BUCKLE, RUCK AND TUCK – THE RESPONSE OF GRAPHITE TO IRRADIATION

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Abstract

The story behind radiation damage in graphite is framed in terms of interstitials and vacancies. First principles calculations all show that interstitials are immobile at low (*e.g.* liquid N_2) temperatures. We have performed the first serious and first principles calculations on dislocations in graphite and found some remarkable results, which give clear explanations for the dimensional change and creep in graphite under neutron irradiation. Dimensional change can be substantial (sometimes exceeding 100%) and creep can be a linear (*i.e.* non-saturating) function of dose. We find that basal dislocations lie at the heart of nearly all these effects, which are not, as was originally thought, exclusively due to the Frenkel pairs formed from irradiation. A more complete explanation lies in prismatic loops and the interactions between basal dislocations, so the structure and energetics of these will be discussed. The physical effects they give are buckling and forming folds, *i.e.* 'ruck and tuck' defects. The findings are expected to be general to layered materials.

Dislocations in graphite

In every material the shear strength is not limited by the inherent shear strength of the perfect crystal where one plane glides uniformly and simultaneously over another, but rather by progressive movement of slip through the crystal, so that at any one time some of the crystal has slipped and some has not. The boundary between the slipped and unslipped region is a line known as a dislocation. The amount of slippage is the Burgers vector, $\boldsymbol{b}$, and it is commonly a lattice vector so that both the slipped and unslipped regions are commensurate with the underlying lattice. Dislocations are classified by $\boldsymbol{b}$ and by their line direction (Table 1). Elegant and pioneering work on radiation damage focused on the aggregation of carbon interstitials in interlayer regions into new sections of graphite planes, *i.e.* interstitial prismatic dislocation loops (Brown *et al.*, 1969, Reynolds and Thrower, 1965). The existence of such loops was proven in transmission electron microscopy. The extra disks of graphene plane are bounded by prismatic dislocations, which have been studied elsewhere (Suarez-Martinez *et al.*, 2007). The loops clearly expand the $\boldsymbol{c}$ direction and can thus cause dimensional change, but the process is irreversible at most temperatures. Annealing would require the emission of interstitials or absorption of vacancies which are both high energy processes.

Table 1. Classes of dislocation in graphite after Fujita and Izui (1961)

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DISLOCATION	$\boldsymbol{b}$	$\boldsymbol{l}$
Basal dislocation	basal	basal
Prismatic edge dislocation	prismatic	basal
Prismatic screw	prismatic	prismatic
Non-basal edge	basal	prismatic

Dimensional change can occur at very low temperatures (*e.g.* 4K) and starts annealing at 70-100K (Kelly, 1980). It is impossible that either recovery mechanism is viable at such low temperatures, and this prompts a new model for dimensional change, which invokes basal dislocations.

These are exemplified by 'perfect' dislocations of $\boldsymbol{b}=\boldsymbol{a}_1$ and $\boldsymbol{l}=\boldsymbol{a}_2$ and $\boldsymbol{b}=\boldsymbol{a}_1$ and $\boldsymbol{l}=\boldsymbol{a}_1$, where the Burgers vectors are basal lattice vectors ($\boldsymbol{a}_1$ or $\boldsymbol{a}_2$). The latter is a screw dislocation and the former has mixed screw and edge character. Edge character implies an extra half plane terminates at the dislocation line. The half plane is a notional crystal plane and in this case is *not* a graphene plane, but rather a prismatic one.

In some materials which have low energy stacking faults (large regions where one plane undergoes a shift of less than a lattice vector with respect to the neighbouring plane) slip can occur in two stages, each stage being a partial dislocation, and the two partials are separated by a stacking fault. In graphite there is a very low energy basal stacking fault (0.85 mJm^{-2}, Telling *et al.* 2003) that creates a local rhombohedral (ABC) stacking within hexagonal AB graphite and allows basal dislocations to dissociate. In the following we omit this detail, although its effects are relatively easily incorporated into the theory.

Structures involved in radiation damage

Calculations within the Local Density Approximation of Density Functional Theory have been shown to be very successful first principles methods for graphite and its point defects (Ewels *et al.*, 2003), demonstrating for example that the energy stored in graphite due to radiation (Wigner energy) is most likely due to recombination of intimate Frenkel pairs – at least for the case of the large release peak normally presented at 200°C. Such calculations have also shown that there are many radiation induced defects (the intimate Frenkel pair, the interstitial and the interlayer divacancy) which give rise to strong interlayer bonds (Telling *et al.*, 2003). The cross-links can lock in basal dislocations and Figure 1 is an illustration of this. Substantial dimensional changes result. In this preliminary calculation the fractional changes found by optimization of atom positions and cell dimensions are $\Delta X_a/X_a = -4\%$, $\Delta X_c/X_c = 48\%$, which are values of basal plane contraction and ***c*** axis expansion consistent with what is observed in neutron irradiation below 250°C.

