# CHAPTER 10: PHASE TRANSFORMATIONS

#### **ISSUES TO ADDRESS...**

• Transforming one phase into another takes time.



- How does the rate of transformation depend on time and T?
- How can we slow down the transformation so that we can engineering non-equilibrium structures?
- Are the mechanical properties of non-equilibrium structures better?

#### Development of Microstructure and Alterations of Mechanical Properties

- Phase Transformations in metals
- Kinetics of Solid State Reactions
- Multiphase Transformations
- Changes in Iron-Carbon Alloys
- Isothermal Transformations
- Continuous Cooling Transformations
- Mechanical Behavior
- Tempered Martensite

# PHASE TRANSFORMATIONS

- The patterns in which atoms are arranged in a solid depend on parameters such as the chemical composition, temperature and magnetic field. A phase transformation is a change in the arrangement of atoms. Prediction of phase transformations helps to conceive novel alloys or processes using calculations & critical experiments.
  - •*Three classes* of phase transformations can be outlined:
    - Simple Diffusion-dependent.
      - no change in number or composition of phases
    - Diffusion-dependent
      - with changing of phase composition and often their number
    - Diffusionless

formation of the metastable phases

# Phase Equilibrium

We are all familiar with *phase transitions* where a substance transforms from one stable phase to another at an equilibrium temperature. For example, ice will be in *equilibrium* with liquid water at 273.15 K and 1 atmosphere pressure, or liquid water will be in equilibrium with water vapor at 373.15 K and 1 atmosphere.

Let us briefly consider the thermodynamic principles involved in phase transitions. We assume that we know nothing about the conditions under which two phases can be in equilibrium. The only things we know are the *criteria for equilibrium* under certain conditions:

- for a closed isolated system that is, the *entropy*, S, seeks a <u>maximum</u>:  $dS_{U,V} \ge 0$
- for a system at constant temperature and volume the *Helmholtz free energy*, A, seeks a <u>minimum</u>:  $dA_{T,V} \le 0$
- for a system at constant temperature and pressure the *Gibbs free energy*, G, seeks a <u>minimum</u>:  $dG_{T,P} \le 0$

# The Enthalpy

**Enthalpy** is an energy-like property or state function, it has the dimensions of energy, and its value is determined entirely by the temperature, pressure, and composition of the system and not by its history.

In symbols, the **enthalpy**, *H*, equals the sum of the internal energy, *U*, and the product of the pressure, *P*, and volume, *V*, of the system:

H = U + PV

According to the law of energy conservation, if the only work done is a change of volume at *constant pressure*, the **enthalpy** change is exactly equal to the heat transferred to the system:

 $C_p = (\delta H / \delta T)_p$ 

## Simple Diffusion-dependent PT

Example: solidification of a pure element

Solidification is undoubtedly the most important processing route for metals and alloys. Consider a pure metal. At the fusion temperature  $T_f$ ,  $\Delta G = 0$  so that:

 $\Delta \mathbf{G}_{f} = \Delta \mathbf{H}_{f} - \mathbf{T}_{f} \Delta \mathbf{S}_{f} = \mathbf{0} \text{ or } \Delta \mathbf{H}_{f} = \mathbf{T}_{f} \Delta \mathbf{S}_{f}$ 

where  $\Delta H_f$  is the latent heat of fusion and  $\Delta S_f > 0$  for melting.

For any temperature other than  $T_f$ ,

$$\Delta G = \Delta H - T\Delta S \cong \Delta H_f - T\Delta S_f = \Delta S_f (T_f - T) = \Delta S_f \Delta T$$

where  $\Delta T$  is **undercooling** 



The *driving force* is therefore proportional to the *undercooling* because the latent heat and the entropy of fusion do not vary much with temperature

• Any molecule near the solid/liquid Interface has a certain number of bonds (in the range 0 to 6) with the solid phase.

• The molecules attached to the interface may become "*melted off*" into the liquid as a result of *thermal fluctuations* (*diffusion*).

• The molecule resists this to a degree which depends on the energy with which it is bound to the solid.

• Since the *maximum binding energy* is given by the *enthalpy of fusion*,  $\Delta H_{\rm f}$ , the value for a molecule exposed to the liquid will be  $n\Delta H_{\rm f}$  / 6, where **n** is the number of bonds.



