

# Physics of Nanomaterials

## Module II

### Properties of Nanomaterials

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#### Learning objectives

*Microstructure and defects in nanomaterials, dislocations, twins, stacking faults and voids, grain boundaries*

*Effect of nanodimension on material behavior, mechanical properties, melting point, diffusivity, grain growth characteristics, solubility, magnetic, electrical and thermal properties of nano materials*

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## 1.How nano-dimension effect the thermal properties of materials?Explain

### EFFECT OF NANO-DIMENSIONS ON MATERIALS BEHAVIOUR

#### 1.Thermal properties

##### a).Decreasing of thermal conductivity

1. In the gas kinetic theory, the relation for thermal conductivity is known:

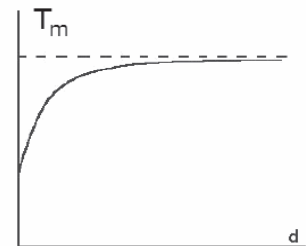
$$K = 1/3 C v l$$

where  $v$  is a particle velocity,  $l$  is a free path length,  $C = cn$  is a heat capacity of unit volume,  $c$  is a heat capacity of single particle,  $n$  is a number of particles.

2. One can apply this simple model for thermal phonons gas in metal regarding the free path length is the free phonon path,  $l = l_{\text{phonon}}$ . For bulk solid of big size  $d > l_{\text{phonon}}$ , the size effect do not arise. However under reducing of the size  $d$  it can become smaller than free path length  $d < l_{\text{phonon}}$ , resulting to a cut of phonon spectra and decreasing of  $K$ .
3. In general, increasing the number of grain boundaries will enhance phonon scattering at the disordered boundaries, resulting in lower thermal conductivity. Thus, nanocrystalline materials would be expected to have lower thermal conductivity compared to conventional materials. However, as the grain sizes assume nanodimensions, their size becomes comparable to the mean free paths of phonons that transport thermal energy.
4. In nanowires, quantum confinement of phonons in 1D can result in additional polarization modes compared to that observed in bulk solids. The strong phonon–phonon interactions and enhanced scattering at grain boundaries result in a significant reduction in thermal conductivity of nanostructures.

##### b).Melting Temperature

1. It is known that atoms in a solid vibrate about their mean position. The amplitude of the vibrations increases with increasing temperature. When the vibration amplitude exceeds a certain percentage of the bond length, melting begins at the surface and propagates through the solid.
2. Atoms at the surface and grain boundary are less constrained to vibrate compared to atoms inside the crystal lattice. As the grain size decreases, the percentage of atoms residing at surfaces and grain boundaries increases significantly. Hence, freestanding nanoparticles may show a lower melting point compared to bulk.
3. In contrast to nanoclusters and nano-agglomerates, nanoparticles within a matrix may, in fact, experience an enhancement in the melting temperature. The matrix exerts a pressure, which can affect the melting temperature of the particles.

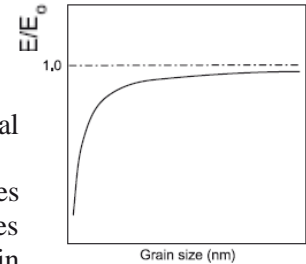


## 2.What is nano-dimension? How nano-dimension effect the mechanical properties? Explain.

### 2.Mechanical properties

1. The elastic modulus of a material is proportional to the bond strength between atoms or molecules. The higher the bond strength, the higher will be the melting point and elastic modulus.
2. The second differential of the interatomic force–distance curve at the position of equilibrium separation distance is known to be proportional to the elastic modulus.

- The elastic properties of crystalline materials are usually considered to be structure (microstructure) independent. If the temperature is increased, the mean separation between atoms increases and the elastic modulus decreases.
- A large increase in vacancy and other defect concentrations can be treated as equivalent to higher apparent temperature. Increasing the defect concentration is thus expected to decrease the elastic modulus. However, the effect of defects on the elastic modulus is manifested only at significantly higher concentration of vacancies.
- Nanomaterials, by virtue of their very high defect concentration, may have considerably lower elastic properties in comparison to bulk materials.
- Elastic moduli were found to be 30%–50% lower than in conventional grain size materials.
- Hardness and strength were found to be very high, with hardness values for nanocrystalline pure metals (~10 nm grain size) up to seven times higher than those for conventional coarse-grained (>1 μm) metals; in general, tensile and compressive strengths in nearly all materials show significantly high values at the nanometre scale.
- Nanoscale multilayers made of metallic or ceramic materials exhibited ultrahigh hardness. The Hall–Petch slope is negative below a critical grain size, showing that hardness decreases with decrease in grain size in the nanoscale grain size regime.
- Ductility (possibly superplastic behaviour) is observed at low temperature in brittle ceramics or intermetallics with nanoscale grain size, possibly due to diffusional deformation mechanisms—an area to be explored.

