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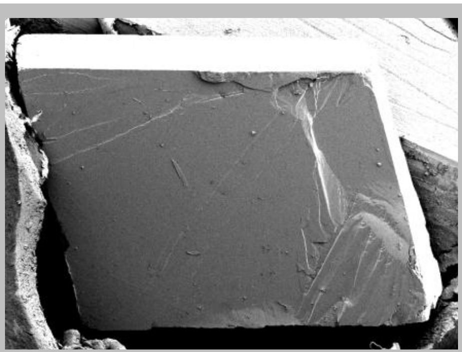

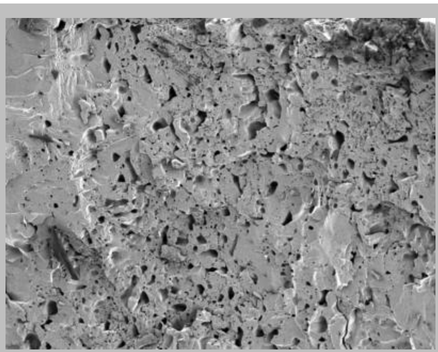

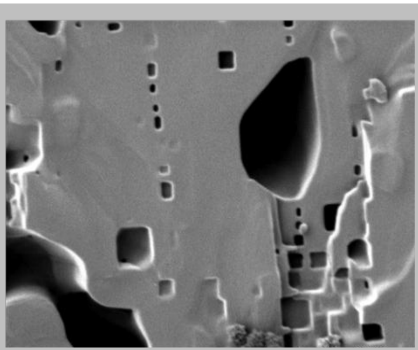

Role of Defects in Thermal Decomposition of Solids

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Sandia National Laboratories

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U.S. DEPARTMENT OF ENERGY

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Motivation – Understanding and Modeling Thermal Decomposition in Solids

- Thermal decomposition of energetics is a physically and chemically complex process
  - Complex chemistry
  - Physical effects – defects, phase changes, etc.
- One of the greatest challenges in EM science: Predictive modeling of cook-off
  - Multicomponent systems (formulations)
  - Multiple length scales
  - Plus chemistry and physics
- Even pure materials are challenging
  - Particularly solids
  - Classic example – ammonium perchlorate LTD
  - Defects drive chemistry – a “hidden variable” that turns a challenging problem into a mystery

