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Internal friction study of dislocation dynamics in neutron irradiated iron, and iron–copper alloys

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ABSTRACT

The temperature dependent internal friction spectra of cold-worked and neutron irradiated iron and iron–copper binary alloys are investigated. By increasing dose, both γ- and Snoek-Köster-relaxation peaks exhibit strong shift towards low temperatures, as a consequence of the reduction of double kink activation energy. This shift is found to be the largest in alloys with the highest copper content. Besides, new modes appear in the spectra at energies of about 410 and 540 K. The 410 K peak intensity increases at the expense of Snoek-Köster peak intensity, indicating that redistribution of carbon takes place under irradiation, most probably as a result of grain boundary segregation. The presence of copper impedes the carbon redistribution by influencing the formation of carbon-vacancy complexes, which causes the grain boundary segregation, and activation of the 410 K relaxation process at larger neutron fluence in comparison with pure iron.

1. Introduction

The motion of dislocations and their interaction with defects are one of the most important causes of mechanical damping in metals. In general, defects induce distortions of the lattice and create the obstacles for dislocations by reducing dislocation mobility. Dislocation–defect interaction depends on the type, size, concentration and position of the defects in the lattice, which in combination with thermal fluctuations creates plethora of possible damping mechanisms [1]. The resulting energy dissipation is known as an internal friction (IF) effect, and can be observed by measuring the time-dependent e.g. anelastic deformation of a solid subjected to an external stress [2]. In contrast to dislocation–point defect interaction which is elaborated both experimentally and theoretically [1,2], the role of extended crystal defects, such as vacancy clusters, self-interstitial atom (SIA) clusters, and secondary phase precipitates, is not yet fully understood. These defects are typically formed by electron or neutron irradiation, as a consequence of complex defect kinetics [3]. Since deformation behavior governs the material performance, the influence of irradiation-induced defects to the dislocation dynamics is especially important in iron alloys which are used in nuclear applications [4].

This work reports the analysis of the temperature dependent IF spectra of plastically deformed, neutron irradiated iron and iron–copper binary alloys, as a part of the PERFECT project. Within this project, the advanced experimental techniques, and computer simulations are performed in combined fashion on the same "REVE" materials [5], in order to enable detailed investigation of the physical properties of nano-defects induced by irradiation. By measuring the IF spectra of cold-worked neutron irradiated pure iron, the influence of irradiation induced matrix damage on dislocation-related relaxation processes can be studied, whereas for Fe–Cu alloys the combined effects of Cu-precipitation and matrix damage could be analyzed.

2. Materials

The materials used in this study are polycrystalline iron alloys: the nominally pure Fe, Fe–0.1%Cu, and Fe–0.3%Cu. The chemical composition of the investigated materials is given in Table 1. The neutron irradiation is performed in the Belgian Reactor (BR2) up to four doses of, 0.026, 0.051, 0.1, and 0.19 displacement per atom, dpa, $(1.5, 3.0, 6.9, 12.5 \times 10^{19}\ \mathrm{n/cm^2})$, at the temperature and pressure of about 300 °C and 150 bar, respectively. The details of the sample preparation and irradiation conditions were published elsewhere [6].

3. Experiment

The internal friction measurements are performed in an inverted torsion pendulum [7] operating in free vibration at about 1.8 Hz (with a typical sample size of $1.3 \times 1.3 \times 30\ \mathrm{mm^3}$), in the temperature range between 100 and 600 K. From the free decay signal, the resonance frequency, ω, and the internal friction coefficient, Q^{-1}, which is proportional to the ratio of the energy dissipated during one cycle to the maximum elastic energy stored

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Table 1
The nominal composition of investigated alloys.

Material	Nominal composition (wt.%)
Pure Fe	(<200 ppm impurities, ∼ 30 ppm C)
Fe–0.1%Cu	0.1%Cu (∼30 ppm C)
Fe–0.3%Cu	0.3%Cu (∼30 ppm C)

in the sample, are determined. The measurements have been performed at a strain amplitude of about 10^{-4}, and in a He atmosphere with a heating rate of about 1.5 K/min. No magnetic field is applied. Prior to the measurements all samples are, in a consistent way, subjected to a torsional cyclic plastic deformation by an angle of $\pi/2$ over a length of 30 mm at room temperature. This corresponds to a local deformation of about 6% ($\pi R/L$).