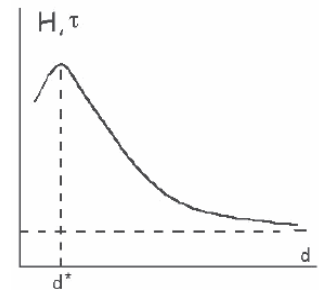


#### Increasing of plastic yield strength and hardness of polycrystal

- In physics of strength the Hall-Petch relation is well known of which accordance a hardness and yield strength are increased under the reduction of the grain size  $d$  of polycrystal:

$$\tau_H = \tau_0 + \frac{K_1}{\sqrt{d}}$$

where  $\tau_0$  deformation strength of monocrystal is,  $\tau_P$  is a strength of polycrystal,  $K_1$  is a coefficient of fracture ductility. The dependence is shown in fig. and successfully used in the industry.



- However in extreme case  $d \rightarrow 0$  this relation do not works. The critical size  $d = d^*$  exists when  $\tau$  approaches its maximal value  $\tau = \tau^*$  and then drops again. The reason is disappearance of dislocation, the carriers of plastic deformation, due to nanoparticle size becomes to be smaller than a dislocation length,  $d < l_{dislocation}$ , because of which all dislocations come to a surface.

### 3.Explain electrical properties variation based on effect of nano-dimension? OR

What is diffusivity? How diffusivity undergoes change with nano-dimension?Explain.

#### 3.Electrical properties:

- Nanomaterials can hold considerably more energy than conventional coarse-grained materials because of their large grain boundary (surface) area. They are materials in which an optical absorption band can be introduced, or an existing band can be altered by the passage of current through these materials, or by the application of an electric field.
- Conventional and rechargeable batteries are used in many applications that need electrical energy. The energy density (storage capacity) of these batteries is usually quite low, requiring frequent recharging.
- Nanocrystalline materials are good candidates for separator plates in batteries because they can hold considerably more energy than conventional ones. Nickel– metal hydride batteries made of

nanocrystalline nickel and metal hydrides are envisioned to require far less frequent recharging and to last much longer.

4. The dielectric properties are significantly enhanced by making these nanocrystalline.
5. The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic properties of the materials.
6. Nanoparticles made of semiconducting materials like Germanium, Silicon and Cadmium are not semiconductor. Nanoclusters of different sizes will have different electronic structures and different energy level separations. So they show diverse electronic properties which depend on its size.

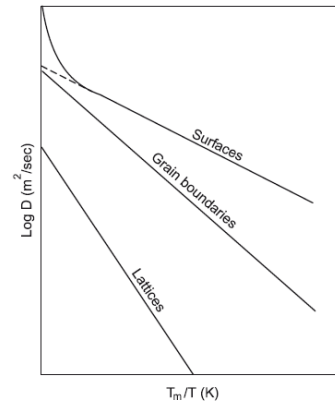
#### Diffusivity:

1. Diffusion kinetics increases with increasing defect content of the material, like vacancy concentration. Grain boundaries and dislocation cores provide easy diffusion paths compared to bulk lattice, because the structure is more open/defective. Thus, fewer atomic bonds have to be disrupted for diffusion along defect cores, resulting in lower activation energy paths.
2. The numerous interfaces in nanocrystalline materials provide a high density of short circuit diffusion paths. Thus, nanocrystalline materials are expected to exhibit enhanced selfdiffusivity in comparison to single crystals or conventional polycrystals with the same chemical composition. This idea was confirmed by self-diffusion measurements in nanocrystalline Cu.
3. The measured diffusivities in nanocrystalline Cu are about 14–20 orders of magnitude higher than lattice diffusion. It is also known to be about 2–4 orders of magnitude larger than grain boundary self-diffusion.
4. It is known that the diffusion coefficient obeys an Arrhenius-type relation with temperature:

$$D = D_0 \exp(-Q/RT)$$

where  $Q$  is the activation energy for diffusion. The activation energy for lattice diffusion ( $Q_l$ ) is higher than that along short circuit paths like dislocation cores ( $Q_d$ ), grain boundaries ( $Q_{gb}$ ) and surfaces ( $Q_s$ ).

$$Q_l > Q_d > Q_{gb} > Q_s$$



5. If  $\log(D)$  is plotted as a function of  $(1/T)$ , the slope will be proportional to the activation energy. Since the activation energy for grain boundary diffusion is much lower than that of lattice diffusion, the slopes of the plot are smaller for grain boundary diffusion (Figure).
6. For the same reason, the difference in the diffusion coefficients between the grain boundary and lattice are much higher at lower temperatures.
7. It can be inferred from the figure that grain boundary diffusion will have a greater effect at lower temperatures. At higher temperatures, the diffusion coefficients of lattice and grain boundary diffusion are nearly the same and, considering the much lower volume fraction of grain boundaries in conventional materials, the effective diffusion coefficient would be largely determined by the lattice diffusion coefficient.