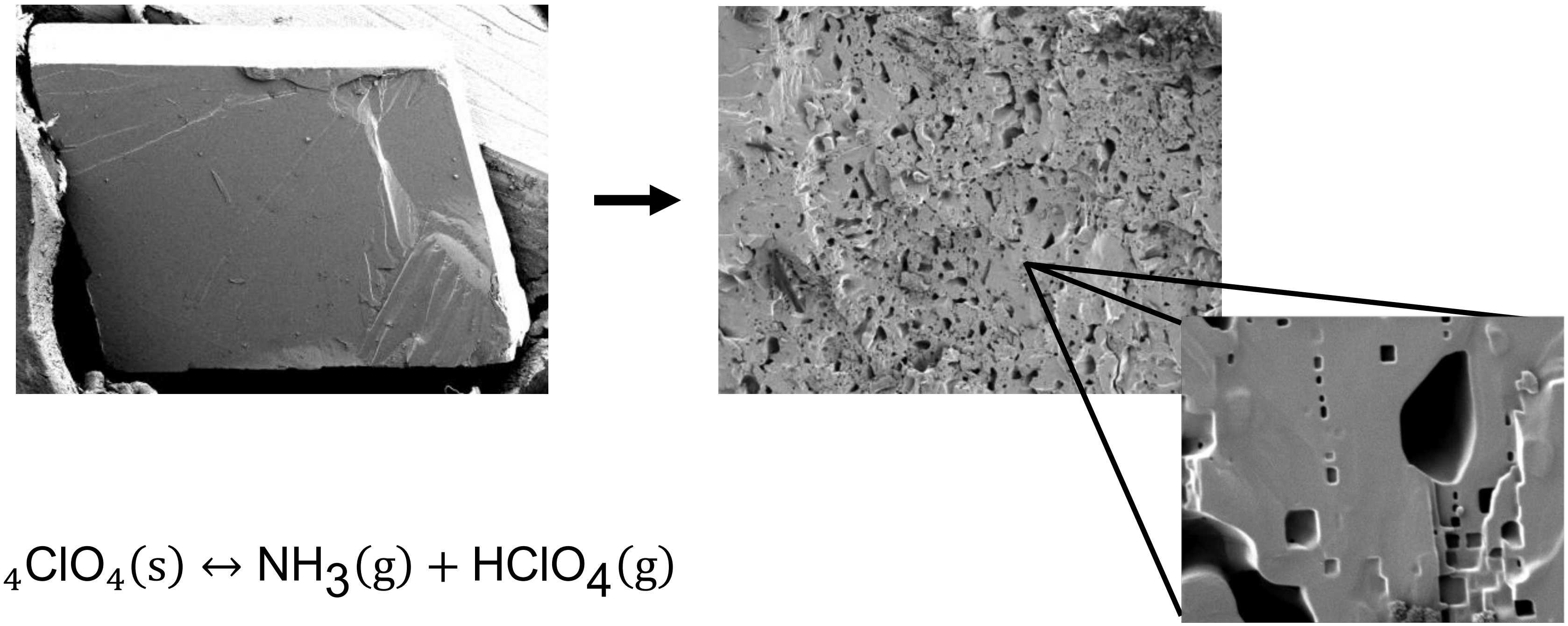
Thermal Decomposition in Solids

- What makes solids difficult?

- Decomposition of solids at low temperatures is often inhomogeneous
  - Decomposition begins at localized sites
  - Often driven by defects
  - Defects can be difficult to quantify
  - Defects initiate chemistry in ways that are hard to interrogate
  - Decomposition chemistry in materials of interest is often complex/multi-step

Example – AP LTD

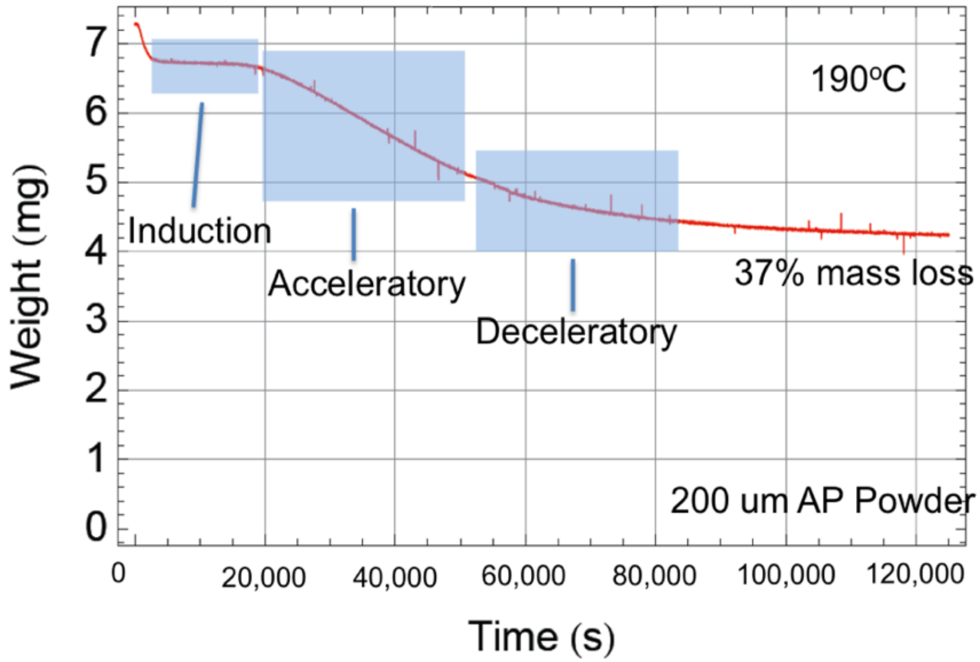
- Ammonium perchlorate low-temperature decomposition is an interesting example in SSD



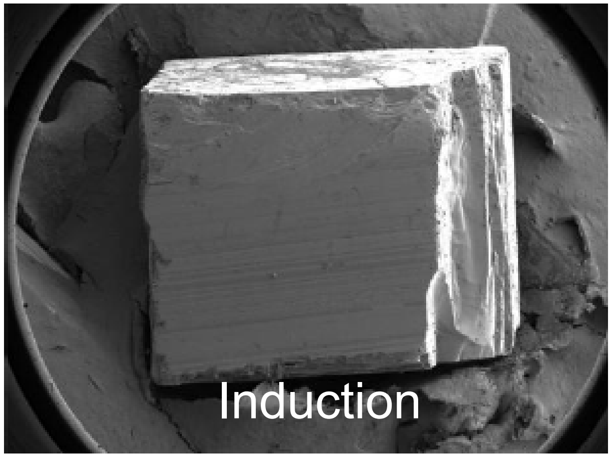
$$NH_4ClO_4(s) \leftrightarrow NH_3(g) + HClO_4(g)$$