4. Results and discussion

The internal friction coefficient, Q^{-1}, as a function of temperature for cold-worked, non-irradiated, and neutron irradiated Fe, Fe–0.1%Cu, and Fe–0.3%Cu is shown in Fig. 1. The non-irradiated IF spectra show the existence of two structures centered at about 345 and 525 K, in a very good agreement with previous measurements [8,9]. The overall shape of the 345 K peak, e.g. the temperature position of the maximum, and the full width at half maximum (FWHM) indicate that this mode originates from the thermal activation of dislocation motion, also known in the literature as the γ-relaxation process. The 525 K peak also appears as the consequence of plastic deformation, and represents typical Snoek-Köster relaxation (SK) of carbon interstitial solute atoms (ISA) in the vicinity of moving dislocations [10].

In irradiated samples new modes appear in the IF spectra, resulting in a complex, broad, four-mode structure, see Fig. 1. All modes have similar FWHM, do not appear in non-deformed samples, and completely disappear in well annealed samples which indicates their link to dislocation motion, see Fig. 2. In order to analyze such complex behavior, we fit the IF spectra with a standard Debye's relaxation equation

$$Q^{-1} \sim \Delta \frac{\omega\tau}{1+(\omega\tau)^2}, \tag{1}$$

generalized to the case of four relaxation processes, including an exponential background. The Δ is the relaxation strength, ω is a frequency, and τ is the relaxation time $\tau = \tau_0 e^{\frac{E}{k_B T}}$ with E being the activation enthalpy (energy). The fact that dislocation motion is not governed by a single relaxation time and manifested by a large FWHM of the IF peaks (∼60 K for the γ-peak), is accounted for in the model by incorporating a Gaussian distribution of the relaxation times, $\Phi(\tau) = \frac{1}{g\sqrt{\pi}} e^{-\left(\frac{\tau}{g}\right)^2}$. The results of the fit are shown as full lines in Fig. 1. The peak positions of all modes (denoted as P_1, P_2, P_3, and P_4) and the integrated peak intensities of P_2 and P_3 modes as a function of dose are presented in Figs. 3 and 4, respectively. New relaxation peaks, P_2 and P_4, appear at high temperature side of both γ- and SK-relaxation peaks (P_1 and P_3 in Fig. 1), and they are marked in dark- and light-gray colors, respectively. The main observations are the following. (a) The P_1 peak position substantially shifts towards lower temperatures for about 30–40 K, with the largest shift in Fe–0.3%Cu. (b) In both Fe–0.1%Cu and Fe–0.3%Cu alloys the P_2- and P_4-peaks appear at the higher dose with respect to pure iron. (c) The intensity of the P_2 mode increases by increasing the dose at the expense of the P_3 mode. (d) The P_3-peak position decreases by increasing the dose mimicking the P_1 shift. The accompanying effects are a decrease of the background and overall decrease of the peak intensities by increasing the dose and copper content, respectively.

4.1. The γ- and Snoek-Köster relaxations

By increasing dose, the P_1 and P_3 peak positions shift towards lower temperatures in a similar way, see Fig. 3. The activation en-

