Annealing of defects in Fe after MeV Heavy ion irradiation

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We report study of recovery dynamics, followed by in-situ resistivity measurement after 100 MeV oxygen ion irradiation, in cold rolled Fe at 300K. Scaling behavior with microstructural density and temperature of sample have been used to establish stress induced defects formed during irradiation as a new type of sink. The dynamics after irradiation has been shown to be due to migration of defects to two types of sinks i.e. stress induced defect as variable sinks and internal surfaces as fixed sinks. Experimental data obtained under various experimental conditions have been fitted to theoretical curves. Parameters thus obtained from fitting are employed to establish effect of electronic energy loss and temperature on recovery dynamics and stress associated with variable sinks.

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Transfer of energy after inelastic collision suffered by swift MeV ions, to lattice atoms, is well established now. The dissipation of ion energy takes place in two stages. The lattice electrons initially pick up large kinetic energies which couple to the lattice atoms through electron-phonon (e-p) coupling. This is seen to induce defect production in several metals (Fe, Ni, Ti etc.) \([1,2]\), where e-p coupling is large, and also in metals where this is not very large such as Cu and Ag \([3]\). Moreover, in metals where very strong e-p coupling exist (Al, Ni and Pt) \([1,4]\) an anomalous reduction in defect density is noticed. This is ascribed to radiation annealing, leading to decay of single interstitials.

Several years ago, quenching-in of vacancies in noble metals was established by Bauerle and Koehler \([5]\), Kimura et al. \([6]\) and De Jong and Koehler \([7]\) by following their annealing behavior employing electrical resistivity measurements. These were later substantiated by transmission electron microscopy (TEM) \([8,9]\). The relative decrease in quenched-in resistivity as a function of time showed S-shaped curves instead of an exponential decay expected due to annihilation of single vacancies with high activation energies of motion. Departure from exponential decay was assigned to formation of divacancies, vacancy clusters and deposition of vacancies at sessile ring sites with low activation energy.

Swift MeV ions, passing through thin specimens, subject the material predominantly to electronic excitations as the ion ranges are sufficiently large. Following e-p coupling, the lattice atoms are agitated around the ion irradiation site, possibly in concentric circles (assuming electronic conductivity to be isotropic for a polycrystalline specimen). Under low flux these circles will not overlap. This will lead to regions which are at high temperature directly in contact with cold regions, contiguous in space. A situation similar to quenching can arise if the hot-cold interface temperature difference is reasonably large, allowing the formation of vacancies. This will probably
be most efficient at natural interfaces, for example, at dislocation and grain boundaries of cold rolled metallic foils.

In this Letter we shall try to establish result of electronic excitation in a pure Fe foils by following time evolution of electrical resistivity after subjecting them to MeV ions. This method not only allows us to confirm defect production through MeV ion irradiation but shed further light on the long term annealing products such as vacancy clusters or sessile rings, as established before employing other procedures [5-7].

Polycrystalline metal foils (99.99% pure, Goodfellow, UK) were irradiated with 100 MeV oxygen ions \(S_e \sim 2MeV/\mu m\) accelerated with the help of a 15 UD pelletron at NSC, New Delhi. A constant flux of \(8.8 \times 10^9\) ions cm\(^{-2}\) sec\(^{-1}\) was maintained normal to the surface of the sample while an in-situ four probe resistivity measurement at constant sampling current monitored the time evolution of defect density. Response Voltage (RV) was collected every t= 0.2 sec using a computer controlled Keithley nanovoltmeter. Foils (10\(\mu m\) thick) of Fe were mounted on mica or sapphire substrates for electrical isolation from the sample holder. Temperature during irradiation, monitored with the help of a thermocouple placed next to the sample, was held constant by thermalising with a large constant flow copper cryostat. The low ion flux maintained on the sample does not produce any temperature rise. This is confirmed by directly measuring on thermocouple. The MeV ions on entering solid targets lose part of their energy to the nuclear \(S_n\) and electronic \(S_e\) subsystems. The two loss processes can be spatially separated by appropriately choosing the thickness of the target. In this study, changes in the intrinsic physical property of the system would be primarily \(S_e\) related as ion range (from TRIM \([10]\) code is 37\(\mu m\)) is much larger than the thickness of Fe foils.