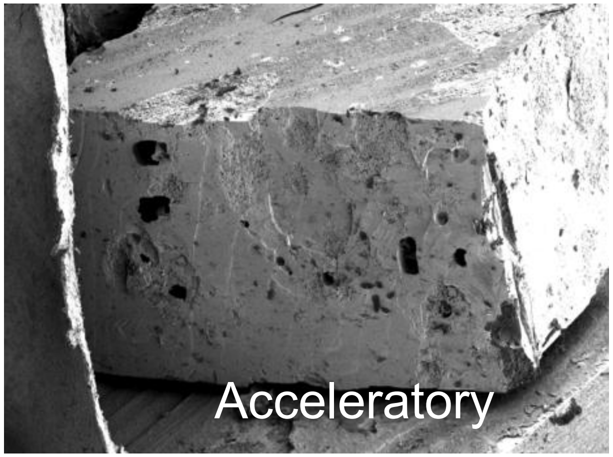
$$NH_4ClO_4(s) \rightarrow H_2O(g) + O_2(g) + N_2O(g) + Cl_2(g) + N_2(g) + NO(g) + NO_2(g) + ClO_2(g)$$

Example – AP LTD

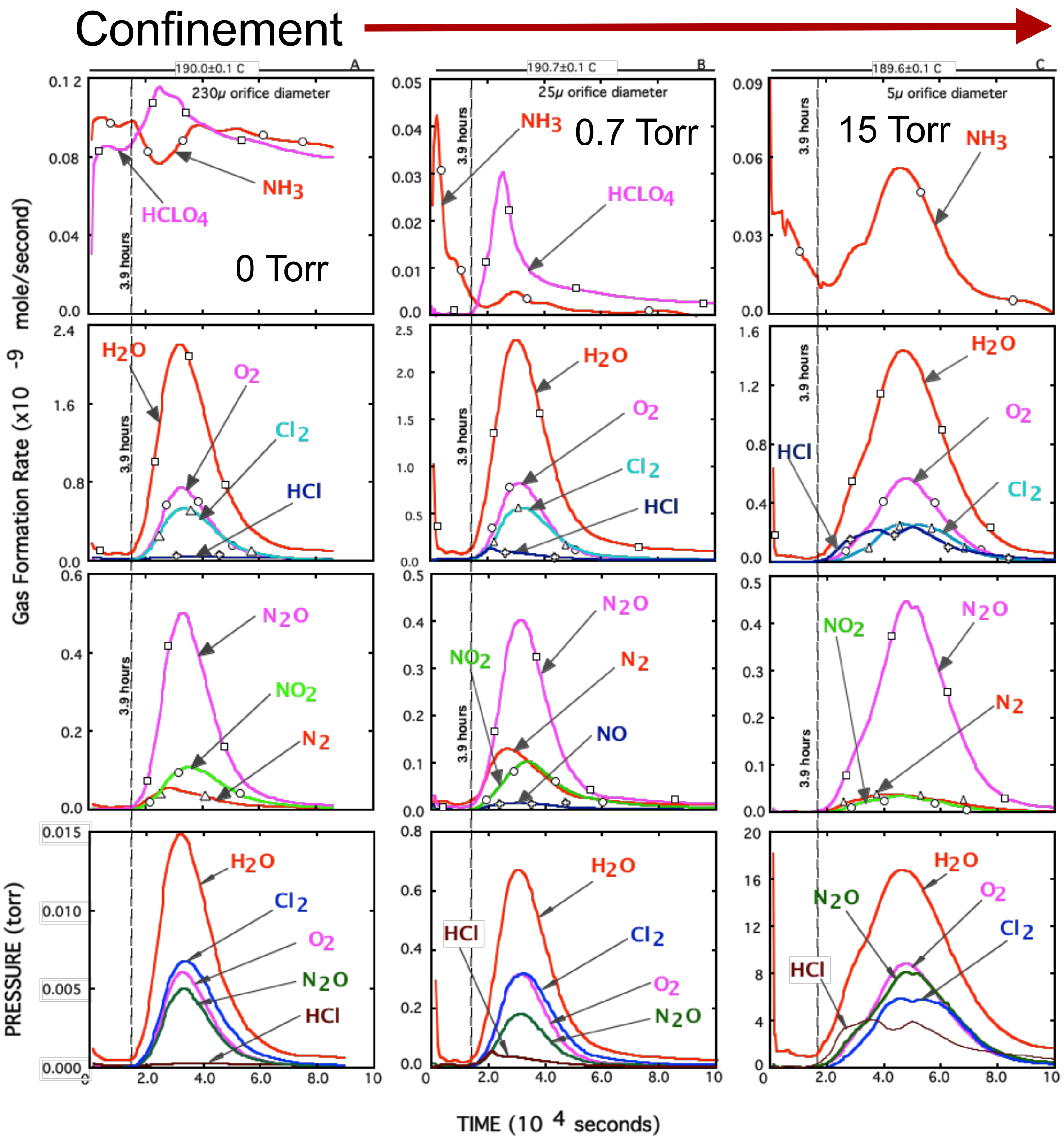


Thermogravimetry data on 200 µm AP powder, 190°C isothermal for ~35 hours





Example – AP LTD

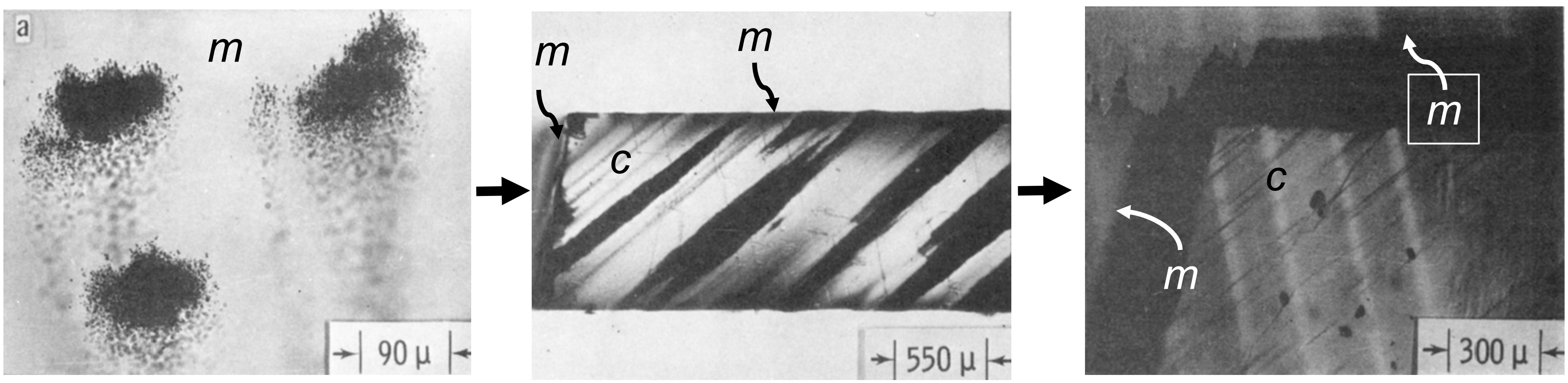


Decomposition kinetics depends on confinement, particle size, impurities, etc.

Minier and Behrens, CPIA Publication **691**, 626 (1999)

Example – AP LTD

- Reacts by nucleation, growth, and interfacial advance process



