MSE 205 Lecture 29

Grain, Particle and Crystalline Size

Recap

The arrangement of atoms in a crystal structure not only depends on the charge on the ion and type of bonding between atoms, but also on the size of the atoms or ions.

The **special arrangement of the ligand atoms which are directly attached to the central atom/ion** forms the coordination polyhedron around the central atom/ion. Tetrahedral, square planar, octahedral, square pyramidal and trigonal bipyramidal are common shapes of coordination polyhedra.

Linus Pauling studied crystal structures and the types of bonding and coordination that occurs within them. His studies found that crystal structures obey the five rules, now known as Pauling's Rules.

Grain Size

As far as material science is concerned grain size refers to that volume of a material within which the crystal structure and the orientation of the crystals is same.

At the grain boundaries, you have a change in orientation of the crystal. Or Grains are volumes, inside crystalline materials, with a specific orientation.

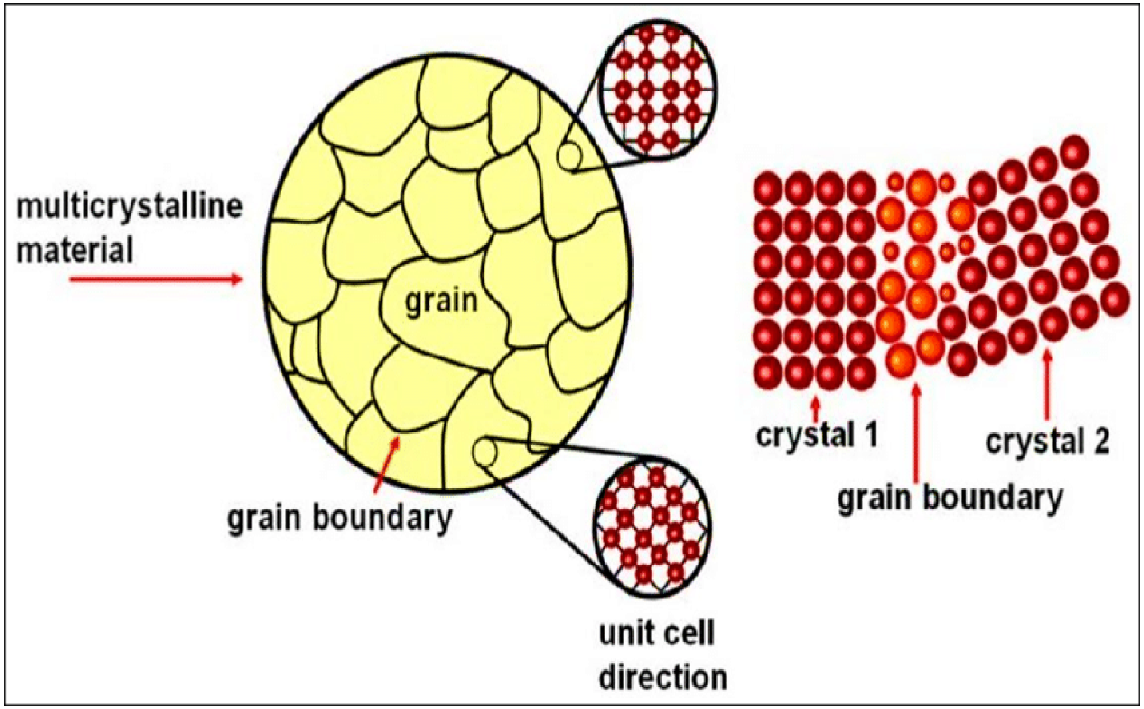
Grain is either a single crystalline or polycrystalline material, and is present either in bulk or thin film form.

