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# SYNERGISTIC EFFECTS OF NEUTRON IRRADIATION AND INTERSTITIAL IMPURITIES ON MECHANICAL AND FRACTURE BEHAVIORS OF FERRITIC STEELS

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## ABSTRACT

Ferritic steels that are generally used in pressure vessels and various reactor support structures in light water reactors exhibit dynamic strain aging (DSA) resulting in increased work-hardening accompanied by ductility loss. DSA is due mainly to interstitial impurity atoms (IIAs) such as C and N that diffuse to the gliding dislocations and lock them resulting in load fluctuations. While there is a possibility of adding this embrittlement known as ***blue brittleness*** to the well-known radiation embrittlement, it has been amply demonstrated that radiation exposure leads to decreased concentrations of IIAs in solution. Thus the critical temperature for DSA increases with increased neutron fluence very similar to the increase observed in dry hydrogen treated mild steel samples with decreased concentration of nitrogen in solution with increased treatment time. We summarize here the mechanical and fracture studies made on three different materials: a mild steel and two ferritic steels (A533B and A516 Grade70). Tensile, 3-point bend and compact tension (CT) specimens were used in characterizing mechanical and fracture behaviors of these materials. Superimposed radiation effects are considered on subsize 3-point bend specimens of A533B and A516 steels. Thin wire samples were used to investigate tensile properties of mild steel at various test temperatures before and after irradiation with special attention to DSA. In addition, effects of interstitial nitrogen are evaluated by heat treating to different times in dry hydrogen atmosphere.

## INTRODUCTION

Ferritic steels used in containment vessels exhibit radiation embrittlement in terms of increased ductile to brittle transition temperature (DBTT) and decreased shelf energy, degrees of which increase with increased exposure to neutron irradiation (Steele, 1983). The radiation sensitivity of these steels is influenced by alloying elements such as P, Cu, Ni, etc and thus the nuclear regulatory commission (NRC) guidelines stipulate the tolerable amounts of these alloying and trace elements (Murty, 1985). While these effects have been considered in detail in manufacturing technology, the role of interstitial impurity atoms (IIAs) are examined for an understanding of the effects on ductility due to dynamic strain aging (DSA) resulting in negative strain-rate sensitivity accompanied by increased work-hardening (Hall, 1970, Chakravarty et al., 1983). Significance of the effects of IIAs and DSA is on the possible decreases in fracture toughness in the upper-shelf regime depending on the applied strain-rate leading to embrittlement in addition to that due to irradiation. Figure 1 depicts such a behavior in A533B steel as reported by Jung and Murty (1987). It is to be noted that the results depicted in Figure 1 were obtained using slow strain-rate testing of sub-size Charpy-type specimens in 3-point bend mode and such dips in toughness are not discernible in regular Charpy tests with relatively high strain-rates (Steele, 1983) since the critical temperature for toughness dip increases with the applied strain-rate following an Arrhernius function with an activation energy equal to that for diffusion of IIAs in iron. While there is a possibility of embrittlement due to DSA adding to that of irradiation, it has been amply demonstrated that decreased concentration of IIAs in solution following radiation exposure postpones such dips to higher temperatures. As neutron radiation fluence increases and/or time and temperature of irradiation increase, the steel may become nonaging (Charit et al, 2007) eliminating such DSA completely.

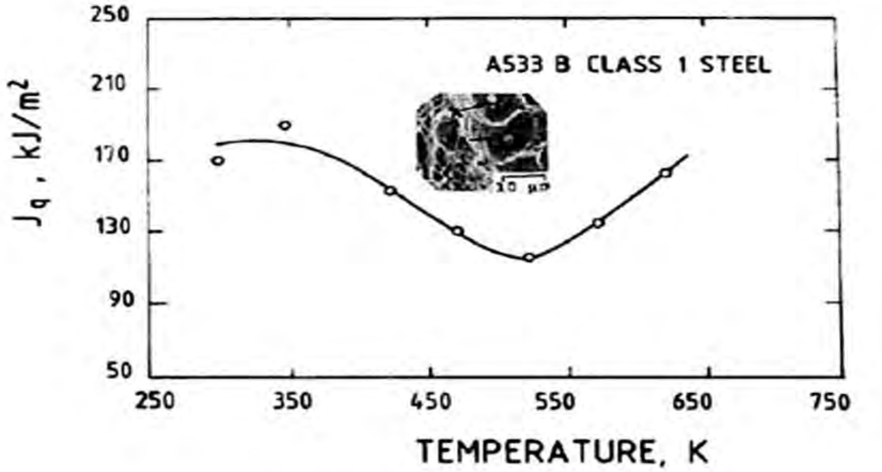


Figure 1. Temperature variation of elastic-plastic fracture toughness depicting dip due to DSA (Jung and Murty, 1987)