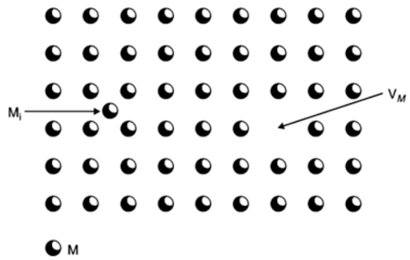
Kraeutle, *J. Phys. Chem.* **74**, 1350 (1970)

Defects in Solids

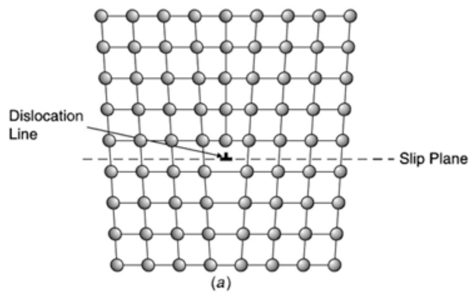
- Defects are often *more important* in properties of solids than the lattice itself
  - Mechanical properties
    - Flexibility
    - Ductility
    - Hardness
    - Fatigue
  - Electronic properties
    - Band structure
    - Conductivity
    - Optical properties – lasers
  - Properties of solids are often manipulated by changing defect profile of material
    - Mechanical working
    - Thermal treatment (annealing, quenching)
    - Doping

