Effect of material defects on the surface of polycrystalline copper in high electric fields

Kristian Kuppart

November 22, 2014

Contents

Introduction

With the rise of available computational power, computational material science has emerged as a field which is both promising[1] and challenging, allowing us to simulate conditions, which would be experimentally hard to attain and to understand the microscopic phenomena that govern the macroscopic behaviour of materials [2]. In particular, atomistic modelling techniques have been used to study vacuum breakdowns caused by material failiure in fusion reactors(viide) and particle accelerators(viide). In Compact Linear Collider CLIC [3] , a new planned electron-positron collider at CERN, planned energies will peak at 5 TeV, with optimal working energy of 3 TeV [3]. To achieve those energies, huge accelerating radio frequency electric fields over 100 MV/m are needed, which can damage the material[**?**], cause the loss of the accelerated beam[4] and are mainly limited by vacuum breakdowns [5],[6]. The driving mechanisms behind those breakdowns are not known, it has been speculated, that they are caused by evaporation of atoms from the surface [7], electron emission [4] or other mechanisms, that lead to plasma formation near the metal surface [7]. The stress induced by the external electric field on the metal surface can be calculated as follows:

$$\sigma = \frac{\epsilon_0 E^2}{2} \tag{0.0.1}$$

Which, when calculated for the excpected field of 100 MV/m is orders of magnitude below the yield strength of copper $\sigma_c = 70$ MPa(viide), a typical material for this kind of accelerating structure[6]. Nevertheless, it has been experimentally shown, that in some regions on the surface, the local field is stronger than the applied macroscopic field by a factor of $\beta = 50 - 100$[8], which can cause evaporation of surface atoms and electron emission from those regions(viide). This microscopic field enhancement is believed to originate from narrow protrusions on the metal surface[5], which are preferred on-sites for evaporation due to higher electric fields and electron emission due to heating from conduction currents. The mechanisms for the development of those field emitters are not well understood, because such protrusions should be well seen under scanning electron microscope and no geometrical protrusion with $\beta > 50$ have been experimentally found[8]. Different mechanisms have been proposed, for example it has been shown by simulations[9], that a pre-existing void underneath the copper surface in a strong external electric field can cause significant surface modification, which in-turn causes enhancement of the local electric field, leading to a self-reinforcing process[9].

The aim of this work is to study the effects of defects in nanocrystalline copper on surface morphology under high applied electric fields. It has been shown(viide), that grain boundaries and triple junctions act as stress concentrators, which can cause dislocation nucleation from those regions. For this purpose, classical molecular dynamics(MD) is used. This thesis is split into 4 chapters: first chapter discusses the origin of different defects found in metals and their potential interactions with the material surface. Overview of molecular dynamics, used algorithms and software is discussed in chapter 2. Description and setups of ran simulations is discussed in chapter 3 and results with analysis is presented in chapter 4. Chapter 5 describes the model to couple together elctrodynamics through Finite Element Method with MD.

1 Background

1.1 Vacuum breakdowns

1.2 Metallic microprotrusion model

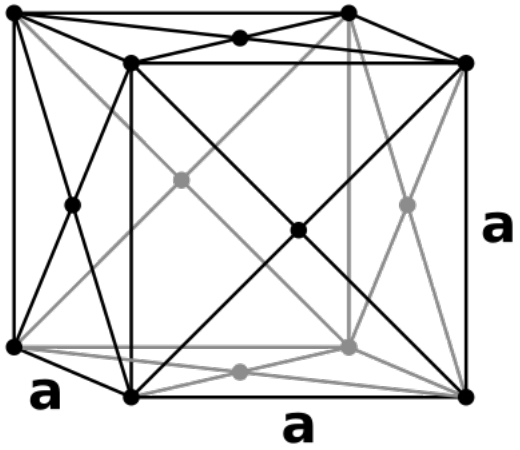
1.3 Processes in field emitters

2 Defects in metals

Microscopic defects found in metals often govern the macroscopic behaviour of the material. Defects are deviations from the perfect crystal lattice, which for copper is face centered cubic structure(fcc). That means, that the unit cell of copper consists of atoms situated at the corners of the unit cell and at the centers of all the cube faces. The length of the side of the unit cell is called the lattice parameter. The smallest distance between atomic sites is $\frac{\sqrt{2}}{2}a$, where a is the lattice parameter. (viide mingile õpikule, dislocations in solids või modelling materials)