Such dips in ductility were noted in A516B steel at around 200C ascribable to DSA while 3-point bend tests exhibited dips in fracture energy at around 250C (Hong and Murty, 1973); effects of strain-rate were not reported. Fracture toughness data determined using compact tension specimens, however, did not exhibit such dips albeit for the presence of a plateau noted in the elastic-plastic toughness ($J_{IC}$) for crack initiation between 200C to 300C (Seok and Murty, 1999). Effects of neuron radiation exposure on energies to fracture determined using both mechanical (tensile and 3-point bend) and fracture (3-point bend, $J_{IC}$) clearly revealed that such dips due to DSA were postponed to higher temperatures as well as becoming relatively shallow. These results again clearly point to the fact that IIAs interact/combine with radiation produced defects thereby resulting in decreased concentrations in-solution.

Fundamental understanding of these phenomena can be obtained by considering simpler materials such as mild steel and pure iron with emphasis on characterizing effects of neutron irradiation on friction ($\sigma_i$) and source ($\sigma_s$) hardening terms comprising the yield stress ($\sigma_y$) (Murty and Oh, 1983):

$$\sigma_y = \sigma_i + \sigma_s. \qquad (1)$$

In this equation, the source hardening represents the stress required to unlock the pinned dislocations and set them free to move while the stress experienced by the mobile dislocations moving through the matrix is the friction hardening. At test temperatures and strain-rates where the dislocation-solute atom interactions become significant (i.e., DSA regime) the source hardening will attain high values which depends on the amount of IIAs in solution. Since neutron radiation exposure results in increased line and areal defects while decreasing the IIAs in solution (due to interaction of IIAs with irradiation defects), one expects to find increased friction hardening accompanied by decreased source hardening. These aspects have important implications to the Hall-Petch coefficients and predictions of the changes in DBTT (Murty, 1999):

$$\Delta DBTT = \frac{1 + \frac{2\Phi^2 \sigma_y}{\sigma_i}\left(\frac{d\sigma_s}{d\Phi}\right)}{1 + \frac{\sigma_y}{\sigma_s}\left(\frac{d\sigma_s}{dT}\right)} \Delta\sigma_i . \qquad (2)$$

In the above equation, $\Phi$ is the neutron fluence ($\phi$t, with $\phi$ being neutron flux) and $\Delta\sigma_i$ is radiation hardening generally varying as square-root of fluence. It is clear that the change in DBTT is directly proportional to the radiation sensitivity of the mechanical properties in particular the increase in the friction hardening due to increased defects arising from radiation exposure. We note in addition that the temperature and fluence dependences of the source hardening are also important parameters albeit they are not commonly observed or determined for many structural alloys. As noted in iron and steels (Hong and Murty, 1993), the source and friction hardenings vary with test temperature and neutron radiation exposure as well as IIAs through DSA. A major objective of the paper is to summarize the mechanical and fracture characteristics of a mild steel and two ferritic steels (A533B and A516Gr70) along with analyses/correlations of the concentration of IIAs with the lower critical temperature for DSA for vacuum annealed, dry hydrogen treated and irradiated mild steel.

## EXPERIMENTAL ASPECTS

Experimental materials consist of a silicon-killed mild steel and two reactor pressure vessel (RPV) ferritic steels (A533B and A516) whose compositions in wt% are included in Table 1. Subsize tensile and V-notched 3-point bend specimens of A533B and A516 Gr70 steels were sealed in evacuated quartz tubes, and irradiated in the PULSTAR reactor at the North Carolina State University. Mild steel wires of 0.001 m diameter and 0.0385 m gage length were used and the material was cold drawn from a rimmed mild steel, and the prepared specimens were annealed under vacuum. Different levels of nitrogen were obtained by annealing in dry hydrogen atmosphere at 948 K for various times followed by vacuum annealing. These samples were irradiated in the heavy-water moderated, high-isotope-flux Australian reactor (HIFAR) at Lucas Heights to different neutron doses. All tensile tests were performed on a hard tensile machine at cross-head speeds varied between $1.8\times10^{-7}$ and $1.0\times10^{-7}$ m/s. 3-point bend tests were performed using a compression jig which transforms a tensile load applied to its ends into a compressive load onto a v-notch specimen supported at 3-points. Areas under load-displacement curves are measured to represent energies to fracture initiation and propagation. This type of arrangement was also suitable for performing $J_{IC}$ tests using unloading compliance technique (Jung and Murty, 1993). Irradiation temperatures were taken as the reactor coolant temperatures and were around 50C to 80C.