Defects in Solids

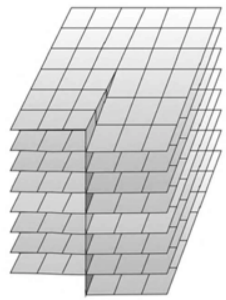
- Come in several varieties:
  - Point defects (0D)
    - Lattice vacancies
    - Interstitial substitutions
    - Substitutional defects
  - Line defects (1D)
    - Dislocations
  - Planar defects (2D)
    - Grain boundaries
    - Stacking faults
    - Surfaces
  - Volume defects (3D)
    - Voids
    - Inclusions
    - Impurity clusters



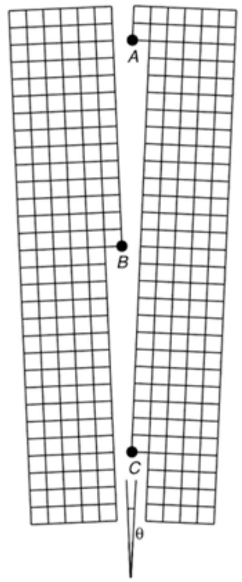
Interstitial defect, Lattice vacancy (0D)



Edge dislocation (1D)



Screw dislocation (1D)



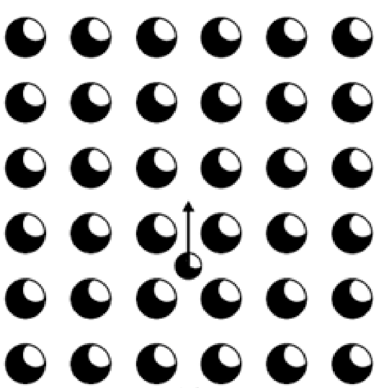
Grain boundary (1D)

R. Tilley, *Defects in Solids*, Wiley (2008)

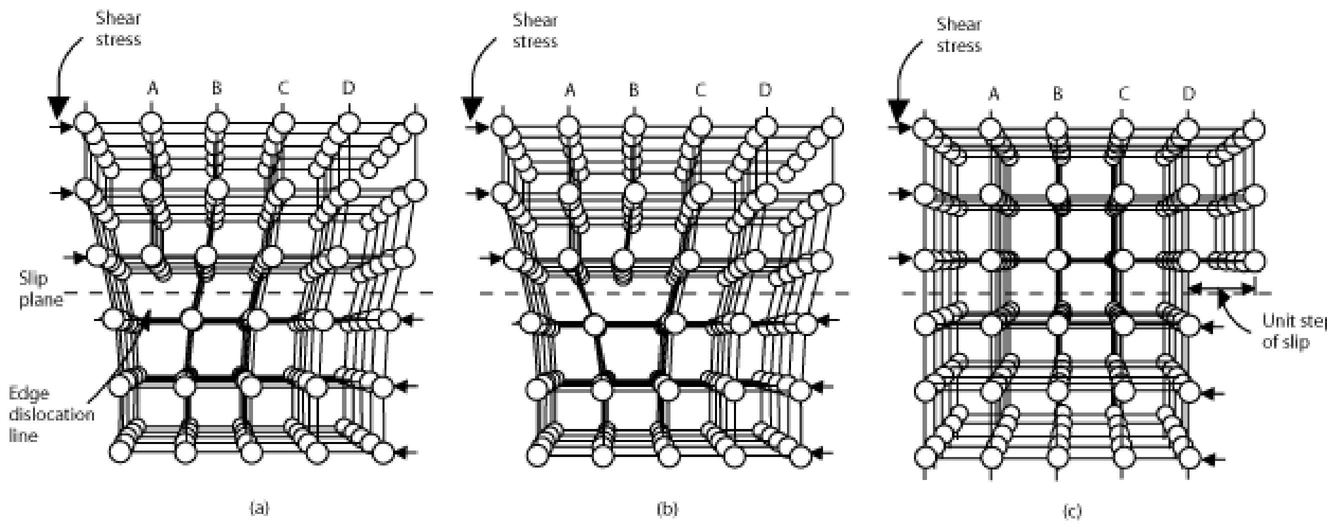
Motion of Defects

- Defects can also *move*, and their motion is important in dynamic processes and material processing

Thermal motion of point defect



Motion of dislocation:
Mechanical -> Stress annealing
Thermal -> Thermal annealing