fcc võre, vask,

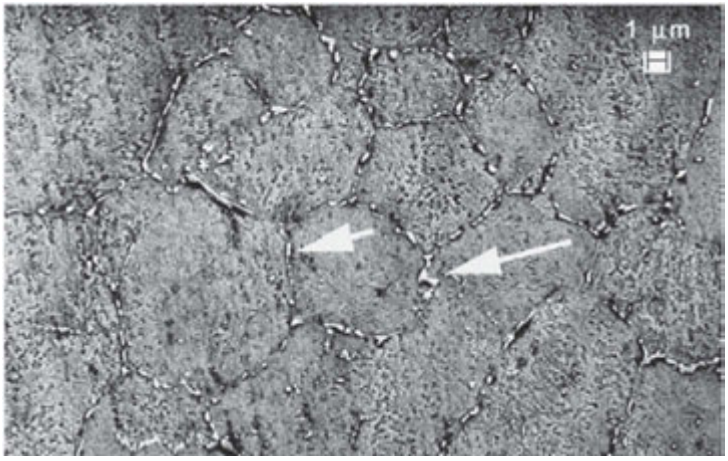
Figure 2.0.1: face-centered cubic lattice



2.1 Polycrystalline materials

In principle, a perfect monocrystal periodic in every dimension is the lowest energy configuration for metals, including copper. Because of the way crystalline materials form, typically through melting and resolidification, they very rarely form one big monocrystal, but instead they consist of small crystallites. Those crystallites are monocrystals with different crystal orientation and are seperated by planar crystal defects called grain boundaries. (viide mingile õpikule, dislocations in solids või modelling materials)

Figure 2.1.1: Polycrystal(viide Tadmor). The arrows point to grain boundaries.



2.2 Dislocations

2.3 Grain boundaries

As mentioned, grain boundaries are planar defects that seperate grains with different orientation and consist of atoms, which have different structure than the bulk crystal they encompass.

2.4 Stacking faults

3 Overview of atomistic simulations

3.1 Classical molecular dynamics(MD)

Although well-established theories about atomistic interactions exist, the so-called first-priciples or ab inito calculations based on quantum mechanics are not sufficient to study phenomena in materials emerging in very different time-and length scales, mainly because of limitations in available computing power.(Võib-olla panen juurde selle tuntud pildi erinevate meetodite kohta, kus ühes otsas kvantmehaanika ja teises FEM?) For that reason, classical molecular dynamics has the middle-ground: it still allows to take the atomic structure of material into account, while being computationally less intensive.

Classical molecular dynamics is a simulation technique developed in the 1950s (viide), that simulates the motion of each individual atom seperately. Atoms are treated as point particles and they interact through a defined potential function, which is a function of coordinates of all atoms. From this potential, inter-atomic forces are derived, which are used to solve Newton's eqution of motion for all atoms. Velocity is also excplicitly calculated, to be able to compute interesting macroscopic parameters like kinetic energy, temperature and pressure. There are many different algorithms for integrating the resulting equations of motion,

3.2 choosing timestep

To be able to simulate an atomic phenomenon, timestep size used must usually be at least an order of magnitude smaller than the smallest characteristic time scale of the phenomenon studied. For metals, this timescale can be estimated using the Debye frequency of the metal(viide), which roughly corresponds to the fastest vibrations of the atoms due to thermal motion:

$$\omega_D = v_s \left(\frac{3N}{4\pi V} \right)^{\frac{1}{3}}$$

where $v_s$is the speed of sound in that metal and $\frac{N}{V}$ is the number density of atoms in the metal. For copper, which has lattice constant of 3.6 Å and speed of sound of 3900 $\frac{\mathrm{m}}{\mathrm{s}}$, this frequency is about one cycle per 0.1 ps. This means, that the timestep size should be below 10 fs. In this thesis, timestep size is chosen to be 2 fs, to reduce numerical errors.

3.3 Embedded atom method(EAM) and EAM potentials

Simple potential described in part 2.1 is not the only potential generally necessary to simulate materials in MD framework. Depending on the nature of the problem, different potentials might be needed, for example to account for chemical bond stretching and bending, and also due to long-range Coulombic forces due to ions. A collection of these potentials for a given problem or substance is called the Force Field(FF). As this thesis concentrates on simulating copper, most of these components are absent and it is possible to simulate the system using a simple pair potential or a more sophisticated addition to those, like Embedded Atom potentials. In EAM formulation, the total energy of the system is given by:

$$E = \frac{1}{2}\sum_{ij} V_{ij}\left(r_{ij}\right) + \sum_{\alpha} U_{\alpha}\left(\rho^{\alpha}\right)$$