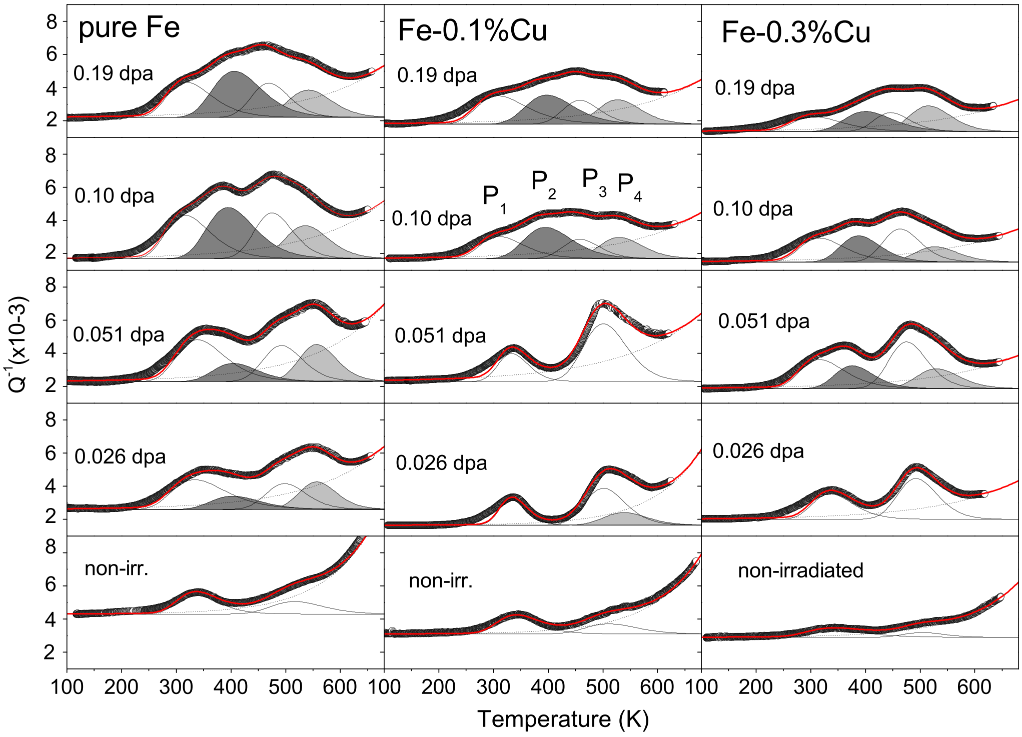

Fig. 1. The internal friction spectra as a function of the temperature of plastically deformed and neutron irradiated Fe, Fe–0.1%Cu, and Fe–0.3%Cu, measured at the frequency of about 1.8 Hz.

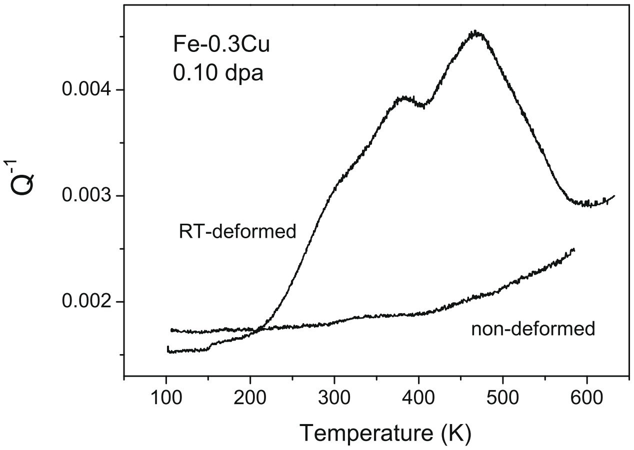

Fig. 2. The internal friction spectra as a function of the temperature of neutron irradiated Fe–0.3%Cu, measured for non-deformed and room temperature deformed conditions.