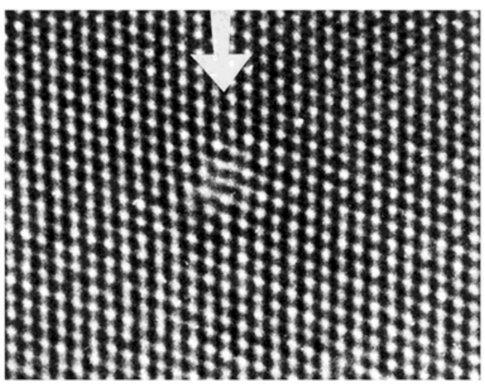
R. Tilley, *Defects in Solids*, Wiley (2008)

www.nde-ed.org

Observing Defects

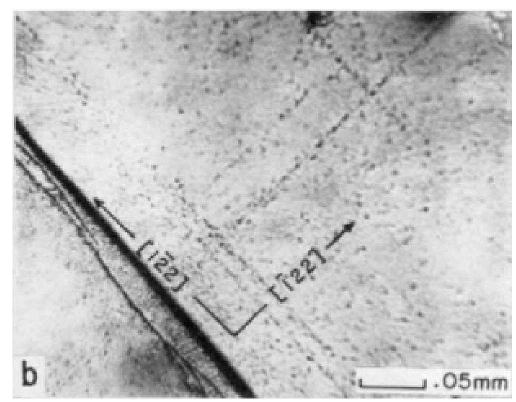
- How can we observe/quantify defects?
- Point defects
  - Conductivity measurements
  - Photoluminescence
- Extended defects (dislocations, grain boundaries)
  - Etching and scanning electron microscopy (SEM)
  - Scanning tunneling microscopy (STM)
  - Tunneling electron microscopy (TEM)
  - X-ray diffraction (quantification of microstrain)

STM of dislocation in CdTe



R. Tilley, *Defects in Solids*, Wiley (2008)

SEM of etched AP

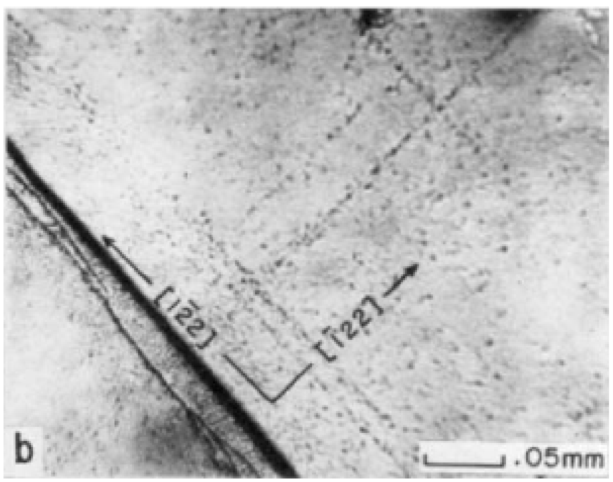


Herley and Levy, *J. Chem. Soc. A* 434 (1971)

Defects and Chemistry

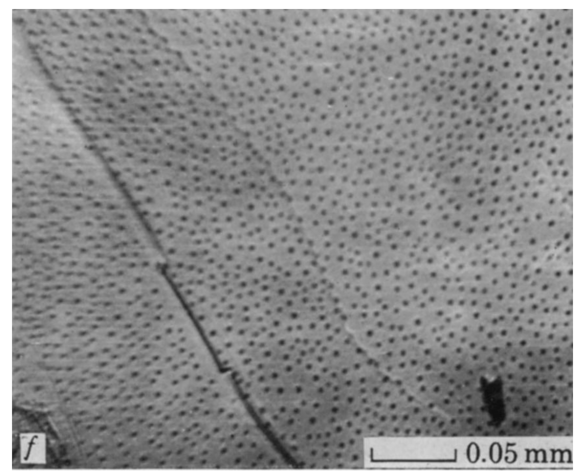
- Defects alter the local environment in the crystal
  - Orientational changes (different relative geometry of molecules)
  - Volumetric changes (more room for molecular motion)
  - Electronic changes (variations in local electronic structure)
- These change the local effective activation energy

Nuclei from etching AP



Herley and Levy, *J. Chem. Soc. A* 434 (1971)

