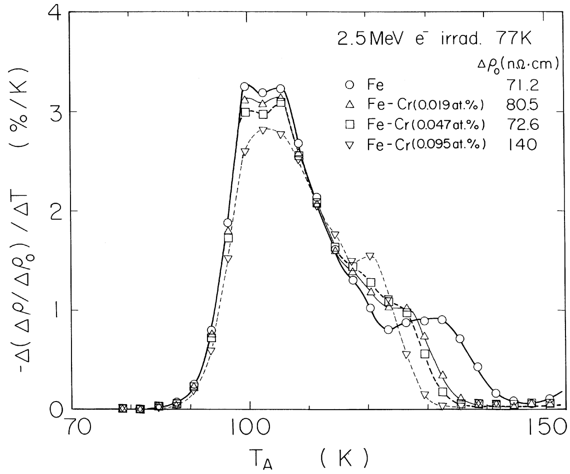

Fig. 5. Differential isochronal resistivity recovery spectra between 77 and 146 K of Fe and Fe–Cr alloys simultaneously irradiated with 2.5 MeV electrons at 77 K. $\Delta\rho_0$ indicates induced resistivity by irradiation.

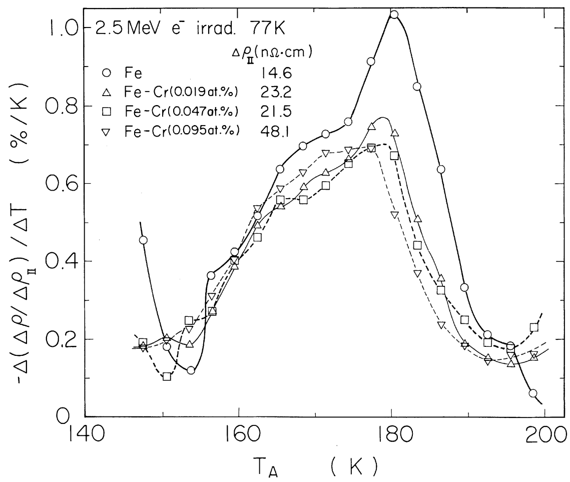

Fig. 6. Differential isochronal resistivity recovery spectra between 146 and 200 K of Fe and Fe–Cr alloys simultaneously irradiated with 2.5 MeV electrons. $\Delta\rho_{II}$ indicates retained resistivity at 146 K.

Fig. 7 demonstrates the recovery spectra of dilute Fe–P alloys between 10 and 100 ppm of solute concentration together with Fe, which spectra indicate a marked similarity to those of Fe–Cr. Despite P is less undersized than Si ($\Omega_{sf} = -13.2$) [16], mixed-dumbbells in Fe–P have been found to be more mobile than self-interstitials. In Fig. 8 are also shown their subsequent recovery spectra between 146 and 200 K. The stage at around 165 K is regarded as corresponding to that at around 180 K in Fe–Cr.

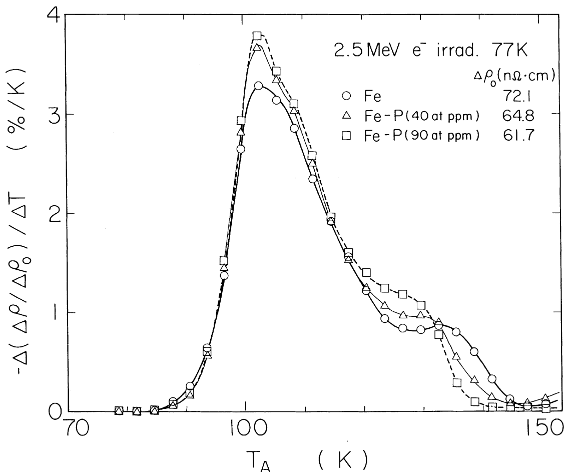

Fig. 7. Differential isochronal resistivity recovery spectra between 77 and 146 K of Fe and Fe–P alloys simultaneously irradiated with 2.5 MeV electrons at 77 K. $\Delta\rho_0$ indicates induced resistivity by irradiation.

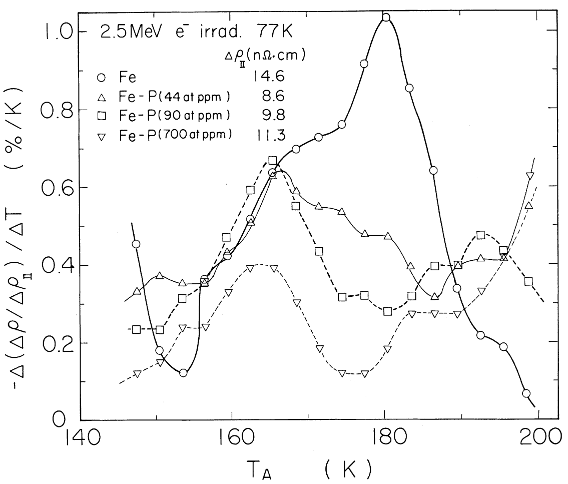

Fig. 8. Differential isochronal resistivity recovery spectra between 146 and 200 K of Fe and Fe–P alloys simultaneously irradiated with 2.5 MeV electrons. $\Delta\rho_{II}$ indicates retained resistivity at 146 K.