In an earlier report we \([11]\) showed evidence of strain induced by electronic energy loss using x-ray topography (XRT) for strain mapping in a Si(001) sin-
single crystal. In polycrystalline metal foils, individual grains can be thought of as “single crystals” with dislocation lines providing natural interfaces. Under stress, generated by ion irradiation at an interface, atoms in a dislocation line can be moved to generate line defects termed as stress induced defects (SID). Motion of atoms at dislocations generated this way is reversible as the stress induced by $S_e$, when removed, initiates a fall of resistivity to its pre-irradiated value. The reversible motion of dislocations under stress, contributes a reversible plastic strain component to the total strain, and can be detected during measurement of strain dependent physical parameters. These defects are different from point defects as has been established by their different scaling behavior with temperature \cite{11}. Under favorable conditions, positive feedback sets in, resulting in formation of dissipative structures \cite{12}. These structures are maintained as long as energy is supplied by the incoming ions. On switching the beam off, these structures decay along with decay of SID’s resulting in jumps in RV. This decay is followed by migration of defects to remnant structures left after the dissociation of dissipative structures at internal surfaces.

In this experiment we try to understand in detail the dynamics involved during defect migration far away from the irradiation event. In Fig.1 we show plot of fraction of defects remaining $(\frac{\Delta RV}{\Delta RV_o})$ vs time ($t$) for cold rolled Fe after 100 MeV oxygen ion beam was switched off at room temperature. The data point at $t = 0$ delineates the SID region from the annealing region and hence signifies starting of annealing behavior. Fraction of defects remaining is defined as

$$\frac{\Delta RV}{\Delta RV_o} = \frac{RV(t) - RV(t = \text{infinity})}{RV(t = 0) - RV(t = \text{infinity})}$$

Polycrystalline metals are characterised by large amount of inherent defect structures like grain boundaries, dislocation lines etc. These structures are
efficient sinks for non-equilibrium defects. Under the influence of thermodynamic forces non-equilibrium defects migrate to sinks. Assuming the number of sinks to remain constant in time, annealing of defects takes place exponentially \[13\]. Under certain thermodynamic conditions a new type of sink is formed, identified in the literature as a variable sink. This sink is characterised by explicit time dependence on the number of sinks. Annealing of defects to variable sinks generate S-shaped decay curves. Presence of both type of sinks in any material would generate decay curves having the characteristics of fixed and variable sink decay. Depending on relative density of each type of sinks, two cases are important: (1) density of variable sinks is larger than density of fixed sinks and (2) density of variable sinks is comparable to density of fixed sinks. In the former case functional form of decrease in defect concentration with time is given as \[6\]

\[ V(t) = \frac{V_o}{(\text{Cosh}(\beta t))^2} \]  

where, \( V_o \) is the concentration of defects before annealing and, \( \beta \) is the rate parameter. In the latter case, the decay process is a combination of first order kinetics due to migration of defects to fixed sinks and decay originating due to variable sinks. Assuming the number of defects migrating to fixed sinks to be independent of concentration of variable sinks and vice versa, decay is solution of two simultaneous differential equations \[13\]. Analysis of the above decay is too involved to allow determination of physical parameters from our experimental curves due to lack of data on concentration of different types of sinks. However an analysis based on fitting procedure is possible by considering the decay to be composed of additive parts as described above. Functional form of the decay would be

\[ V(t) = \frac{V_o}{(\text{Cosh}(\beta t))^2} + Ae^{-t/\tau} \]  

where \( A \) is the constant of proportionality.
Good fitting was obtained for decay dynamics in Fig.1 with equation 2. Fitting to the experimental data was helped by the following observations: (1) tail of decay curve is dominated by the exponential function and provides the slope of exponential fall and (2) initial decay is dominated by variable sink and hence would provide an estimate of $\beta$. The solid line represents a theoretical fit to the experimental data (circle). Curves a and b represent the individual contribution of variable sink and fixed sink to total recovery dynamics. Ratio of $V_0$ and $A$, $R_{V_0/A}$ is a quantity signifying contribution of variable sink with respect to fixed sink. Values obtained for the quantities $R_{V_0/A}$, $\beta$ and $\frac{1}{\tau}$ from fitting are 23.89, 0.136633 ± 0.0005 sec$^{-1}$ and 0.059 ± 0.014 sec$^{-1}$ respectively.

It is well known that point defects exist in metals at all temperatures but the concentration is in thermal equilibrium and hence low. In order to study properties of defects like energy of migration, energy of formation etc. and their effects on physical properties of a host metal, defects are engineered in excess or non-equilibrium concentrations. The process of allowing non-equilibrium concentration of defects at a given temperature to come to equilibrium is termed as annealing. Recent investigation of Ti [2,14] under high energy ion irradiation showed phase transformation from $\alpha$ phase to metastable $\omega$ phase. It is known that Ti undergoes this kind of transformation when subjected to high static pressure of 8 Gpa [15,16] for about 24 hours. Similarities observed in effects due to irradiation and pressure supports us in using kinetics observed under quenching to kinetics observed under irradiation. In our experiment we engineer non-equilibrium concentration of defects using high energy ion irradiation. Behavior of RV after switching the beam off would fall in the regime of annealing theory and plots obtained would be termed as annealing plots.