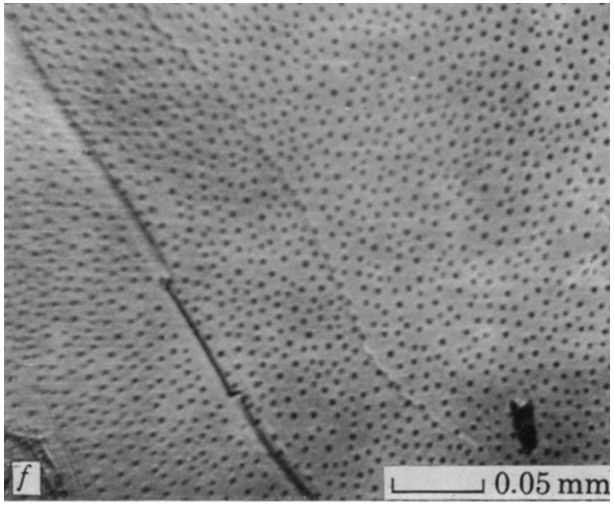
Nuclei from thermal decomposition of AP



Herley and Levy, *Proc. Roy. Soc. A* **318**, 197 (1971)

Defects and Kinetics – Nucleation

- What do we know about the kinetics of solid decomposition in solids?
- Nucleation is the formation of discrete product sites in solid
- Many types depending on chemistry:
  - Single-step
    - One-step reaction establishes nucleus
  - Instantaneous
    - Fast; all nuclei are formed at onset of reaction
  - Linear
    - Slow; concentration of nuclei linear in time
  - Multi-step
    - Requires multiple steps; power law behavior
  - Branching
    - Each nucleus creates more nuclei. Exponential



c face of AP crystal showing nuclei; Herley and Levy (1970)

** Discussion of kinetics derived from Galwey and Brown, *"Thermal Decomposition of Ionic Solids"*, Elsevier (1999)

Defects and Kinetics – Nucleation

- Accordingly, rate laws are different:
  - Exponential $$\frac{dN}{dt} = k_N N_0 \exp(-k_N t)$$
  - Linear $$\frac{dN}{dt} = k_N N_0$$
  - Instantaneous $$\frac{dN}{dt} = \infty$$
  - Power Law $$\frac{dN}{dt} = C\eta t^{\eta-1}$$
  - Branching $$\frac{dN}{dt} = k_N N_0 \exp\big((k_B - k_T)t\big)$$

N_0: Number of potential reaction sites
k_N: Nucleation rate constant
k_B: Branching rate constant
k_T: Termination rate constant
η: # of steps in reaction

Defects and Kinetics – Growth of Nuclei

- Nuclei grow, forming a *reaction interface*
- Rates of *interface advance* are usually constant:

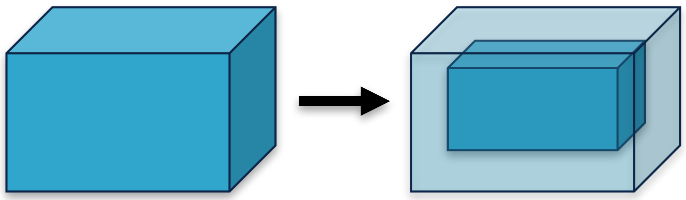
$$\frac{dr}{dt} = k_G(t - t_0)$$

- Growth may be 1, 2, or 3 dimensional.
- Combining nucleation and growth rates enables development of rate laws for reaction.

Solid State Decomposition Models – Geometric Effects

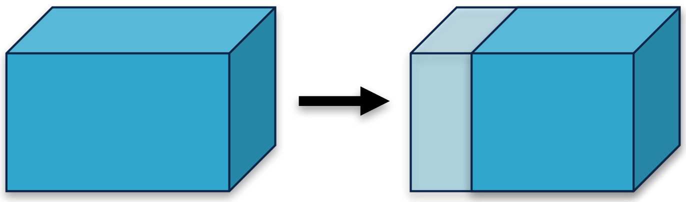
- Geometry plays an important role in SSD
  - Single crystals vs. powders, etc.

- How does reaction advance?
  - Contracting volume
    - Cube/rectangle/sphere
    - Rapid nucleation on *all* surfaces



$$\alpha = [abc - (a - 2k_a t)(b - 2k_b t)(c - 2k_c t)]$$

  - Contracting area
    - Cylinder/rectangle/disc
    - Rapid nucleation on *specific* surfaces



$$1 - (1 - \alpha)^{\frac{1}{n}} = kt$$

Solid State Decomposition Models – Diffusion and Particle Size Effects

- Several expressions developed for diffusion

$$\alpha = (k_D t)^{1/2} \text{ (Parabolic law)}$$

$$\alpha = k_1 \ln(k_2 t + k_3)^{1/2} \text{ (Logarithmic law)}$$

$$\alpha = k_1 t + k_2 \text{ (Linear law)}$$

- Can also develop expressions for particle size effects:

$$\alpha(t, a) = 1 - [1 - t/(\rho a/k)]^3$$

Particles of radius *a* with interface rate k/ρ

Current Work on AP

- How can we use all of this to our advantage?