Table 1. Chemical compositions of the materials studied (in wt. %)

| **Material** | **C** | **Mn** | **Si** | **S** | **P** | **Cu** | **Mo** | **Cr** | **Ni** | **Irradiation** |
|---|---|---|---|---|---|---|---|---|---|---|
| A533B | 0.25 | 1.38 | --- | 0.02 | 0.01 | 0.13 | 0.61 | - | 0.60 | PULSTAR |
| A516Gr.70 | 0.20 | 0.98 | 0.02 | 0.02 | 0.02 | 0.24 | 0.03 | 0.20 | 0.16 | PULSTAR |
| Mild Steel | 0.05 | 0.39 | 0.001 | 0.012 | - | 0.09 | - | 0.004 | 0.03 | HIFAR |

## RESULTS AND DISCUSSION

Effect of test temperature on fracture toughness is already shown in Figure 1 and the effect of applied strain rate was shown to result in shifts of the dips in toughness occurring at higher temperatures with increased strain-rates following an Arrhenius relation with an activation energy of 128 kJ/mole (Jung and Murty, 1993):

$$\dot{\varepsilon} = Ae^{-128kJ/RT} . \tag{3}$$

This activation energy is higher than that for diffusion of IIAs (C and N) in iron and the increase is believed to arise from the additional binding energy of C and N with manganese and vanadium. This relation clearly demonstrates that at the relatively high strain-rates corresponding to those encountered in Charpy testing one does not observe such dips in Charpy energy within the normal temperature regions studied. Interestingly, the effect of neutron radiation exposure was seen to result in increased critical temperature for the occurrence of such dip in $J_{IC}$ (Figure 2) that was explained to be due to the interaction of IIAs with radiation-produced defects resulting in reduced concentration of IIAs *in solution*. Similar findings were noted in the mechanical and fracture properties of A516Gr70 steel as depicted in Figure 3 which demonstrates the reduced effect of DSA on toughness following radiation exposure meaning that irradiation results in decreased concentration of IIAs available for locking the dislocations. Indeed in the temperature region of DSA in the unirradiated material neutron radiation exposure resulted in increased ductility contrary to the usually noted radiation embrittlement similar to that reported in Nature by Murty (1984).

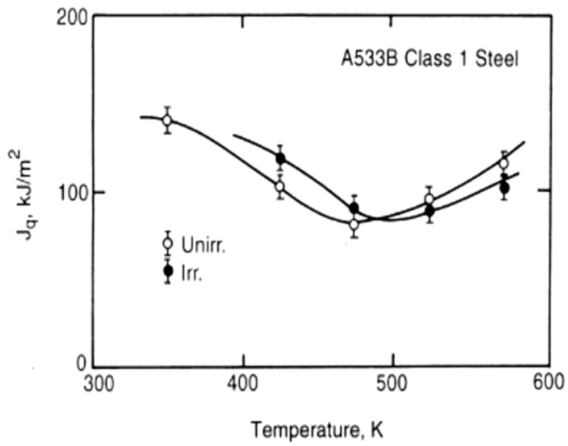


Figure 2. Effect of radiation exposure on temperature variation of Jq (A533B)

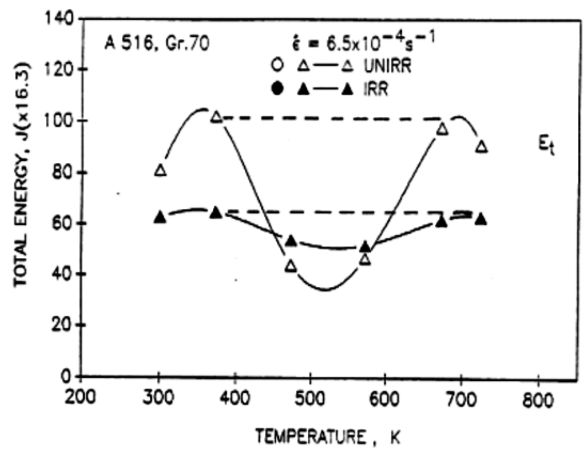


Figure 3. Effect of radiation exposure on temperature variation of Fracture Energy (A516)