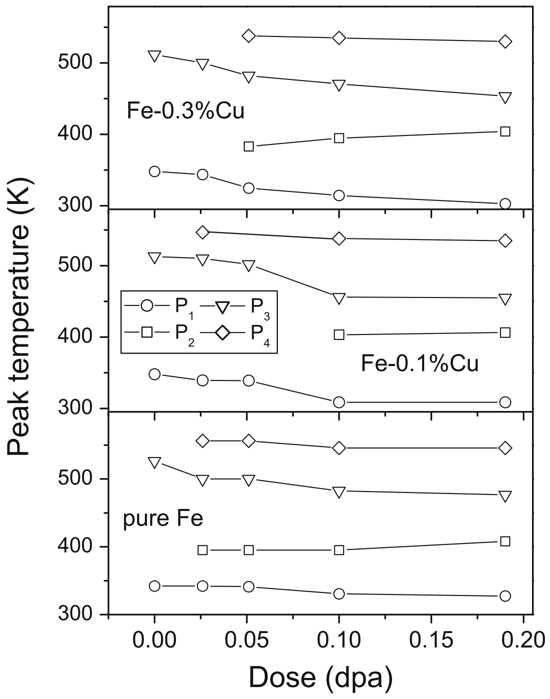

Fig. 3. The internal friction peak positions as a function of dose.

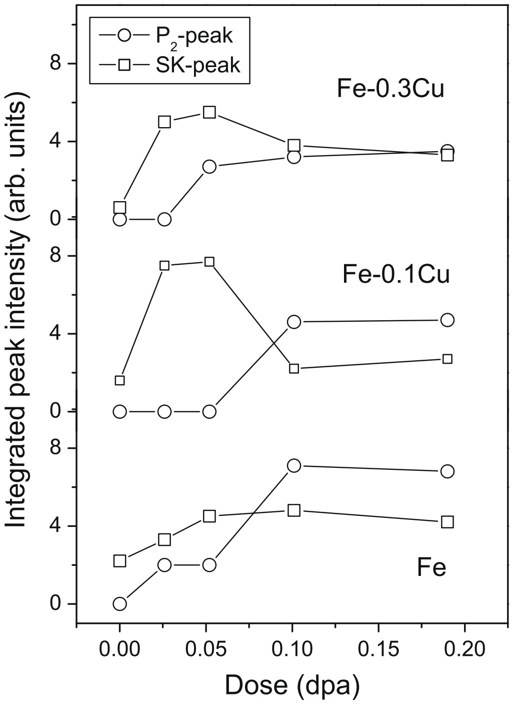

Fig. 4. The E_2- and SK-peak integrated intensities as a function of dose.

ergy of Snoek-Köster-relaxation process can be written as, $E_3 \sim E_1 + E^C_{migr.}$ [11], so the P_3 peak shift can be fully assigned to the shift of the γ-relaxation peak (P_1). The γ-relaxation originates from thermally-activated dislocation motion, which occurs via nucleation and diffusion of the kink–antikink pairs (kink-pairs) [12]. A kink is a short segment of dislocation line crossing the Peierls energy valleys. This process ensures that the dislocation segment can overcome the Peierls barriers [13], and relieve the stress in the material. Its activation energy can be written as $E_\gamma = 2H_K + H_K^M - 2k_BT$ [11], where H_K and H_K^M are kink nucleation and migration enthalpies, respectively. Therefore, the shift of the γ-peak towards low temperatures could be due to reduction of either H_K or H_K^M. According to the literature [14], the migration enthalpy of the kink in pure iron is estimated to be 0.001 eV, which is much smaller than the shift of the γ- and SK-peaks. Therefore, the shift of the γ-peak should be attributed to the change of H_K. Neutron irradiation causes the formation of SIA and vacancy clusters which is fully confirmed in these samples by transmission electron microscopy (TEM) [15] and position annihilation spectroscopy (PAS) [16]. According to recent *ab initio* and kinetic Monte Carlo simulations, these clusters are practically immobile around room temperatures [3], forming strong obstacles for dislocation motion. Consequently, the change of the Peierls potential and/or kink interaction energy could affect, under these irradiation conditions, the H_K, causing the peak shifts.

Interestingly, by increasing dose, the SK-peak intensity exhibits first increase and then decrease, see Fig. 4. The increase is mainly related to early irradiation stage, e.g. there is a large intensity increase from non-irradiated to irradiated conditions, while the decrease is observed in the samples irradiated to 0.1 and 0.19 dpa. Since the SK-relaxation corresponds to joint thermally-activated motion of carbon atoms and dislocations, the SK-peak intensity change can be associated to the existence of carbon redistribution caused by irradiation. However, precise origin of microstructural process which is responsible for the observed carbon redistribution is not possible to uniquely determine from the IF measurements. Typically, carbon redistribution takes place as a consequence of carbon migration from and to the grain boundary. Moreover, the initial SK-peak increase could also occur as a consequence of the destruction of less stable Fe-carbides (cementite) by cascades. Then, at the high dose, the carbon migration may occurs due to combined effects of thermal fluctuations and vacancy formation, leading eventually to the carbon grain boundary segregation and decrease of the SK-peak intensity.