- Quantify defects in AP samples
  - Single crystals
  - Powders
  - Recrystallized powders
- Quantify dislocation densities using XRD
  - Dislocation densities can be calculated from XRD parameters[1]:

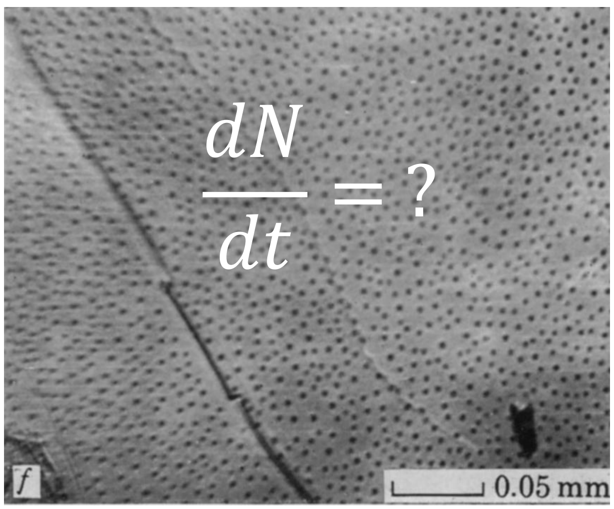
$$\rho = \frac{2\sqrt{3}\langle\varepsilon^2\rangle^{1/2}}{Db}$$

ε is lattice strain, b is magnitude of Burgers vector, D is crystallite size

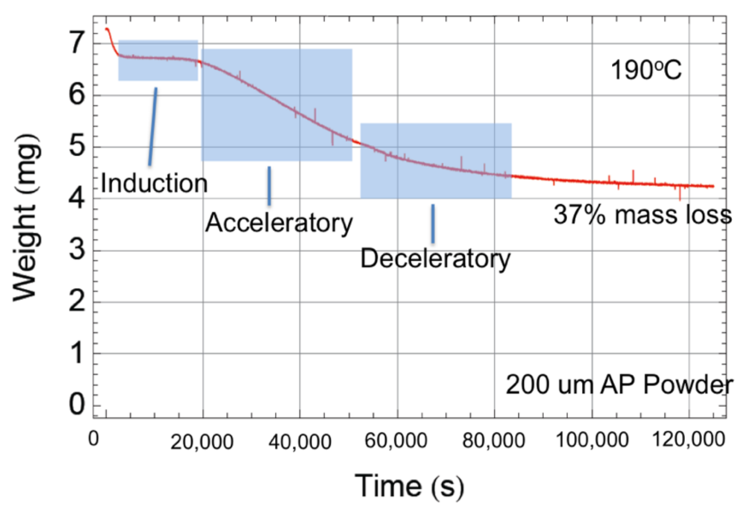
[1] Yang, *et al.*, *Acta Materialia* **82**, 41 (2015)

Current Work on AP

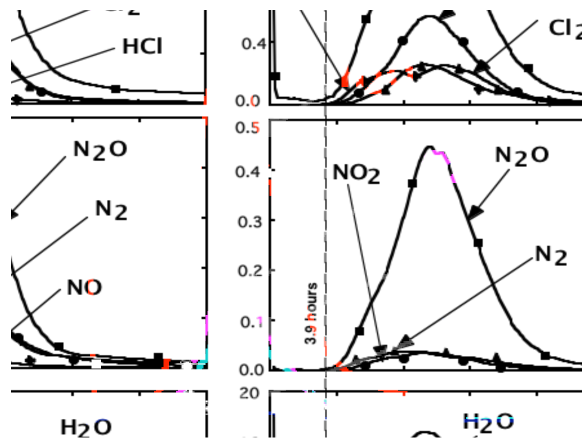
- Dislocation densities can be correlated with decomposition kinetics
  - Length of induction period and kinetics
  - Density of nuclei as a function of time (SEM)
  - Characteristics of acceleratory period (length, product spectrum) from thermogravimetry and mass spectrometry (STMBMS)



SEM of nuclei
Herley and Levy (1970)



Thermogravimetry data
(STMBMS)



Product rates
(STMBMS)

Current Work on AP

- Work on aged samples
- 20-year-old naturally-aged AP powders
  - Defect quantification
  - Decomposition kinetics
  - What are effects of aging?
- Thermal annealing
  - How does heating alter dislocation densities?
  - Heat samples, quantify with XRD, observe decomposition kinetics

Acknowledgments

Thank you to:

US DoD/DOE Joint Munitions Program