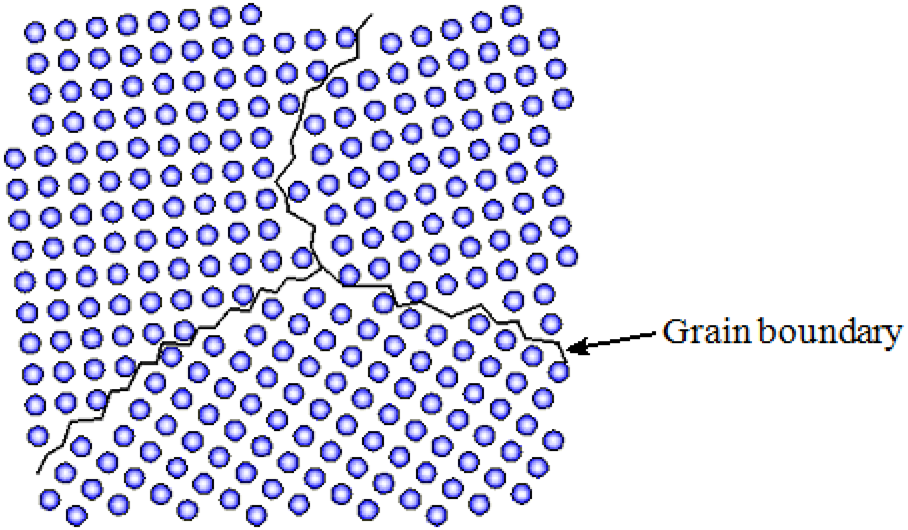
In case of single crystal, the whole crystal can be called as a single grain. Here it can be considered as a particle.

Grain Size

A **grain boundary** is the interface between two **grains**, or crystallites, in a polycrystalline material. **Grain boundaries** are 2D defects in the crystal structure, and tend to decrease the electrical and thermal conductivity of the material.

A finer **grain size** means more **grain** boundaries, and more **grain** boundaries means a greater resistance to dislocation. It is the measured ability of a **material** to withstand serious plastic deformation, making the **material** less ductile


multicrystalline material
grain
grain boundary
unit cell direction
crystal 1
crystal 2
grain boundary


Grain boundary

Grain Size and Hall-Petch Relationship

The **Hall–Petch relationship** tells us that we could achieve strength in materials that is as high as their own theoretical strength by reducing grain size. In other words, the strength increase trades off with ductility in nanostructured metallic materials.

$$\sigma_{yp} = \sigma_o + \frac{k}{\sqrt{d}}$$

Where,

σ_{yield} = Yield stress

σ_o = Friction stress or resistance to dislocation motion

k_y = Locking parameter or the hardening contribution from the grain boundary

d = Grain diameter

How is grain size determined?

One of the simplest techniques to estimate an average **grain size** is the intercept technique. A random straight line is drawn though the micrograph. The number of **grain** boundaries intersecting the line are counted. The average **grain size** is found by dividing the number of intersections by the actual line length.

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Average **grain size** =1/(number of intersections/actual length of the line).

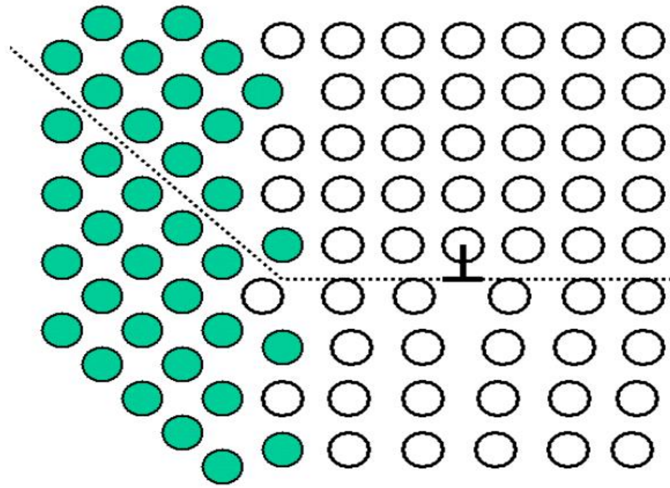
What happens if grain size increases?

If the **grain size increases**, accompanied by a reduction in the actual number of **grains** per **volume**, then the total area of **grain** boundary will be reduced. is radius of the sphere. This driving pressure is very similar in nature to the Laplace pressure that **occurs** in foams.

How does grain size affect strength?

Smaller **grains** have greater ratios of surface area to volume, which means a greater ratio of **grain** boundary to dislocations. The more **grain** boundaries that exist, the higher the **strength** becomes.

Strengthening by grain-size reduction (I)



Grain boundaries are barriers to dislocation motion: slip plane discontinues or change orientation.

Small angle grain boundaries are not very effective.

High-angle grain boundaries block slip and increase strength of the material.

Particle size

On the other hand Particle size is a macro phenomenon. It is the size of the particles which may have 1 or several grains within it.