• The probability of an interfacial molecule being melted off, i.e. the fraction of this type of molecule which will be detached, is given by a *Boltzmann expression*:

$$f(n) = \exp(-\frac{n \triangle H_f / 6}{kT})$$

•A smooth interface will be one for which there are few remaining molecules with n=1 and many with n=5. Using the expression  $\Delta H_{\rm f} = \Delta S_{\rm f} T_{\rm f}$ , and assuming that the temperature is close to  $T_{\rm f}$ , the ratio can be written as:

$$\frac{f(1)}{f(5)} = \exp(\frac{2/3 \triangle S_f}{k})$$

•A high value ( $\geq 10$ ), obtained when  $\Delta S_f / k$  is greater than about 5-6, will give a smooth interface





•If all adsorption sites are equivalent, then a simple model can be used to relate solidification velocity to undercooling An adsorption event is assumed to be similar to a normal *diffusive jump* in the liquid

• The advance *velocity* from *adsorption* events can be written as the product of jump distance,  $\lambda^*$ , vibration frequency,  $\omega_0$ , and the probability of making a diffusive jump

$$V_{ads} = \lambda_* \omega_0 \exp(-\frac{\Delta G_{mL}}{kT})$$

• Account must also be taken of *desorption* events. These are less frequent (if the interface is undercooled) because of the larger energy barrier

$$V_{des} = \lambda_* \omega_0 \exp(-\frac{\Delta G_{mL} + \Delta G_f}{kT})$$

The net velocity is given by the difference between these two.

$$V = \lambda_* \omega_0 \exp(-\frac{\Delta G_{mL}}{kT}) [1 - \exp(\frac{\Delta G_f}{kT})] = \lambda_* \omega_L [1 - \exp(-\frac{\Delta G_f}{kT})]$$

• Elementary diffusion theory relates the jump frequency to the diffusion coefficient and the jump distance

$$\omega_L = \frac{D_L}{\lambda_L^2}$$

•Assuming  $\lambda^* \cong \lambda_L \cong d$  (molecular diameter), the velocity can be written as

$$V = \frac{D_{I}}{d} \left[ (1 - \exp(\frac{\Delta G_{f}}{kT})) \right]$$

which is often termed the *Wilson-Frenkel equation*. Since  $\Delta G_f$  is given by  $\Delta H_f \Delta T / T_f$  and assuming  $\Delta T$  is small, so that the approximation  $1 - \exp(-x) \cong x$  for small x can be used, this equation reduces to:

$$V \cong \frac{D_L}{d} \frac{\Delta H_f}{kT_f^2} \Delta T = B \Delta T$$

#### Typical data:

$D_{I}$	*	510 <sup></sup>	m²/s	
$\Delta H_{f}$	~	10 <sup>-20</sup> 310 <sup>-10</sup>	J I molecule m	$B \cong 10^{-2} m/sK$
Τ,	~	10 <sup>3</sup>	K	,2=10 <i>m</i> ,811
k	~	1.4 10 <sup>-23</sup>	J I (K molecule)	

Even a relatively high velocity of ~ 1 mm/s thus requires a (kinetic) undercooling of *only about 0.1K*. Conversely, if a melt is significantly undercooled before a crystal forms, the initial growth rate will be *very fast*.

#### **KINETICS of SOLID STATE TRANSFORMATION**

#### • *Kinetics -* a time dependence of transformation rate.

Example: typical kinetics for variety of solid-state transformation at constant temperature



Two stages of transformation process: *Nucleation* – formation of extremely fine particles, i.e. *nuclei*, of *new phases Growth* – increase of nuclei size

- Can be described by so-called *Avrami Equation*:
  - fraction  $\pi$ y=1-e transformed time
- By convention, the rate of transformation **r** is taken as the reciprocal of time required to reach half completion:



#### **Homogeneous Nucleation**

#### *Homogeneous Nucleation* – precipitation occurs within a **homogeneous medium**.



The small clusters of crystallized solid forming from a liquid metal. These arise due to the random motion of atoms within the liquid



•By assuming that solid phase nucleates are spherical 'clusters' of radius, *r*, one can define the excess of free energy change for a single nucleus,  $\Delta G_{(r)}$ :

$$\angle \Delta G_{(r)} = \frac{4}{3} \pi r^3 \Delta G_{\rm tr} + 4\pi r^2 \gamma_{\rm SL}$$

where  $\gamma_{SL}$  is the solid/liquid interfacial energy.