In order to justify SID as variable sinks we compare annealing plots of
Fe foils after 200 MeV silver ion irradiation for different temperatures and microstructural density. In Fig.2a we show $\Delta RV / \Delta RV_o$ vs t for cold rolled and annealed Fe. Annealed Fe shows an exponential decay after an initial rise whereas cold rolled Fe shows an S-shaped decay characteristic of variable sinks. Under high energy ion irradiation individual ions deposit large amount of energy in a local region. This region thermalises in time scales of the order of $10^{-12}$ sec thus simulating conditions similar to quenching. Variable sinks have been observed in quenched gold, with divergent models being proposed of their geometry and process of production [5-9]. Under irradiation, if variable sinks originate due to quenching then annealed Fe should also show S-shaped decay. But this is certainly not observed. We have shown already established of SID in annealed Fe [11]. Another aspect is the time required to fall to half its initial value i.e. $t_{1/2}$, which defines the sharpness of the decay. This is less in the case of 80K annealing than at 300K. Finally, in Fig.2b we show plots of $\Delta RV / \Delta RV_o$ vs t in cold rolled Fe at two different irradiating and annealing temperatures of 300K and 80K. Observation of S-shaped decay curves at 300K could be attributed to migration of defects to remnant structures left after release of dissipative structures or to low concentration of SID. Similar decay curves are seen in absence of dissipative structure formation at 80K. This together with absence of S-shaped decay in annealed Fe conclusively proves role of SID as variable sinks.

After having established the contribution of SID towards variable sinks we proceed to analyse the effect of $S_e$ on recovery dynamics. In Fig.3a we show annealing plot of $\Delta RV / \Delta RV_o$ vs t for cold rolled Fe after 200 MeV silver ion irradiation ($S_e \sim 15 MeV/\mu m$) at 300K. Samples were irradiated for 30 minutes before measurements were taken. Experimental data (circle) fitted well to pure variable sink decay dynamics given by equation 1 (solid line). Values obtained for different parameters $V_o$ and $\beta$ from fitting are 1.0 and
0.116 ± 0.00049 sec\(^{-1}\) respectively. Change in functional form to pure variable sink decay after silver irradiation, from a combination decay after oxygen irradiation, could be attributed to difference in flux or to difference in \(S_e\) values. In Fig.3b we show annealing plots of \(\frac{\Delta R_{V}}{\Delta R_{V_o}}\) vs t for cold rolled Fe at two ion currents of 1.3 nA and 1.8 nA. Decrease in \(t_\frac{1}{2}\) is observed for increase in ion flux. Theoretical fitting to the data showed increase in value of \(\beta\) with decrease in \(t_\frac{1}{2}\). Increase in value of \(\beta\) has been attributed in the literature to increase in concentration of variable sink \([13]\). Hence flux has the effect of increasing the concentration of variable sink but not to change the functional form of decay. It is also observed that same value of \(\beta = 0.136633\) sec\(^{-1}\) is obtained in silver irradiation with one order of lower flux than oxygen irradiation. Silver ions dissipate higher \(S_e\) and present larger stress across the boundaries thus creating a large fraction of SID. These SID’s with a range of activation energies are formed across dislocation lines, reducing the fraction of fixed sinks. This shows that ions with higher \(S_e\) transfer larger energy to the lattice and are more efficient in creating SID. This also explains pure variable sink recovery dynamics under silver irradiation.

Variation of recovery dynamics with temperature has been established in the literature \([13]\) is due to (1) nature of defects created and (2) mobility of defects. The former would affect parameters \(R_{V_o/A}\) and \(\beta\) and latter \(\frac{1}{\tau}\). In Fig.4 we show \(\frac{\Delta R_{V}}{\Delta R_{V_o}}\) vs t for cold rolled Fe under silver irradiation, at 80K. Good agreement with the experimental data was found employing equation 2. A solid line shows the theoretical fit to experimental data (circles). Individual contribution of variable and fixed sinks are represented by curves a and b respectively. Fitting gives the values of \(R_{V_o/A}\), \(\beta\) and \(\frac{1}{\tau}\) as 2.0, 0.1905 ±0.002 sec\(^{-1}\) and 0.0837 ±0.003 sec\(^{-1}\) respectively. On comparing with recovery dynamics at 300K (Fig.3b) the following observations are recorded: (1) change in functional form of recovery dynamics and (2) increase in value of \(\beta\). At lower
temperatures grain become weaker than grain boundaries, making it difficult to create SID at internal surfaces. Thus we have decrease in concentration of variable sinks with respect to its concentration at 300K. The decrease in variable sinks increases the fraction of fixed sinks and results in combination decay with a lower value of $R_{V_0/A}$. Parameter $\beta$ is a function of the concentration of variable sink, rate constant ($\frac{1}{\tau}$) and concentration of conventional point defects. Decrease in rate constant with decrease in temperature is well known in published literature [13]. Increase in $\beta$ at lower temperature is a result of substantial increase in concentration of conventional point defects.

