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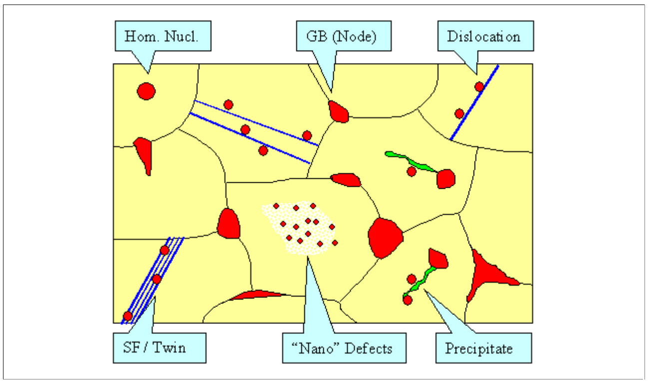
Nucleation Science

Science

5. Precipitation and Structures

General Stuff

- Having patiently worked through the preceding modules, you now know that new phases nucleate heterogeneously at defects, and rarely grow very large. So what can we expect the **structure** to look like?
    - Well - there are plenty of structural pictures in the Hyperscript. Here I only will make a few very general and some very special remarks, to sort of close the topic.
- In a run-of-the-mill poly crystal, full of grain boundaries, dislocations, stacking faults, and what not, we expect a precipitate structure roughly as shown below.



Possible precipitate structure.

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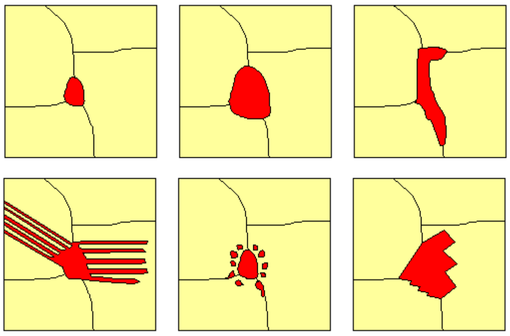
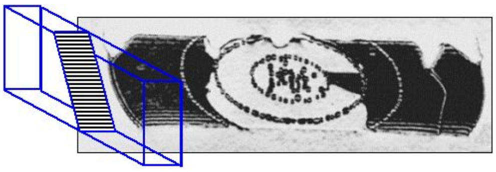
    - Grain boundary nodes are powerful nuclei, as are straight stretches of grain boundaries. Precipitates of some *other* kind that happen to be around, are good nuclei, and so are precipitates of the *same* kind that came into being perhaps on an earlier processing treatment.
      Pretty much all defects will serve as nuclei, and that includes "nano" defects that you cannot see, not even in an electron microscope (see below). How efficient a certain defect will be in nucleating a certain precipitate under certain circumstances depends very much on details, of course.
      Homogenous nucleation is not forbidden either, it's just unlikely.
- Now we need to get one step beyond just *nucleating* a second phase. We now look at the **growth of the second phase**.
    - True, everything said so far would simply imply that the precipitate tries to be spherical or "UFO" shaped. So, when it grows, it just changes from a small sphere / UFO to a big sphere / UFO?
      Does it? Well - it might. Then it might not.
      The reason is that so far we only tried to minimize some surface or interface energies. That is fine as long as the precipitate is rather small. But even at the still small (spherical) size of 20 nm radius, only about 5 % of the atoms are at the surface - check the table! When we look at 100 nm and beyond, the surface just doesn't matter all that much any more. Other things now might matter more.
      The figure below gives some ideas about what a small precipitate can develop into. Rest assured that in real three-dimensional crystals much more can happen.



What a small precipitate can evolve into.

Precipitate about to grow	Just getting bigger	Following favored GB's
Self-organized structure	Forming "colonies"	Facetting

- The figures are rather self-explaining. All of that (and more) has been observed. An example of "colony" formation is shown below in a "TEM" picture.
  - The point defects precipitating in this case are silicon *self-interstitials*. The precipitate they form is a little disc of silicon atoms, wedged in between the planes of the crystal, and otherwise known as a dislocation loop with a stacking fault.
    We have a whole system of loops, truncated by the surfaces of the thin sample, that were nucleated by some (invisible) small defect right in the center of the system. Some of the loops show a kind of zebra pattern, some show nothing at all (i.e. are invisible in this picture), and that is perfectly normal and we know how to deal with that.
    The interesting things are those tiny little circlets arranged at random in the center and otherwise following a circular pattern. They are "colony" loops, nucleated at the perimeter of one of the old big loops. There is nothing special to that - they just illustrate on of the options given in the figure above



**Precipitation of silicon self interstitial in dislocation loops,
and colonies of small secondary loops.**

  - The inset just illustrates the geometry. We are looking *through* a thin sample (that's why the big circular loops are truncated). The loops are inclined in the sample - that's why their projection produces ellipses.
- Notice how cunningly I guided you into the big question coming up now?

What happens in *real* perfect crystals where heterogeneous nucleation should not be possible?

Special Stuff

- In perfect *brain* crystals there are by definition no defects so you can't have heterogeneous nucleation at defects. True enough - but what do you want to nucleate now? There are no foreign atoms in need of precipitation, after all
  - Right. But we still have vacancies and self-interstitials that must be there at high temperatures. When the crystal cools down they become supersaturated and need to disappear. Since there are no other defects that can absorb the little guys, they must go for the second best option and form agglomerates. But how do they handle nucleation?
    We asserted that homogenous nucleation never takes place, and heterogeneous nucleation can't happen either. We have a problem.
  - Before I get to this, let's consider if there actually are *real* crystals that are perfect.
    Yes, there are. The big silicon crystals on which all micro-electronics depends, are rather perfect. They are "grown" at high temperatures and when they cool down we must expect that something happens.
    Right. And what happens is explained to some extent right here.

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