The critical radius  $r^*$  (defined as the radius at which  $\Delta G_{(r)}$  is maximum) is given by:

$$r^* = \frac{-2\gamma_{\rm SL}}{\Delta G_{\rm v}} = \frac{-2\gamma_{\rm SL}T_{\rm m}}{\Delta H_{\rm v}\Delta T}$$

The associated energy barrier to homogeneous nucleation,  $\Delta G^*$  is:

$$\Delta G^* = \frac{16 \pi \gamma_{\rm SL}^3}{3 \Delta G_{\rm v}^2} = \frac{16 \pi \gamma_{\rm SL}^3 T_{\rm m}^2}{\Delta H_{\rm v}^2 \Delta T^2}$$

Important : the temperature-dependence of these terms are:  $r^* \propto 1/\Delta T$  and  $\Delta G^* \propto 1/\Delta T^2$ 

#### **Heterogeneous Nucleation**

Heterogeneous Nucleation



The nuclei can form at preferential sites (e.g. mould wall, impurities or catalysts). By this, the *energy barrier to nucleation*,  $\Delta G^*$  can be *substantially reduced*.



•Let us consider that a solid cluster forms on a mould wall. In this case, one can define the excess of free energy change for a nucleus,  $\Delta G_{(r)}$  as follows:

$$\Delta G_{(r)} = V \Delta G_{\pi} + A_{\rm SL} \gamma_{\rm SL} + A_{\rm SM} \gamma_{\rm SM} - A_{\rm SM} \gamma_{\rm ML}$$

<u>Note</u> that as compared to homogeneous case two new interface should be taken into account i.e. **solid-mould** and **liquid mould** 

• It can be shown that the critical radius  $r^*_{het}$  for heterogeneous nucleation *is equal* to  $r^*_{hom}$ :

$$r_{\rm het}^* = \frac{-2\gamma_{\rm SL}}{\Delta G_{\rm v}} = r_{\rm hom}^*$$

• And:

$$\underline{\qquad} \Delta G_{\text{het}}^* = \frac{16 \pi \gamma_{\text{SL}}^3}{3 \Delta G_{\pi}^2} S(\theta) = \Delta G_{\text{hom}}^* S(\theta)$$

where  $S(\theta)$  is a geometrical factor and  $\theta$  is a **wetting angle**:

$$S(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4}$$

#### **Nucleation Rate-Temperature Diagram**



- The overall nucleation rate is a product of two opposite working factors:
  - the driving force for solidification *increases* with T decrease;
  - while the diffusion that is responsible for the clustering process *decrease* with T decrease.
- These explain the "knee-shaped" nature of the transformation curve with maximum at some value below T<sub>f</sub>

#### **KINETICS of SOLID STATE TRANSFORMATION**

#### • *Kinetics -* a time dependence of transformation rate.

Example: kinetics of solid-state transformation as a function of temperature



Nucleation time decreases and transformation rate increases with increase of temperature

#### activation energy

$$r = Ae^{-Q/RT}$$
 - Arrhenius expression

Thermally activated process

#### Overall Transformation Rate-Temperature Diagram



- The overall transformation rate is a product of two factors:
  - nucleation;
  - *growth*, which is thermally activated process, typically described by Arrhenius function
- Note that for many practical engineering materials we must account for additional factors, such as *mechanical strain* associated with solid-state transformation

# Diffusion-dependent PT with changing of phase composition

# Example:

**Eutectoid** Transformation in Steels

# Iron Carbon (Fe-C) System: Eutectoid Reaction



- *Iron* are alloys with less than 0.008 wt% of carbon *Steels* are carbon-iron alloys with carbon in the range 0.008 wt.% to2.14%.
- *Cast irons* contain 2.14 6.7wt% of carbon
- Iron and carbons combined to form *Fe-Fe<sub>3</sub>C* at the 6.67 % C end of the diagram.

• **Eutectoid**: 0.76 wt%C, 727°C

 $\gamma \Leftrightarrow \alpha(0.022 \text{wt}\%\text{C}) + \text{Fe}_3\text{C}$ 

• Eutectic: 4.30 wt%C, 1147°C L⇔γ (2.14 wt%C)+Fe<sub>3</sub>C

#### **Cementite Crystal Structure**



**Iron carbide** is a <u>chemical compound</u> with the formula  $Fe_3C$  (or  $Fe_2C$ :Fe),

<u>orthorhombic</u> crystal structure Iron atoms are blue, carbon - black

#### **Eutectoid Reaction: Pearlite**



## NUCLEATION AND GROWTH

• Again: transformation rate is a result of nucleation <u>and</u> growth of crystals.