In annealing theory sinks are modeled without a stress field. Relaxation time ($\tau$) is known to be influenced by the stress field of sinks and temperature of annealing [13]. In order to establish that stress fields are associated with SID we study annealed Fe after irradiation. Figure 5 shows $\frac{\Delta R_{V}}{\Delta R_{V_0}}$ vs t after the beam has been switched off. It is assumed that in samples with low SID concentration, annealing starts immediately after switching the beam off. In Fig.5 we see an initial rise which could possibly be due to breakdown of irradiation induced clusters. This rise has been neglected for the moment and the decay part fitted to the desired function. An exponential function is in excellent agreement with the experimental data (circle). Fitting gives the value of $\frac{1}{\tau}$ as 0.0953 $sec^{-1}$. Dislocation lines are source of variable sink and in annealed Fe low density of dislocations result in low density of variable sinks. In presence of an insignificant density of variable sink, the decay dynamics is exponential in form. The value of $\tau$ obtained from the fitting is 10 sec. This value is in absence of stress field associated with SID. Assuming that decrease in $S_e$ effects the ratio of variable sink to fixed sink only, value of $\tau$ in presence of SID is 20 sec (Fig.3a). Such a large increase in $\tau$ for same sample temperature can be only associated to stress field of SID.

Although we have shown recovery following quenching and heavy ion ir-
radiation to have similar overall behavior, their dynamics differ on two accounts. Firstly, under irradiation cold rolled Fe showed a S-shaped recovery curve which on annealing show exponential decay (Fig.2a). Whereas in the quenching experiment reported in the literature [5-7], annealed gold shows S-shaped recovery curve while cold rolled gold wire shows exponential decay. Secondly, under irradiation the time scale of recovery is in order of seconds whereas in quenching it is of the order of hours. The former difference is due to different nature of variable sinks created under the two processes while for the latter, difference in time scales can be attributed to the nature of stress field associated with SID.

In conclusion, we have suggested that new stress induced defects (SID) behave like variable sinks following heavy ion irradiation. Recovery of defects was a result of their migration to two types of sinks, fixed and variable. It was also found to be sensitive to $S_c$ and temperature of the sample. Stress associated with SID have been shown to effect the relaxation time of defect migration to sinks.

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Figure Captions

- Fig.1 : Recovery curve in cold rolled Fe followed by in-situ resistivity measurement after 100 MeV oxygen ion irradiation at 300K. Experimental data (circle) is found to have S-shaped decay characteristic of variable sink. Solid curves a and b represent the contribution of variable sink and fixed sink to total decay. Time (t=0) here and in all subsequent plots for cold rolled (300K) corresponds to starting of annealing behaviour after SID decay [11].

- Fig.2 : Comparative recovery curves for (a) microstructural density and (b) temperature of recovery, after 200 MeV silver ion irradiation in thin Fe foils. These curves have been analysed in detail in subsequent figures. Due to absence of SID time (t=0) for annealed Fe (a) and cold rolled Fe at 80K (b) corresponds to beam switch off.

- Fig.3 : Recovery curves in cold rolled Fe after 200 MeV silver ion irradiation at 300K, where, (a) decay is found to be controlled by pure variable sinks and (b) functional form of decay is unaffected by ion flux.

- Fig.4 : Recovery curves in cold rolled Fe after silver irradiation at 80K. Contribution of variable sink (curve a) decreases and that of fixed sink (curve b) increases when compared to recovery at 300K. Ion current was 1.5nA.

- Fig.5 : Recovery curve in annealed Fe after silver irradiation at 300K. Solid line is the exponential fit to experimental data data (circle). The ion current was 3.0nA.
\[ \frac{\Delta RV}{\Delta RV_0} \]

Time (sec)

- cold rolled
- Annealed
(b)

\[ \frac{\Delta RV}{\Delta RV_0} \]

Time (sec)

- 80K
- 300K
Graph showing the relationship between $\Delta RV/\Delta RV_0$ and time (sec).
The graph shows the time (sec) on the x-axis and $\Delta RV/\Delta RV_0$ on the y-axis. Two curves are plotted, one for 1.8 nA (squares) and one for 1.3 nA (circles), demonstrating the effect of different currents on the variable $\Delta RV/\Delta RV_0$.
