Energy barriers for carbon diffusion in ferrite under heterogeneous stress

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Context & objectives

- The diffusion of carbon in iron controls the kinetics of many transformations in steels (such as, cementite precipitation, martensite ageing, massive austenite-ferrite transformation and bainite formation).
- Diffusion of carbon in defect-free ferrite (the body-centred cubic structure of iron): a fairly well known mechanism, extensively studied and characterized.
- When other defects are present: both the diffusion mechanism and its kinetics are affected. Case of dislocations: they create very large and non-uniform stresses, inducing important effects on the energy barrier of impurities.
- Diffusion and segregation of interstitial carbon to dislocations introduced by plastic deformation in ferritic iron: leads to the growth of so-called Cottrell atmospheres around the dislocations (responsible for static strain aging in ferritic steels).
- Atomistic simulations provide a good alternative for studying the diffusion processes in the presence of stress:
  - Molecular dynamics (MD): could serve as a perfect framework if not so limited in accessible time span (typically, a few ns).
  - Atomistic Kinetic Monte-Carlo (aKMC) method: very well adapted for studying the diffusion of atomic species, based on knowledge of the different escape pathways and the corresponding escape rates.
  - The presence of an imposed stress field modifies the barriers for carbon diffusion in iron because it influences the energy and the atomic configurations of both the diffusion mechanism and its kinetics, as well as the corresponding escape rates.
- In this work, the effect of an heterogeneous stress field on diffusion energy barriers is addressed: a novel method, called LinCoSS (Linear Combination of Stress States), which is very fast and easy to implement alternative to existing approaches [1].

Results

Crystallographic structure

- Anisotropic elasticity theory:
  - Total energy of a periodic simulation box with volume \( V \), containing a point defect with elastic dipole \( P_{D} \), and submitted to a homogeneous strain \( \varepsilon_{0} \):
    \[
    E^{tot}(\varepsilon_{0}) = E^{tot}(0) + P_{D}^{2} \varepsilon_{0} + \frac{\nu}{2} P_{D}^{2} \varepsilon_{0}^2
    \]
  - \( \Delta E(\varepsilon_{0}) = E^{tot}(\varepsilon_{0}) - (E^{tot}(0) - P_{D}^{2}) \)
  \((P_{D}^2)\) is deduced from atomistic simulations

Methods for calculating energy barriers under stresses

- Linear Combination of Stress States (LinCoSS):
  - It is based on the decomposition of a complex stress state into a linear combination of uniaxial and pure shear stress states:
    \[
    \left[\begin{array}{c}
    \sigma_{xx} \\
    \sigma_{yy} \\
    \sigma_{zz} \\
    \sigma_{xy} \\
    \sigma_{xz} \\
    \sigma_{yz}
    \end{array}\right] = \left[\begin{array}{c}
    \sigma_{xx,x} \varepsilon_{xx} + \sigma_{xx,y} \varepsilon_{yy} + \sigma_{xx,z} \varepsilon_{zz} + \sigma_{xy} \varepsilon_{xy} + \sigma_{xz} \varepsilon_{xz} + \sigma_{yz} \varepsilon_{yz} \\
    \sigma_{yy,x} \varepsilon_{xx} + \sigma_{yy,y} \varepsilon_{yy} + \sigma_{yy,z} \varepsilon_{zz} + \sigma_{xy} \varepsilon_{xy} + \sigma_{xz} \varepsilon_{xz} + \sigma_{yz} \varepsilon_{yz} \\
    \sigma_{zz,x} \varepsilon_{xx} + \sigma_{zz,y} \varepsilon_{yy} + \sigma_{zz,z} \varepsilon_{zz} + \sigma_{xy} \varepsilon_{xy} + \sigma_{xz} \varepsilon_{xz} + \sigma_{yz} \varepsilon_{yz} \\
    \sigma_{xy} \varepsilon_{xx} + \sigma_{xy,y} \varepsilon_{yy} + \sigma_{xy,z} \varepsilon_{zz} + \sigma_{xy} \varepsilon_{xy} + \sigma_{xz} \varepsilon_{xz} + \sigma_{yz} \varepsilon_{yz} \\
    \sigma_{xz} \varepsilon_{xx} + \sigma_{xz,y} \varepsilon_{yy} + \sigma_{xz,z} \varepsilon_{zz} + \sigma_{xy} \varepsilon_{xy} + \sigma_{xz} \varepsilon_{xz} + \sigma_{yz} \varepsilon_{yz} \\
    \sigma_{yz} \varepsilon_{xx} + \sigma_{yz,y} \varepsilon_{yy} + \sigma_{yz,z} \varepsilon_{zz} + \sigma_{xy} \varepsilon_{xy} + \sigma_{xz} \varepsilon_{xz} + \sigma_{yz} \varepsilon_{yz}
    \end{array}\right]
    \]
  - One may assume that the effect of an arbitrary stress field on the energy barriers could be simply evaluated by a linear combination of the effects induced by each stress field component:
    \[
    \Delta E(\sigma) = \Delta E(\sigma_{x}) + \Delta E(\sigma_{y}) + \Delta E(\sigma_{z}) + \Delta E(\sigma_{xy}) + \Delta E(\sigma_{xz}) + \Delta E(\sigma_{yz}) - 5\Delta E(0)
    \]

Simulation methods

Atomistic Kinetic Monte-Carlo method:

- Residence time algorithm:
  - time spent in a state \( t \) before transition to an adjacent state \( j \):
    \[
    \tau = \frac{\ln(\Gamma)}{\sum_{j} R_{ij}}
    \]
  - Transition rates: \( R_{ij} = \phi \exp(-\Delta E_{ij}/kT) \)
  - Each aKMC time step is associated with a jump (transition \( i \rightarrow j \))
  - Accessible time span: minutes, hours ...
  - Appropriate method for studying diffusion phenomena in the solids

Climbing-Image Negated Elastic Band (CI-NEB) method:

- State-of-the-art method for locating saddle points on PES knowing the initial and final state configurations, measuring the corresponding energy

Conclusion

The presence of an imposed stress field modifies the barriers for carbon diffusion in iron because it influences the energy and the atomic configurations of both the stable position (octahedral site) and the saddle point position. We propose a novel method for determining the barriers for carbon diffusion under heterogeneous stress field, called LinCoSS:

- LinCoSS is very accurate up to relatively high stresses: more accurate than elasticity theory since it provides a better description of the effect of pure shear stress on the energy barriers.
- Coupled to a KMC algorithm, it could serve as a good framework for modelling carbon diffusion in bcc iron in the presence of any kind of defect (dislocation, vacancy, grain boundary, precipitates, etc.), provided that the stress field induced by the defect does not overpass 3-4 GPa.
- LinCoSS could also be generalized to the case of vacancy diffusion or to the diffusion of other substitutional atoms.

References