It is impossible to have a grain having multiple particles because the smallest thing we could have would always represent one single grain.

Particles are chunks/pieces (usually very small, below 1 mm) of solid matter, ensembles of atoms.

Particles can be as small as two atoms (the nitrogen particle for example, N_2

Particle size

Particle size is a notation for the comparative dimension of solid particles.

But when we are talking about the metal, the crystal contains the internal boundaries. Any of the enclosed part by these boundaries, called as grain and its size is called as a grain size.

Generally inside the particle, we can get grains.

Particles can be polycrystalline, single crystal or amorphous. A 100 nanometer particle of gold, for instance, can be made of:

•a single gold crystal

•many grains with a grain size <100 nm,or of amorphous gold.

What is particle size analysis used for?

Particle size analysis is **used** to characterise the **size distribution** of **particles** in a given sample. **Particle size analysis** can be applied to solid materials, suspensions, emulsions and even aerosols. There are many different methods employed to measure **particle size**.

How do you measure particle size on a microscope?

Microscopy can be used as an absolute method of **particle size** analysis, since it is the only method in which individual mineral **particles** are observed and **measured** . The image of a **particle** seen in a **microscope** is two-dimensional and from this image an **estimate** of **particle size** must be made.

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many grains with a grain size <100 nm,
or of amorphous gold.

What are the different methods of reducing the particle size?

Mechanical techniques to decrease the particle-size of solids are generally classified in three categories: dry**-milling**, wet**-milling**, and high-pressure homogenization.

Crystallite size

Crystallite size is the smallest - most likely single **crystal** in powder form. The crystallite size commonly determined by XRD.

Grain is either a single crystalline or polycrystalline material, and is present either in bulk or thin film form. Therefore, particle is under no circumstances smaller than crystallite size.

Crystallite size

Crystallite Size is Different than Particle Size.

A particle may be made up of several different crystallites or just one crystallite so in this case (particle size = crystallite size). Crystallite size often matches grain size, but there are exceptions

Crystallites are coherent diffraction domains in X-ray diffraction.

Crystalline size sometime was written as sub-grain size,and a particle consists of lots of grains or sometimes one crystal.

How do you measure crystallite size?

Scherrer **formula** is used to **calculate** the average **size** in vertical direction of crystal.

$D=K\lambda/(\beta \cos \theta)$.

For cubic crystal structure, K =0.94, λ is wavelength of X-ray. $\boldsymbol{\beta}$ = the full width at half maximum intensity of the peak (in Rad) – you can **calculate** it using Origin software.

SCHERRER FORMULA

Scherrer Formula (1918)

$$T = \frac{K\lambda}{B\cos\theta_B}$$

T = crystallite thickness
λ (X-ray wavelength, Å)
K (shape factor) ~ 0.9
B, θ_B in radians

Accurate size analysis requires correction for instrument broadening:

$$B^2 = B_M^2 - B_R^2$$

B_M: Measured FWHM (in radians)
B_R: Corresponding FWHM of bulk reference (large grain size, > 200 nm)

Note- K actually varies from 0.62 to 2.08

Peter Dier's Rule

According to Peter Dier's Rule, Crystallite is smaller than grain, grain is smaller than particle. Particle consists of grains and grain consists of crystallites

How size can be measured?

Grain size is measured from microstructures using SEM technique where the individual grains and grain boundaries can be observed.

But a particle is more like a morphology whose size can be analysed using particle size analyser and particle size distribution from sieves or andersen pipette.

A particle can be individual grain or multiple grains with grain boundaries which can be seen in SEM images.

Crystallite size measured from scherrer equation from XRD peaks which means the size in which particular crystalline plane is oriented. This is equivalent to grain size (the crystalline plane inside a grain is oriented in same direction) but different from particle size.

Summary

Crystalline size is smaller than grain or particle size.

Inside a grain or particle we have many crystals of identical orientation. Particle size and grain size are not same.

one particle can have several grains. unless you produce a particle which is single crystal.

Crystallite size is the smallest - most likely single crystal in powder form. The **crystallite size** commonly determined by XRD. **Grain** is either a single crystalline or polycrystalline material, and is present either in bulk or thin film form. . Therefore, **particle** is under no circumstances smaller than **crystallite size**.