#### 4.Explain Grain growth characteristics based on effect of nano-dimension?

##### 4.Grain growth characteristics

1. Consider a sphere of radius  $r$ . Its surface area is proportional to the square of its radius, while the volume is proportional to the cube of the radius. Thus, the ratio of the surface area to the volume of a sphere, for example, can be seen to be inversely proportional to the radius. Thus, the smaller the crystallite size, the larger is the surface area per unit volume. Nanocrystalline materials have a

significantly larger surface area per unit volume fraction of grain boundaries compared to microcrystalline solids.

2. Grain boundaries are higher energy regions in materials. Thus, there is always a driving force for reduction in the grain boundary surface area per unit volume. This can happen only by coarsening of smaller grains involving migration of grain boundaries. Such a reduction in grain boundary surface area per unit volume is the major driving force for grain coarsening in nanocrystalline materials, in order to reduce the net energy of the system. However, grain boundary mobility is predominantly a diffusion limited process and hence depends to a large extent on composition and temperature, amongst other considerations. Grain growth has an exponential dependence on the temperature as shown in the equation below:

$$r^n = r_0^n + \exp\left(\frac{-Q_{gb}}{RT}\right)$$

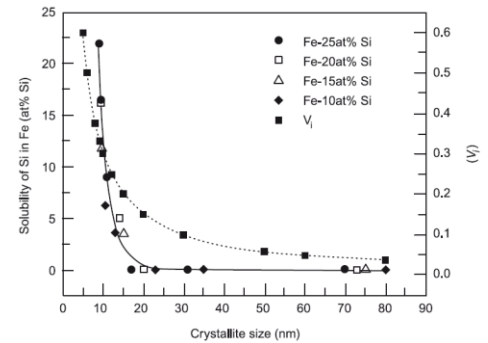
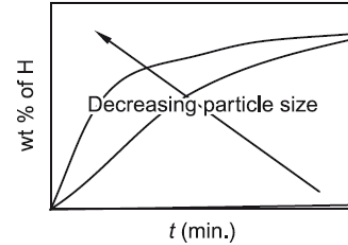
where  $r$  is the radius of the crystal,  $r_0$  a material constant,  $Q_{gb}$  is the activation energy for grain boundary migration, and  $n$  is an exponent factor and is typically 2 for microcrystalline grains.

3. Although the above expression has been derived for microcrystalline solids, it has also been found to be applicable to nanocrystalline materials. However, the activation energy for grain growth in nanocrystalline solids is expected to be lower.
4. In addition, in nanocrystalline solids, owing to the higher driving force for grain growth (larger reduction in grain boundary surface area per unit volume possible by growth of nanocrystalline grains), the exponent factor,  $n$ , is normally much higher than 2. Both the above factors lead to enhanced grain coarsening kinetics in nanocrystalline solids.
5. Thus, it can be seen that nanocrystalline solids cannot be stable at high normalized temperatures ( $T/T_m$ ) for any given material.
6. If the nanocrystalline grains grow larger at high temperatures, all the advantageous properties of nanomaterials envisaged cannot be utilized in service.
7. Thus, nanocrystalline solids are in general not suitable for high temperature applications. However, there is progress in grain boundary engineering to reduce grain coarsening kinetics of nanocrystalline materials.
8. Grain boundary migration can be reduced by pinning the grain boundaries either with secondary particles (Zener pinning) or by vacancy clusters.
9. Grain boundaries being higher energy sites, there is a driving force for several secondary phases to be located there. Grain boundary migration would thus incur an additional energy to break the bonding with such particles, acting as a source of inhibition for grain growth.
10. The effective pinning ability of secondary phases is obviously dependent on both the volume fraction as well as the size of the particle. It is clear that for effective Zener pinning, the particles should be stable at high temperatures and should not undergo coarsening themselves.
11. This can also be achieved by having dispersoids of secondary phases like ceramics (that are insoluble in the matrix even at elevated temperatures) decorating the grain boundaries of nanocrystalline materials.
12. An effective means of synthesizing such a solid is by powder metallurgy processes involving ball milling and consolidation techniques.
13. If the dispersoid phase is insoluble in the matrix, it is obvious that the ceramic second phase would be both stable at high temperatures and will not undergo coarsening of itself. Thus, such a technique can be an effective route for achieving grain boundary pinning to enhance the service temperature applicability of nanomaterials.
14. There is another way of grain boundary engineering to restrict grain growth. This involves enabling a grain boundary with a composition different from that of the bulk. Thus, grain boundary migration will also have to simultaneously involve diffusion of all involved chemical species to ensure the same composition of grain boundary.
15. Such a solute drag effect can act as a rate limiting step for grain boundary migration. A heterogeneous composition can be obtained, for example, by grain boundary segregation effects.