4.2. The 410 and 540 K relaxations

The peak P_2 ($E_2 = 410$ K) appears at the temperature which is about 60 K higher in energy then the γ-relaxation peak, see Figs. 1 and 3. The peak position remains approximately constant, while intensity increases by increasing dose. It is important to note that the large intensity increase of the P_2-peak appears at high dose, in contrast to intensity increase of the SK-peak. Moreover, the P_2-intensity increase seems to occur at the expense of the SK-peak. Accordingly, if the decrease of SK-peak indicates the carbon grain boundary segregation, the P_2-mode can be assigned to the relaxation process related to grain boundary carbon. The relaxation peak with similar activation energy, assigned to carbon redistribution has been also observed in irradiated reactor pressure vessel (RPV) steels [17].

Another possibility is that P_2 mode occurs as a consequence of the modified Peierls energy for dislocation due to presence of large immobile SIA clusters and voids. However, this scenario can be discarded since the estimated volume fraction of the crystal affected by such obstacles is less than 0.1% [18]. In this case, the P_2-peak intensity should be much smaller then the P_1-peak intensity, which is not observed.

The P_2 peak could also originate from the SK type-of relaxation, corresponding to migration of defect clusters in the vicinity of thermally-activated dislocations, analogous to the case of heavy interstitials. However, for these irradiation conditions it is expected that most defect which are formed are large and immobile, thus could not contribute to this type of relaxation. Moreover, it is not clear how large and spatially extended defects could participate in such process, which is essentially valid only for the point defects.

Therefore, we assigned the 410 K peak to relaxation process involving grain boundary carbon.

The P_4-peak at about 540 K accompanies the appearance of the P_2-peak, indicating their common origin. However, both the activation energy as well as intensity of this mode do not change by increasing dose in contrast to all other modes. At the moment it is not clear what could be the origin of this relaxation process.

4.3. The copper effects

The formation of irradiation-induced copper precipitates influences the shift of the γ-relaxation process. The γ-peak shift if found to be the largest in the sample with the highest copper content, of about 45 K in Fe–0.3%Cu irradiated to 0.19 dpa. In this case, the change of kink-pair activation energy is about 50% larger in comparison with pure iron (the maximum shift in nominally pure iron is about 30 K), which points to equally important contribution of copper precipitation to the dislocation pinning and hardening as those related to the matrix damage.

The presence of large irradiation-induced defects such as SIA's, and copper precipitates is also observed in the background of the IF spectra. These obstacles represent strong pinning points for dislocations by reducing the dislocation length, which leads to a decrease of damping [19]. This is manifested in the IF spectra as a strong reduction of the overall background, clearly visible in all materials at high temperatures.

As already mentioned, in Fe–0.1%Cu and Fe–0.3%Cu alloys the activation of P_2-, and P_4-relaxation processes is postponed until high dose, see Figs. 1 and 2. This behavior can be also understood as a consequence of the presence of copper. Following the proposed scenario for the P_2-relaxation process, it can be concluded that the presence of copper prevents the carbon grain boundary segregation. This effect could be correlated with copper affecting the vacancy distribution. Namely, at the low dose, besides forming vacancy-carbon complexes, the vacancies partially segregate at copper sites which effectively reduce the carbon redistribution in comparison with pure iron. As a result, carbon grain boundary segregation occurs at the high dose, namely at 0.1 and 0.052 dpa in Fe–0.1%Cu, and Fe–0.3%Cu, respectively.