- In general nucleation rate increases ~  $\Delta T$
- Growth rate increases ~T

• Examples:



T just below T<sub>E</sub> Nucleation rate low Growth rate high

T moderately below T<sub>E</sub> Nucleation rate med. Growth rate med.



T way below T<sub>E</sub> Nucleation rate high Growth rate low

## PEARLITE MORPHOLOGY

#### Two cases:

e.g. 600 ° <T<sub>transf</sub><727 ° C</li>
 --Larger T: diffusion is faster
 --Pearlite is coarser.



- 540 °C<T<sub>transf</sub> <600°C
  - --Smaller T: diffusion is slower
  - --Pearlite is finer.







- Larger ∆T: colonies are smaller

## *Temperature-Time-Transformation* (*TTT*) Diagram

#### Example:

TTT diagrams (or isothermal transformation diagrams) for eutectoid reaction in Fe-C System

#### Eutectoid Reaction: Temperature-Time-Transformation (TTT) Diagram

 <u>Example</u>: TTT diagrams or isothermal transformation diagrams for eutectoid reaction in Fe-C System



 TTT diagram is generated from numbers of percentage transformation-versus-time
 (PTT) diagrams. One of the PTT is shown on the figure.

- Note that at T=675°C it takes 105 s for full transformation, while at T=540 °C only 3 seconds!!
  - And now you know why?!!

#### **TTT Diagram and Steel Structure**



At relatively high  $T < T_E$  *diffusion is fast* enough to produce relatively long and thick lamellae.

• A slow cooling path leads to coarse pearlite formation, which once formed, remains stable upon further cooling

Q: What will be at higher under cooling ? Answer: Fine pearlite !!

## PEARLITE MORPHOLOGY

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   --Smaller T: diffusion is slower
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- Larger ∆T: colonies are smaller

## And if one increases $\Delta T$ even more!?

### More fine Microstructures will form:

Bainite !!

## OTHER PRODUCTS: Fe-C SYSTEM (1)

TTT Diagram





Bainite – a fine structure formed at temperatures below 400° C
-bainite formation is also diffusion dependent process Example of bainite microstructure: α-ferrite strips with long cementite (Fe3C) rods

#### Summary: TTT Diagram and Steel Structure

Structure of products depends on the its specific thermal history



• Important! Although they possess *different* microstructure they do have the *same* phase composition and relative amount of phases

#### ONE MORE PRODUCT: Fe-C SYSTEM



(ferrite Fe<sub>3</sub>C (cementi **60** μ**m** 

• *Spheroidite* is a structure formed as a result of long term (> 24 h) heat treatment of bainite or pearlite structures

<u>Spheroidite microstructure</u>: spherical cementite (Fe<sub>3</sub>C) particles in a – iron matrix;

• Driving force of PT is the *reduce of interfacial area*, which proceeds by additional carbon *diffusion* with *no change* in the composition and relative amount of phases – thus it is *Simple* Diffusion Dependent transformation!

# Diffusionless (Displacive) PT

Example: Martensitic transformation in eutectoid steels

## **Diffusionless Transformations**

*Martensitic transformation* is a <u>diffusionless spontaneous</u> process occurring when *quenching* rate is rapid enough to prevent diffusion controlled mechanisms.
<u>Example</u>: Specific transformation in eutectoid steel during quenching of austenite to temperature lower than ~215° C





•<u>Martensitic microstructure</u>: the martensitic phase needles in γ-Fe matrix

#### What is the nature of this unique PT? What is the PT rate?

#### For simplicity let us consider first pure iron system. At temperature (~910 C) we do have transformation: $\gamma$ (f.c.c) $\rightarrow \alpha$ (b.c.c.)

which is also *diffusionless*!!!



Pure Iron Phase Diagrams (P=1atm)

#### The Displacive F.C.C. $\rightarrow$ B.C.C.



# And what is going on the level of the *Crystalline Lattice*?



# The unit cells of the F.C.C and B.C.C. iron

# Two adjacent F.C.C. cells make a distorted B.C.C. cell

If this is subjected to the "Brain strain" it becomes an undistorted B.C.C. cell

## **Diffusionless Transformations**

• For steels, the martensitic transformation involves the *sudden reorientation* of C and Fe atoms from fcc structure of  $\gamma$ -Fe to a body-centered tetragonal (bct) unit cell of matrensite



The bct unit cell relative to the fcc lattice



Note: the open circles are Fe atoms, while the solid circles represent an *interstitially dissolved* carbon atoms

# **Characteristics** of Transformations

Diffusive
Atoms move over distances of 1 to 10 <sup>6</sup> interatomic spacings.
Atoms move by thermally activated diffusion from site to site.
Atoms hop randomly from site to site (although more hop "forwards" than "backwards") ("civilian" transformation).
Speed of transformation depends strongly on temperature; transformation does not occur below 0.3 T <sub>m</sub> to 0.4 T <sub>m</sub> .
Extent of transformation depends on time as well as temperature.
Diffusion allows compositions of individual phases to change in alloyed systems.
Sometimes have crystallographic relationships between phases.