## 5. Explain solubility based on nano-dimension?

### 5. Enhanced solid solubility

1. The solubility of a solute A in a solvent B is controlled by the chemical potential,  $\mu_A$ , of A in B. The chemical potential and hence the solubility of A in B may be enhanced (or reduced) in nanocrystalline materials in comparison to single crystals or glasses with the same chemical composition.
2. The solubility of H in nanocrystalline Pd (at concentrations  $<10^{-3}$ ) is increased by a factor of 10 to 100 relative to a Pd single crystal. Similar effects have been observed in Mg and with the Mg-based alloys that have become popular for hydrogen storage applications.
3. Figure shows a schematic of how the hydrogen adsorption increases with a decrease in particle size. This result has significant technological importance.
4. A similar effect was observed for Bi in Cu. The solubility of Bi in crystalline Cu is less than  $10^{-4}$  at  $100^\circ\text{C}$ .
5. In contrast, the solubility of Bi in nanocrystalline Cu is about 4%, corresponding to a solubility enhancement by about 10,000 times relative to crystalline Cu.
6. It is found that a diameter of 20 nm seems to be the threshold value to observe significant extended solid solubility, i.e., the solubility being greatly promoted with decreasing grain size when the size of the matrix nanoparticles is less than 20 nm.
7. Figure demonstrates this phenomenon in the Fe-Si system. It can be clearly seen that the solubility of
8. Si in Fe is almost negligible up to a crystallite size of Fe of about 20 nm, below which there is a sudden dissolution of Si.
9. The figure also shows that this solubility can be correlated to the grain boundary volume in nanocrystalline materials, which follows a similar trend. It has also been possible to alloy conventionally immiscible systems by optimizing the process conditions to achieve nanocrystalline grains.



## 6. What is the effect of nano dimension on magnetic properties? Explain. OR What is GMR? Explain? What is the effect of nano dimension on GMR?

### 6. Magnetic Properties:

1. The magnetic moment of nano particles is found to be very less when compared them with its bulk size. Actually, it should be possible that non-ferromagnetic bulk exhibit ferromagnetic-like behavior when prepared in nano range. Bulk Gold and Pt are non-magnetic, but at the nano size they are magnetic.
2. The main driving force for this increased interest is their application potential in vital areas like ultrahigh density magnetic storage devices, magnetic random access memory (MRAM), ferrofluids, spintronics, magnetic semiconductors, nanogranular magnetic materials, etc.
3. With this increased interest comes the realization that the shape and size of the nanoparticles 200 nm 200 nm take centre stage in determining their magnetic properties.

4. The strength of a magnet is decided by its coercivity and saturation magnetization values. They increase when the grain size decreases and the specific surface area per unit volume of the grains increases.

### Giant magnetoresistance (GMR)

1. The phenomenon of significant decrease in electrical resistance when materials are exposed to a magnetic field is known as giant magnetoresistance (GMR) effect.
2. This phenomenon is usually observed in bulk composites consisting of ferromagnetic and non-magnetic phases or in thin film multilayers of these materials, as shown in figure.
3. A significant decrease in resistance from the zero-field state is evident in these materials when the external magnetic field leads to adjacent ferromagnetic layers, aligning in an antiparallel fashion due to weak anti-ferromagnetic coupling between layers.
4. It was observed in both nanocrystalline thin films and equiaxed granular nanocrystalline materials.
5. In case of granular materials, GMR is observed when small ferromagnetic single-domain particles with randomly oriented magnetic axes are embedded in a non-magnetic matrix.
6. The explanation for the GMR is spin-dependent scattering of the conduction electrons at the ferromagnetic/non-magnetic interfaces and, to a lesser extent, within the magnetic grains.
7. **The GMR is inversely proportional to the average particle diameter.**
8. The effect can be up to 100% in multiple stacks of ultrathin films. This effect was first observed in Fe/Cr multilayer ultrathin films and is also commonly observed in Cu/Co nanocomposites.
9. This effect has wide application in magnetic reading heads for computer hard discs and in position sensors.