Where V_{ij} is the energy of pairwise interaction of particles with indices i,j and U_{α} is the energy associated with embedding an atom to the environment governed by the functional ρ^{α}, which itself is a function of all the coordinates of the atoms. There are different physical explanations how to justify different parametrizations of functionals $U_{\alpha}$and ρ^{α}, but the simplest explanation is that $V_{ij}$is the Coulombic interaction between the atomic cores of atoms i,j and that $U_{\alpha}\left(\rho^{\alpha}\right)$ is the energy needed to embed an atom in a background electron density ρ^{α}, which is simply taken as the linear superposition of electron densities from neighbourghing atoms. This assumes that the contribution to the electron density ρ^{α} from a neighbourghing atom depends only on the distance from that atom, with no angular dependence, which is not strictly true. Yet it is possible to get satisfying results with this method when simulating elements with filled d-orbitals, like copper.

3.4 Statistical mechanics ensembles

Nose-Hoover thermostat, N-H barostat, maybe discuss other methods(simple velocity rescaling, Langevin, Berendsen, trouble with those)

3.5 periodic boundary conditions

z-direction thin but periodic, grains resemble tubes or cylinders

3.6 Analysis methods for crystalline structures

3.6.1 Centrosymmetry parameter(CSP)

As mentioned in chapter 1, defects in crystal lattice play an enormous role in material properties, and as such, it is important to be able to extract the information about defects from the data of the sample under study. As MD methods do not keep track

of defects internally, it is necessary to apply algorithms that do so as part of the post-simulation processing(Stukowski 2012 igale poole). Although there are many ways to analyse possible defects in the sample studied, here are presented two methods, that are used in this thesis: analysis of Centrosymmetry Parameter, usually abbreviated CSP, and Common Neighbour Analysis. Centrosymmetry Parameter assigns a scalar to each atom by looking at it's nearest neighbours [10]:

$$CSP = \sum_{i=1}^{N/2} \left| \boldsymbol{r}_i + \boldsymbol{r}_{i+\frac{N}{2}} \right|^2$$

Where N is the number of neighbours for each atom, for fcc crystals $N = 12$. Here $\boldsymbol{r}_i$and $\boldsymbol{r}_{i+\frac{N}{2}}$ are position vectors from the central atom to a pair of neighbours, which lie symmmetrically with respect to the central atom, hence the notation i and $i + \frac{N}{2}$. CSP is nearly 0 for atoms in their regular positions corresponding to a perfect crystal and is non-zero for atoms near or part of a defect. One of the advantages of CSP is that it has rotational symmetry, that is it depends only on the neighbourhood of an atom, not on the orientation of particular crystal. The disadvantages include not being able to distinguish between different defects and sensitivity to noise due to thermal displacements of atoms from their equilibrium sites, which means, that at higher temperature(milline?) the distributions of CSP of fcc atoms and defect atoms, like in stacking faults, begin to overlap.

3.6.2 Common Neighbour Analysis(CNA)

4 Simulations

4.1 Setup

The system that is used in this work originates from a previous simulation conducted in University of Helsinki Department of Physics by Ossi Saresoja *et al.* as described here: [**?**]. The autors simulated explosive welding process between monocrystal copper and iron plates, after which, polycrystalline structure with $10-20$ nm grain size appeared in both materials. The starting point for simulations in current thesis is the copper part of the material, with iron atoms removed. The system partly resembles a material after a breakdown event, because both vacuum breakdown and explosive welding essentially cause a shockwave to propagate from the material surface, causing massive plastic deformation.(Viide otsida selle kohta!) The sample consists of about 7.65 million copper atoms forming a thin slab about 400 nm long in x-direction, 50 nm wide in y-direction and 4 nm thick and periodic in z-direction. As the snapshot of the sample is taken right after the welding process and is in a highly compressed state, measures have to be taken to release the initial stresses in the material and to reduce the amount of defects present. For this purpose, three methods are used in this thesis to aquire a sample that could be used in further simulations:

1. Equilibrate the sample by relaxing the internal potential energy of the sample without creating velocities for the atoms, then use a thermostat to reduce the temperature to 300 K.

2. Perform energy minimization on the system at 0 K using Conjugate Gradient(CG) minimization scheme(Citation here, if I don't discuss it elsewhere), raise temperature to 300 K and equilibrate.