#### COOLING EX: Fe-C SYSTEM (1)

#### • Co = Ceutectoid



Case I

Temperature-time path # 1: Rapid Hold Rapid cool to: for: cool to: 350°C 10<sup>4</sup>s Troom

-At 350 C γ-Fe isothermally transforms to bainite in ~600 s
-Thus in 10<sup>4</sup> s 100% of specimen is bainite
-No other transformations are possible during quenching up to room temperature

#### COOLING EX: Fe-C SYSTEM (2)

•  $C_{o} = C_{eutectoid}$ 

#### Case II



Temperature-time path # 2: Rapid Rapid Hold cool to: for: cool to: 10<sup>2</sup>s T<sub>room</sub>

- At 250 C it takes ~150 s to transform to bainite - Thus in  $10^2$  s 100% of specimen is still austenite - Progressive rapid cooling to room temperature leads to the formation of 100 % of martensite

#### COOLING EX: Fe-C SYSTEM (1)

• C  $_{o}$  = C  $_{eutectoid}$ 

#### 800 Austenite (stable) 600 100%B S В 400 ()°C) 70000 100%A 500 200 M + A **10**<sup>5</sup> **10**<sup>3</sup> **10**<sup>-1</sup> 10 Time (s)

#### **Case III**

Temperature-time path # 1:

Rapid	Hold	Rapid	Hold	Rapid cool to:
cool to:	for:	cool to:	for:	
650°C	<b>20</b> s	400°C	10 <sup>3</sup> s	Troom

-At 650°C in 7s γ-Fe begins isothermal transformation to pearlite and after 20s ~50% of specimen has pearlite structure;
Rapid cooling to 400°C does not significantly contribute to the changing of phase composition
While 10<sup>3</sup> s treatment at this temperature completely converts remaining austenite to bainite.

-Finally, cooling down to room temperature results in no further transformations occur.

~50% Pearlite+ 50% Bainite

#### Continuous Cooling Transformation (CCT) Diagram



- The positions of transformation curves on CCT diagrams are shifted slightly *downwards* and towards the *right* as compared to TTT diagrams: the transformations start and end are delayed.
  - Also, specifically for considered eutectoid composition in plane steel the *bainite* does not form during continuous cooling to room temperature.

#### **CCT Diagram and Cooling Curves**



Microstructure depends on cooling rate: *slow* cooling – *coarse* pearlite *moderately rapid* cooling – *fine* pearlite Critical cooling rates,  $\omega$ , exist that define the characteristic regions of product microstructure:  $\omega < 35$  C/s – pearlite;  $\omega > 140$ C/s - martensite



#### Transformation Diagrams and Alloying Elements



Plain carbon steel : carbon is prime alloying element

*Alloy steel* : e.g. type 4340 with alloying elements: *Ni, Cr, Mo* 

*Critical cooling rates* for alloy steel: compare with plane carbon steel

#### Mechanical Behavior of Iron Carbon Alloys and their Microstructures

 Type of microstructures:
 – Pearlite

coarse fine

- Bainite
- Spheroidite
- -Martensite







#### MECHANICAL PROP: Fe-C SYSTEM (1)



• More wt%C: TS and YS increase, %EL decreases.

#### MECHANICAL PROP: Fe-C SYSTEM (2)

• Fine vs coarse pearlite vs spheroidite



- Hardness: fine > coarse > spheroidite
- %AR: fine < coarse < spheroidite

#### MECHANICAL PROP: Fe-C SYSTEM (3)

• Fine Pearlite vs Martensite:



• Hardness: fine pearlite << martensite.

## **TEMPERING MARTENSITE**

reduces brittleness of martensite, reduces internal stress caused by quenching



- produces extremely small Fe<sub>3</sub>C particles surrounded by  $\alpha$ .
- decreases TS, YS but increases %AR

#### SUMMARY: PROCESSING OPTIONS