Thin mild steel wires provide a suitable example to investigate the DSA phenomena and radiation effects since their geometry is highly suitable for deformation to proceed by a single Luders band as well as for reduced induced radioactivity (Murty and Hall, 1976). The vacuum annealed wire samples were irradiated in HIFAR to various fast (>1 MeV) neutron fluences ranging from $4 \times 10^{16}$ to $1.4 \times 10^{19}$ n/cm$^2$. Tensile tests were carried out on a hard screw driven machine for recording load drops during DSA. Load-elongation curves for mild steel before and after radiation exposure were presented before (Murty and Hall, 1976) which clearly pointed out that radiation exposure resulted in increased critical temperature for DSA, reduced serration height with increased neutron fluence and reduced temperature range of DSA (Figures 4 and 5). These were thought to arise from reduced concentration of IIAs in solution. Correlations were made on the DSA phenomena between neutron irradiated and partially denitrided mild steel that clearly demonstrated these effects (Figure 6).

Table 2. Concentration of IIAs in-solution in irradiated mild steel

| **Fluence n/cm$^2$** | **Concentration of N in-solution, at%** | **$T_C$ K** | **$\sigma_{LY}$ at $T_C$ MPa** |
|---|---|---|---|
| 0 | 0.016 | 393 | 147.0 |
| 75min* | 0.0096 | 403 | 121.5 |
| $4 \times 10^{16}$ | 0.0095 | 423 | 171.5 |
| $3 \times 10^{17}$ | 0.008 | 433 | 176.4 |
| 140min* | 0.0044 | 423 | 112.7 |
| 180min* | 0.002 | 453 | 99.96 |
| 300min* | 0.0014 | 495 | 83.3 |
| $2 \times 10^{18}$ | $1 \times 10^{-9}$ | 523 | 215.6 |
| $1.4 \times 10^{19}$ | $1 \times 10^{-10}$ | 530 | 323.4 |

* dry hydrogen treatment at 675C

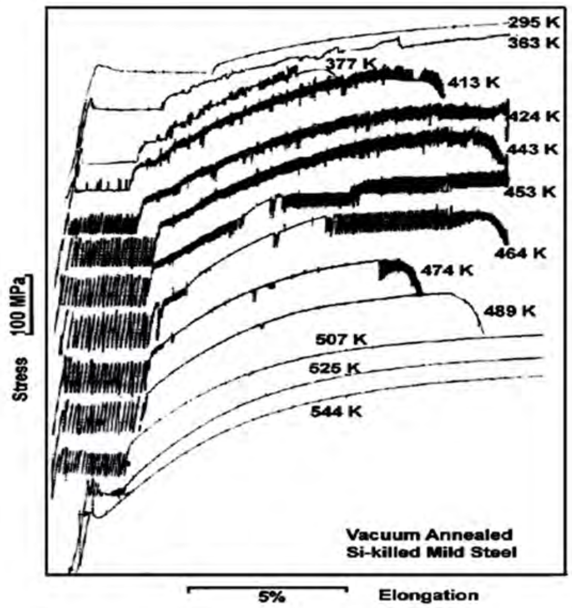


Figure 4. Load-elongation curves for mild steel at varied temperatures depicting serrations