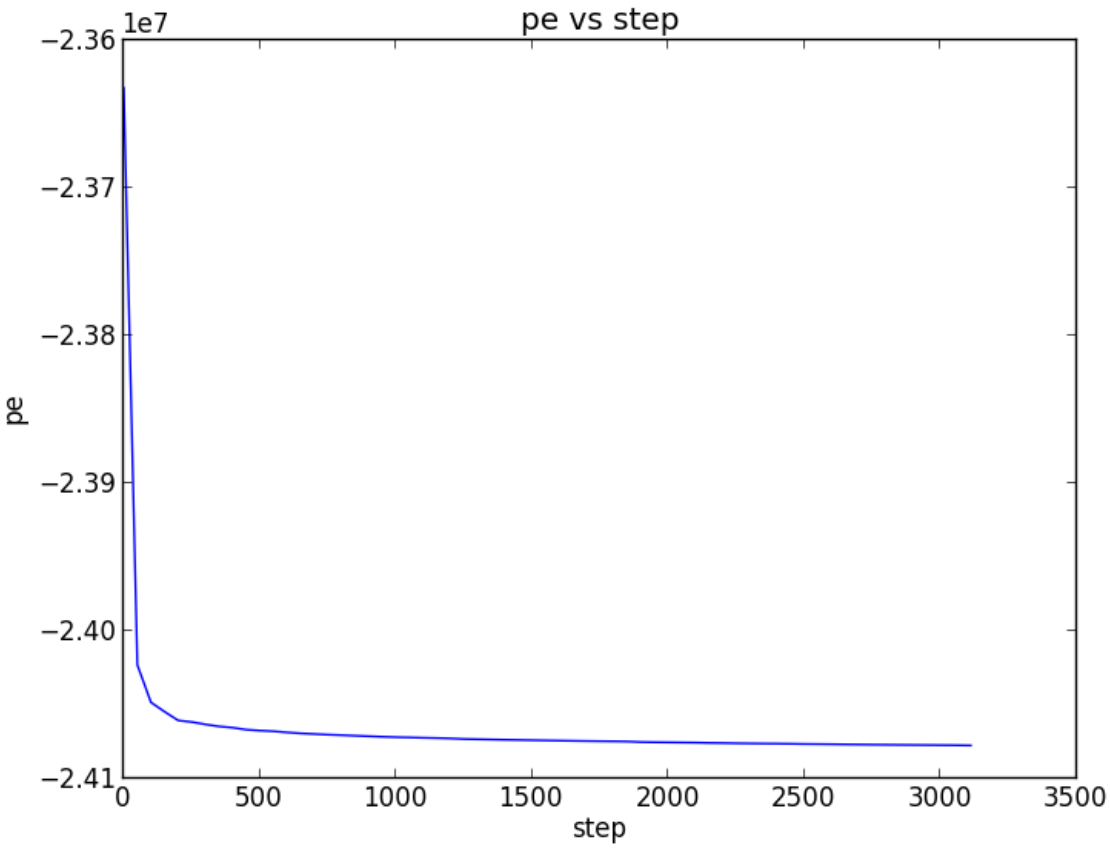
3. Take the equilibrated structure aquired in previous section, anneal it to a higher temperature and then slowly reduce the temperature back to 300 K.

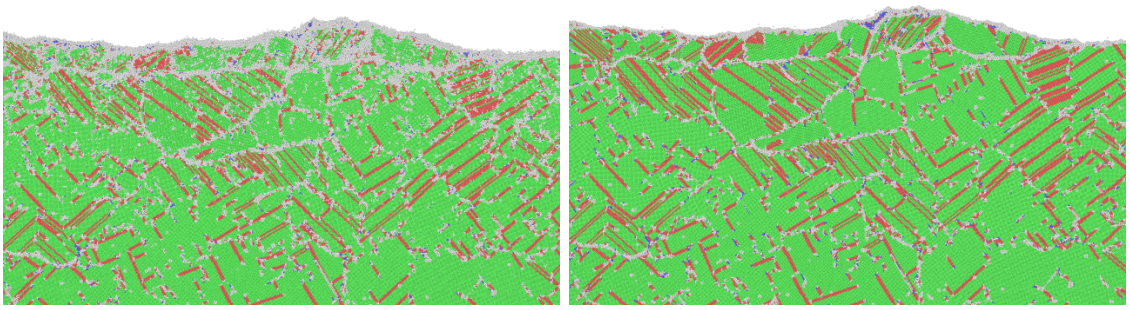
Figure 4.1.1: Initial sample

4.2 minimization

To perform minimization, the atoms forming the jet were removed, as it basically consists of evaporated atoms. The remaining sample consists of 6.85 million atoms: while further simulations were carried on a much smaller systems, This step was performed on a larger system to be able to identify interesting regions and to cut out an interesting sample after minimization,. Energy minimization was performed using Conjugate Gradient method with quadratic line search algorithm, which tries to minimize the forces acting on the atoms, while making sure, that the total energy is not increased. As mentioned, the system is intially compressed, so additionaly the simulation box size was allowed to dynamically change in the periodic z-direction. As can be seen from the CNA picture(lisa pilt!), the amount of stacking faults and point defects has reduced. The minimizer terminated because line-search parameter α reached 0, in other words, the minizer could not reduce energy any further.(Citation α kohta) This means, that the sytem had reached a local energy minimum, but this method offers no way to assess the quality of this local minimum.