The existence of irradiation-induced carbon redistribution, e.g. carbon grain boundary segregation, could cause the effective decrease of hardening. In fact, our result indicate that two competing mechanisms contribute to the irradiation-induced hardening process. First one is related to the matrix damage and copper precipitation, and the second one originates from the carbon redistribution. At the low dose, both hardening mechanisms contribute, especially in copper rich alloys. This is due to formation of copper precipitates, and due to increase of fresh supply of carbon as a consequence of neutron induced carbon redistribution. At the high dose, the contribution to the hardening from copper precipitates reaches saturation [16], and the carbon is removed from the iron matrix due to grain boundary segregation. Therefore, at the high dose the second mechanism prevail, which could lead to the irradiation-induced effective softening in these materials. The reported yield strength data of the same set of materials [6] support these conclusions. The initial yield strength increase depends on the copper content. It is the largest for the largest copper content. However, after initial increase, the hardening reaches a plateau, and even decreases for the highest dose, see Fig. 1 in [6]. The existence of softening supports the explanation based on the interplay between two hardening mechanisms, in a very good agreement with the internal friction data.

5. Conclusions

As a conclusion, the internal friction spectra of cold-worked and neutron irradiated iron and iron–copper binary alloys provide the evidence for two hardening mechanisms. The fist contribution, related to the matrix damage and copper precipitation, is manifested by the decrease of the γ-peak energy and overall decrease of the damping e.g. internal friction background. The second hardening mechanism occurs due to carbon redistribution, triggered by neutron irradiation, and it is characterized by the intensity interplay of SK and P_2 peaks. Under certain conditions, which are met in these materials and irradiation conditions, these two mechanisms could lead to the effective softening at high dose.

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References

[1] J.P. Hirth, J. Lothe, in: Theory of Dislocations, John Willey and Sons, New York, 1982.
[2] A.S. Nowick, B.S. Berry, Anelastic Relaxation in Crystalline Solids, Academic, New York, 1972.
[3] C.C. Fu, J. Dalla Tore, F. Willaime, J.L. Bocquet, A. Barbu, Nature Mater. 4 (2005) 68.
[4] S.B. Fisher, J.E. Harbottle, N. Aldrige, Phil. Trans. R. Soc. Lond. A 315 (1985) 30.
[5] L. Malerba, E. van Walle, C. Domain, S. Jumel, J.C. Van Duysen, in: Proceedings of the 10th International Conference on Nuclear Engineering, ICONE-10, The American Society of Mechanical Engineers, 2002.
[6] K. Verheyen, M. Jardin, A. Almazouzi, J. Nucl. Mater. 351 (2006) 209.
[7] M.J. Konstantinović, Phys. Rev. B 78 (2008) 052104.
[8] H. Mizubayashi, H. Konmüller, A. Seeger, J. Phys. c10 (1985) 309.
[9] V. Hivert et al., Phys. Stat. Sol (a) 42 (1977) 511.
[10] W. Köster, L. Bangert, R. Hahn, Arch. Eisenhüttenw. 25 (1954) 569.
[11] A. Seeger, J. Phys (Paris) Colloq. 42 (1981) C5–201.
[12] A. Seeger, P. Schiller, Acta Metall. 10 (1962) 348.
[13] R. Peierls, Proc. Phys. Soc. 52 (1994) 34.
[14] H. Schultz, Matt. Sci. Eng. A 141 (1991) 149.
[15] M. Hernandéz-Mayoral, D. Gómez-Briceño, J. Nucl. Mater., submitted for publication.
[16] M. Lambrecht, L. Malerba, A. Almazouzi, J. Nucl. Mater. 378 (2008) 282.
[17] A. Munier, M. Maamouri, R. Schaller, O. Mercier, J. Nucl. Mater. 202 (1993) 54.
[18] The volume fraction in nominally pure Fe is estimated to be $V \sim d^3 n_d < 0.001$, where $d \sim 8$ nm is the diameter of SIA cluster, and $n_d \sim 4 \times 10^{21} m^{-3}$ is their number density, after [15].
[19] A. Granato, K. Lücke, J. Appl. Phys. 27 (1956) 583.