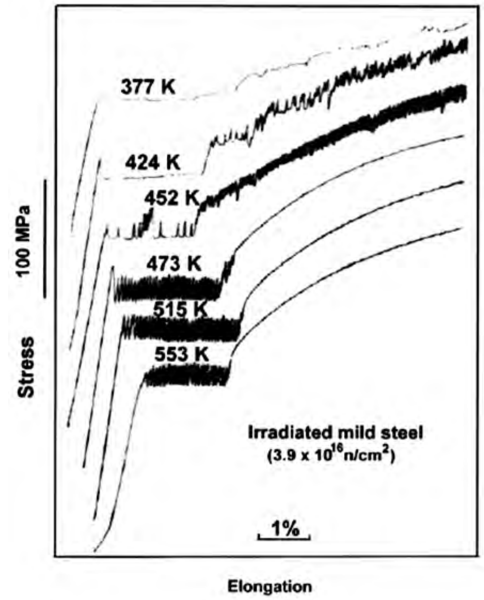


Figure 5. Load-elongation curves for irradiated steel depicting reduced DSA

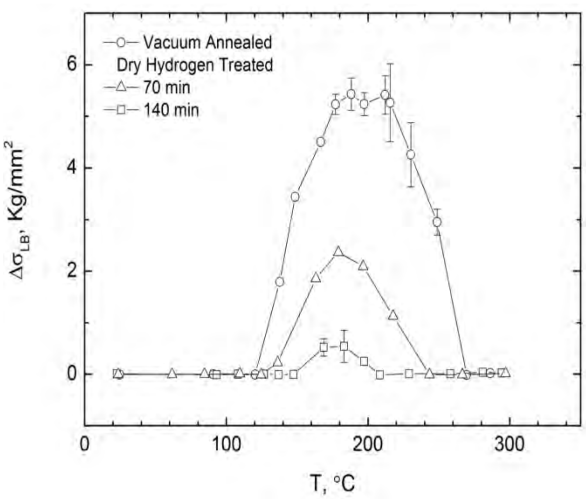


Figure 6. Effect of nitrogen concentration on serration height versus test temperature

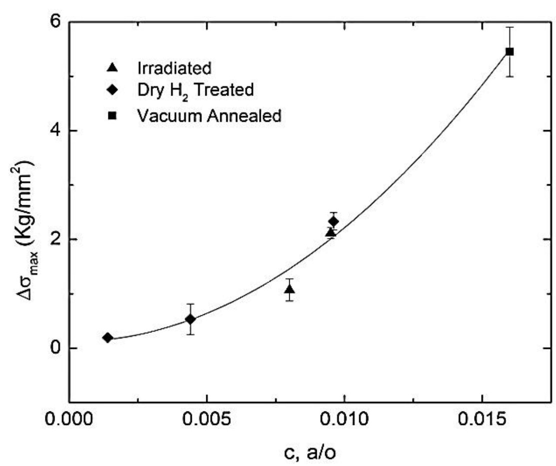


Figure 7. Effect of nitrogen concentration on $\Delta\sigma_{max}$ for irradiated and denitrided steel

From detailed analyses on static strain-aging kinetics of the neutron irradiated and denitrided mild steel samples, Murty and Charit (2008) were able to estimate (by interpolation/extrapolation) the concentration of IIAs in neutron irradiated mild steel. Table 2 summarizes these results for both irradiated and partially denitrided mild steel. It is interesting to examine the effect of IIA concentration in solution on the lower yield stress ($\sigma_{LY}$) at the lower critical temperature ($T_C$) as depicted in Figure 8. We note from the denitrided mild steel data that the lower yield stress at the $T_C$ decreases with decrease in nitrogen concentration. Irradiated test data are more complex since while decreased concentration of IIAs occurs with neutron irradiation, radiation-induced defects result in increased hardening. This clearly implies that the effect of reduced IIAs in-solution needs to be taken into account to evaluate the intrinsic radiation hardening in steels. Corresponding increase in the lower critical temperature for the appearance of serrations with radiation exposure and/or denitriding follows the models predicting the concentration dependence of the critical temperature for the appearance of serrations (Van den Beukel and Kocks, 1982). Accordingly,

$$c = KD^{-2/3} \text{ or } Q = \frac{3}{2}\frac{\partial \ln c}{\partial(1/kT_C)}, \tag{4}$$

where Q is the activation energy for locking of the dislocations by IIAs. Figure 9 is an Arrhenius plot of the concentration versus the lower critical temperature where we note that the line corresponding to the partially denitrided steel yields an activation energy of ~60 kJ/mole identifiable with that for diffusion of nitrogen in iron. However, neutron irradiated steel data yields a much smaller value of ~36 kJ/mole the reasons for which are currently not clear; however, in-situ annealing of radiation damage at higher temperatures could be one of the reasons.

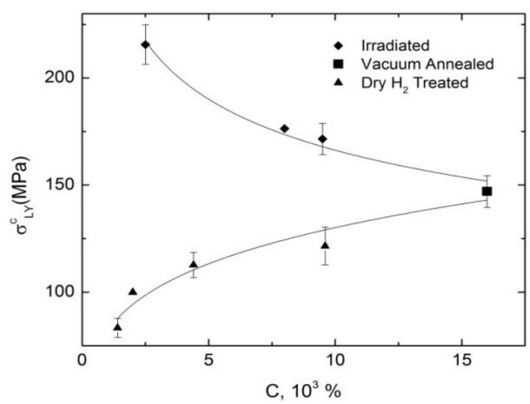


Figure 8. Effect of nitrogen concentration on $\sigma_{LY}$ at $T_C$ for irradiated and denitrided mild steel