Figure 4.2.1: Potential energy during minimization





(a) before the minimization

(b) after the minimization

4.3 temperature ramping

After the initial minimization, a smaller sample was cut out of the system. The reasons for that were two-fold: first, only parts of the system exhibit an interesting polycrystalline structure and second, simulating the whole system would not be computationally feasable. The resulting sample consists of about 1.5 million atoms and is 100 nm long in the x-direction, 40 nm wide in y-direction and 4 nm thick in z-direction. The bottom layer was kept fixed during the temperature ramping, because without it, the system deformed undesireably during the simulation. To raise the temperature to 300 K, velocities were first created for the atoms corresponding to a temperature of 10 K with a gaussian profile. Because the velocity creating algorithm uses a random number generator, net linear and angular momentum have to be zeroed to prevent the sample as a whole from moving. After that, a Nose-Hoover thermostat was used to increase the temperature to 300 K with a simulation time of 100 ps. A Nose-Hoover barostat was also used to allow the sample to expand in the periodic direction and to keep the external pressure component p_{zz} at 0 Pa.

4.4 equilibration

After the temperature ramping, equilibration was performed for 100 ps with N-H thermostat and barostat, which kept the temperature at 300 K and p_{zz}at 0 Pa. In MD simulations, an equilibration is called a simulation during which, the conditions imposed on the material, for example temperature and pressure, are not changed and dynamics is run for some time to allow the system to relax to a lower energy through thermal fluctuations. This is necessary, because very rarely the conditions can be changed as slowly as needed for the system to remain in equilibrium and is often done after a simulation with changing conditions.

4.5 annealing

To process the material further, simulated annealing was used, to further remove the defects present. Annealing consists of 3 steps:

1. Raising the temperature to some higher temperature, than used in other simulations. In this work, temperatures $0.4T$, $0.6T$ and $0.8T$ are used, where T is the melting point of copper for this potential: $T = 1320K$(viide).

2. keeping the temperature elevated for some time

3. slowly reduce the temperature back to working temperature

   The idea of this procedure is to first increase the energy of the system so that it would overcome the the energy barrier that confines it to it's current local minimum of the potential energy surface and let it reach an equilibrium state corresponding to a higher temperature.

4.6 Applying force

5 Coupling electrostatics and MD

Bibliography

[1] How supercomputers will yield a golden age of materials science - scientific american.

[2] Ellad B. Tadmor. *Modeling materials: continuum, atomistic, and multiscale techniques*. Cambridge University Press, Cambridge ; New York, 2011.

[3] M Aicheler and European Organization for Nuclear Research. *A Multi-TeV linear collider based on CLIC technology: CLIC Conceptual Design Report*. CERN, Geneva, 2012.

[4] A. Descoeudres, T. Ramsvik, S. Calatroni, M. Taborelli, and W. Wuensch. dc breakdown conditioning and breakdown rate of metals and metallic alloys under ultrahigh vacuum. *Physical Review Special Topics - Accelerators and Beams*, 12(3):032001, March 2009.

[5] H. Braun, S. DÃ¶bert, I. Wilson, and W. Wuensch. Frequency and temperature dependence of electrical breakdown at 21, 30, and 39 GHz. *Physical Review Letters*, 90(22), June 2003.

[6] W. Wuensch. Observations about RF breakdown from the CLIC high gradient testing program. 2006.

[7] S. Parviainen, F. Djurabekova, H. Timko, and K. Nordlund. Electronic processes in molecular dynamics simulations of nanoscale metal tips under electric fields. *Computational Materials Science*, 50(7):2075–2079, May 2011.

[8] A. Descoeudres, Y. Levinsen, S. Calatroni, M. Taborelli, and W. Wuensch. Investigation of the dc vacuum breakdown mechanism. *Physical Review Special Topics - Accelerators and Beams*, 12(9):092001, September 2009.

[9] A. S. Pohjonen, S. Parviainen, T. Muranaka, and F. Djurabekova. Dislocation nucleation on a near surface void leading to surface protrusion growth under an external electric field. *Journal of Applied Physics*, 114(3):033519, July 2013.

[10] Alexander Stukowski. Structure identification methods for atomistic simulations of crystalline materials. *Modelling and Simulation in Materials Science and Engineering*, 20(4):045021, June 2012.