In Fig. 9 is compared the recovery curve of Fe–Be with Fe between 77 and 146 K, Be being the most undersized of solutes examined ($\Omega_{sf} = -26.2$) in the present experiments [16]. The distinct discrepancy in the peak position of I_D between Fe and Fe–Be is due to a transient temperature rise in Fe–Be during irradiation. This stage and another stage at around 170 K also describe the characteristics similar to those of Fe–P and Fe–Cr. As concerns the lower temperature stage, the position of the peak shifts toward lower temperature for Fe–Be than for Fe–P. Consequently, for the undersized solutes, it has been found that an increase of the volume-size misfit tends to enhance the mobility of mixed-dumbbells.

In both fcc and bcc metals, it has generally been believed that undersized solutes combine with self-interstitials and the resulting mixed-dumbbells are thermally more stable than self-interstitials. As indicated in Figs. 7 and 9, however, this appears inapplicable to the mixed-dumbbells in Fe–P and Fe–Be. It seems reasonable to assume that the ferromagnetic ordering contribution to the thermal stability of a self-initial is extremely important in Fe. As for 3d magnetic transition element solutes with a slightly oversized size-factor (Fe–Cr, Fe–Mn, Fe–Co, Fe–Ni), Lucasson et al. pointed out a positive correlation between the mobility of a mixed-dumbbell and the magnetic moment disturbance at surrounding Fe atoms due to a substitutional solute on the basis of their recovery measurements [17]. From the experimental [18] and the theoretical [19] work, in the case of Fe–Co and Fe–Ni, the solute with a positive local moment enhances the magnetic moment of surrounding Fe atoms, which results in a positive change in total magnetization. On the contrary, for Fe–Cr, a negative solute moment increases the nearest neighbor Fe

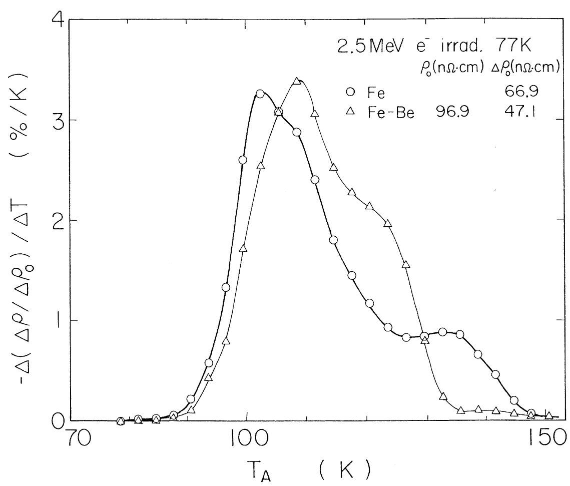

Fig. 9. Differential isochronal resistivity recovery spectra between 77 and 146 K of Fe and Fe–Be alloy simultaneously irradiated with 2.5 MeV electrons at 77 K. $\Delta\rho_0$ indicates induced resistivity by irradiation.

moment and decreases the next nearest neighbor Fe moment, and brings about a negative change in total magnetization as a result. For Fe–Mn, the reduction of total magnetization is also found in spite of the differences in the details of the magnetization between the experimental and theoretical work. Hence the thermal stability of mixed-dumbbells in Fe–Co and Fe–Ni corresponds to the increase of total magnetization, whereas the thermal instability of those in Fe–Mn and Fe–Cr corresponds to the decrease of total magnetization.

All of the undersized solutes studied in the present experiments have no d-electron. Both the experimental and the theoretical studies [20,21] ascertained that a substitutional Si in ferromagnetic Fe produces a magnetic vacancy at its site and a negligible change in saturation magnetization at surrounding Fe atoms. Such a fairly lacalized magnetic disturbance as this also arises for a Be solute and may be expected for a P solute [22]. Hence the difference in thermal stability of mixed-dumbbells between non-transition metal solutes is not directly related to the valency of solutes or to the magnetic disturbance due to substitutional solutes.

The magnetic disturbance in the vicinity of a mixed-dumbbell must greatly differ from that of a substitutional solute. In its heavily compressed configuration, the shorter interatomic distance may change the effective filling of d-band of surrounding Fe atoms and the resulting magnetic perturbation because of the overlapping and screening effects existing between the solute wave function and the spin-orbitals of neighboring Fe atoms. However the details of the magnetic disturbance induced by a mixed-dumbbell as well as a self-interstitial have not been elucidated experimentally or theoretically, leaving the problem to the future studies.

4. Conclusions

The conclusions obtained from the recovery spectra of Fe dilute alloys electron irradiated are as follows:

1. The oversized Mo solutes trap migrating self-interstitials and release them above stage I_E.
2. The undersized Si solutes trap migrating self-interstitials and the resulting mixed-dumbbells migrate and annihilate above stage I_E.
3. The mixed-dumbbell in Fe–Cr (Cr; slightly oversized) migrates below I_E.
4. The mixed-dumbbells in Fe–P and Fe–Be are thermally unstable and migrate below I_E in spite of the fact that P and Be have undersized volume-size factor in Fe.
5. For undersized solutes, it has been revealed that the thermal stability of mixed-dumbbells tends to enhance with decreasing volume-size misfit of solutes.

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