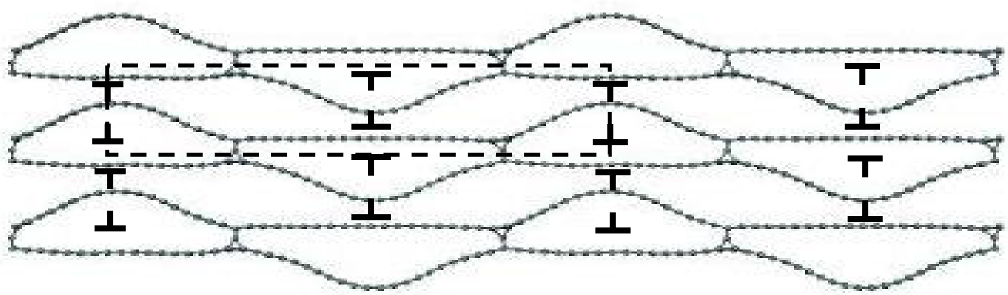

Figure 1. Basal edge dislocations with edge character trapped between cross-linking defects. Broken line depicts the supercell used in calculations. Dislocations are represented by the **T** character.

The effects of radiation damage include increasing basal electrical and thermal resistivity and these have been monitored for cryogenic irradiation and subsequent annealing. In the electrical case these increases could be attributed to enhanced scattering of in-plane charge carriers by defects (such as the spiro-intersitial) which bond into the planes, thereby removing p orbitals of the host atoms they bond to from the π system. Intriguingly the first stages of annealing see an increase in basal resistivity, rather than a decrease (Kelly, 1981) and the present model of buckling indicates a possible explanation (Heggie *et al.*, 2007). During irradiation at low *T* buckling can become so extreme that interstitials cannot adopt their usual cross-linking spiro structure. The result is adatoms which bond only to one plane and these can form the spiro structure after a gentle anneal has reduced the buckling. They thus increase the concentration of scattering centres and resistivity.

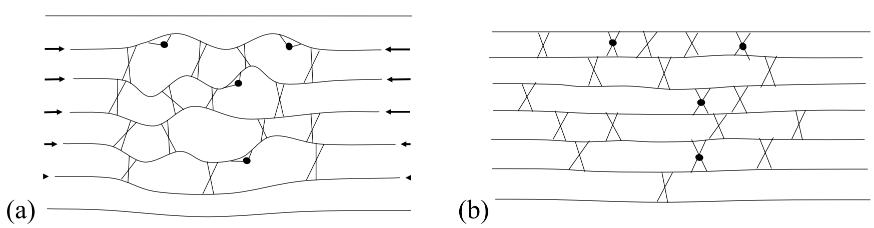

Figure 2. Low temperature damage and annealing (a) schematic of radiation damage at cryogenic temperatures. Crosses represent cross-linking defects, e.g. spiro-interstitials and solid circles adatoms which convert into spiro-interstitials (b) after gentle anneal.

It is to be expected that the majority of cross-linking defects anneal out at 200-250°C, forming the major part of the nominal 200°C peak of Wigner energy. Given that production, movement and trapping of basal dislocations are implicit in the low temperature processes, then it is highly likely that production and movement will occur at higher temperatures, albeit without the pinning points. Dislocations can, however, mutually trap and one such mutually trapped structure is given in Figure 3. Basal edge dislocations gliding on neighbouring planes come together and annihilate, but in so doing deposit material at the point of annihilation because their half planes overlap (they extract material if sense of dislocation is reversed). This extra material gives rise to a fold in the planes (a 'ruck and tuck' defect). It is difficult to reproduce this defect in a first principles calculation because of the size of supercell required (a thousand atoms or so), but molecular mechanics reveal that this kind of defect can produce dimensional changes which are largely volume conserving and of the same order of magnitude as observed experimentally.

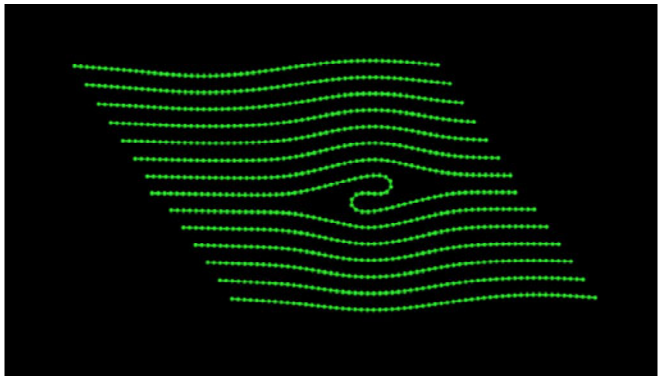

Figure 3. A ruck and tuck defect arising from mutual trapping of basal dislocations on neighbouring planes.

Conclusions

An alternative to the generally accepted model for the principal effects of neutron radiation on graphite has proposed. It invokes basal edge dislocations and their interactions with point defects (at temperatures below 250°C) and with each other at higher temperatures. It is to be expected that there are profound implications in this work for graphites in general, including graphite intercalation compounds and non-carbon analogues of graphite, which could be straightforwardly *h*-BN and MgB_2 or less directly layered molybdenum and tungsten oxides and sulphides. More distant possible extensions are to clays and Langmuir-Blodgett films.

Acknowledgments

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