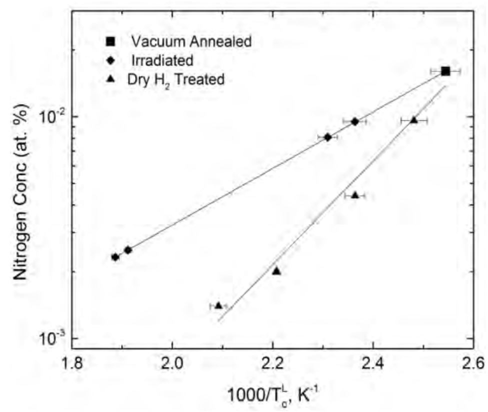


Figure 9. Arrhenius plots of nitrogen concentration in mild steel

It is now well established that serrating yielding in iron-based alloys is due to the locking of the dislocations by IIAs through Cottrell type of drag according to which the solute atmospheres form around the moving dislocations when their speed is less than the critical break-away velocity ($v_c$) given by,

$$v_c = \frac{4D}{\ell} = \frac{4DkT}{A}, \tag{5}$$

where D is the diffusivity of the IIAs in-solution, *l* is the effective radius of the solute atmosphere and A is the Cottrell drag constant (~$1.84 \times 10^{-20}$ dyn/cm$^2$). Using Orowan equation then, one can relate the lower critical temperature ($T_C$) for DSA to the applied strain-rate from which the density of mobile dislocations ($\rho_m$) can be estimated:

$$\dot{\varepsilon} = 4\rho_m b \frac{DkT_C}{A}, \tag{6}$$

where b is the Burgers vector and D is diffusivity of IIAs at $T_C$. Thus evaluated $\rho_m$ values are plotted in Figure 10 and indicate a range of $10^{11}$ to $10^{13}$ m$^{-2}$ that are expected to be reasonable thereby lending further support to the Cottrell type of locking by solute atoms rather than Snoek type. As expected, the density of mobile dislocations decreases with decreased concentration of nitrogen which is consistent with the corresponding decrease in the lower yield stress as noted in Figure 8. Another interesting aspect is on the effect of nitrogen concentration on the disappearance of serrations as noted in Figure 6 that clearly indicates that disappearance of serrations is also correlated with the concentration of IIAs. This is similar to the report on iron and steels by Keh et al (1968). Results on irradiated steel samples however did not reflect this (Murty and Hall, 1976) apparently due to annealing of radiation damage at higher temperatures.

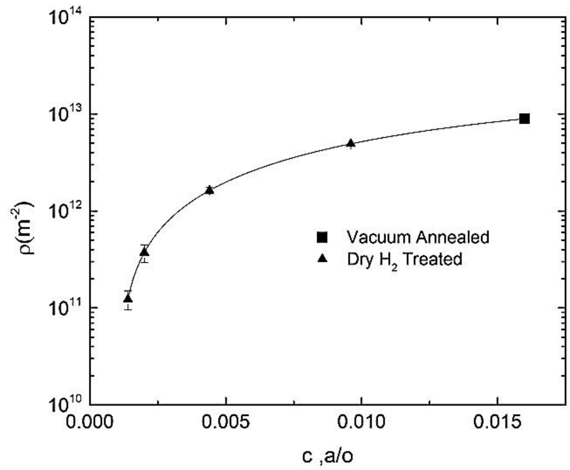


Figure 10. Effect of nitrogen concentration on dislocation density evaluated using Cottrell locking

## SUMMARY AND CONCLUSIONS

Effects of dynamic strain aging due to interaction of interstitial impurities such as C and N on mechanical and fracture characteristics of ferritic steels are described with emphasis on superimposed radiation hardening and embrittlement. Neutron radiation exposure was noted to result in decreased amounts of IIAs in solution, a finding reached from correlations with mechanical properties of partially denitrided mild steel. Occurrence of DSA was seen to result in decreased toughness that is a function of the applied strain-rate, and the kinetics of DSA were governed by the diffusion of IIAs in iron. Radiation exposure and partial denitriding resulted in increased critical temperature for DSA, reduced serration height and decreased temperature range of DSA. Maximum serration height was shown to be dependent on the concentration of IIAs in solution and the results from irradiated and denitrided steels followed the same trend (Figure 7). DSA in mild and RPV steels is identified to be due to Cottrell drag and the density of mobile dislocations derived for mild steel using models based on Cottrell drag are seen to be of reasonable magnitude.

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