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ENR116 Engineering Materials

Module 3 Metals

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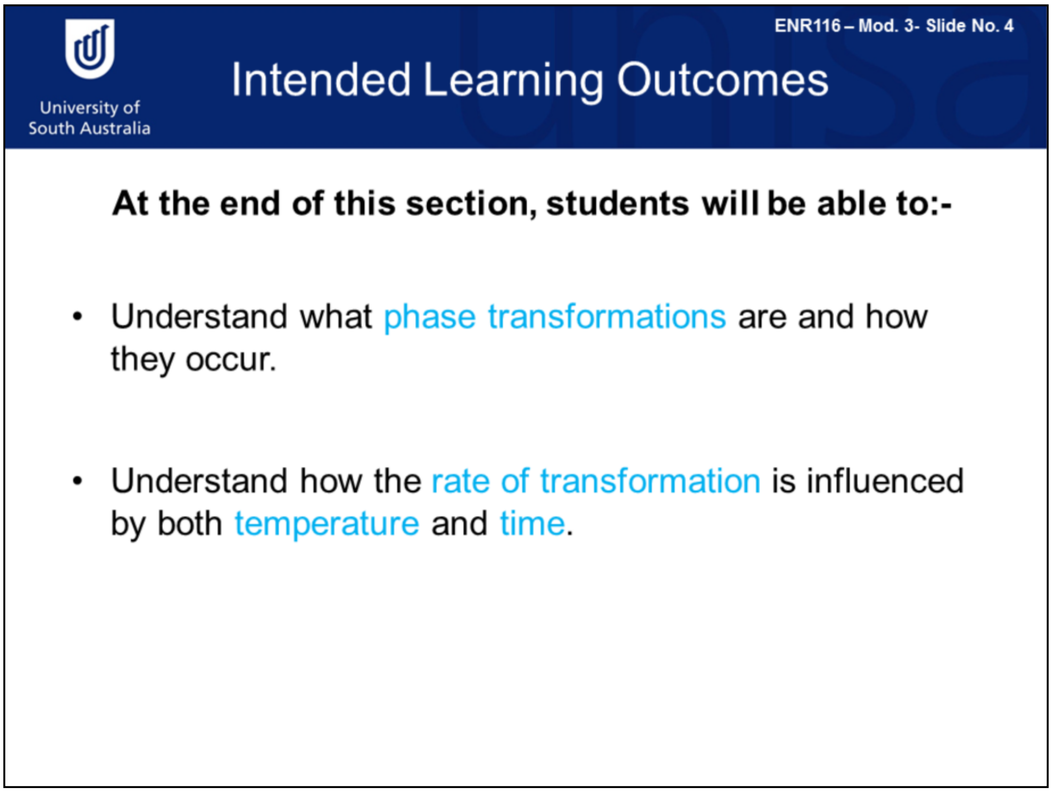
Phase transformations



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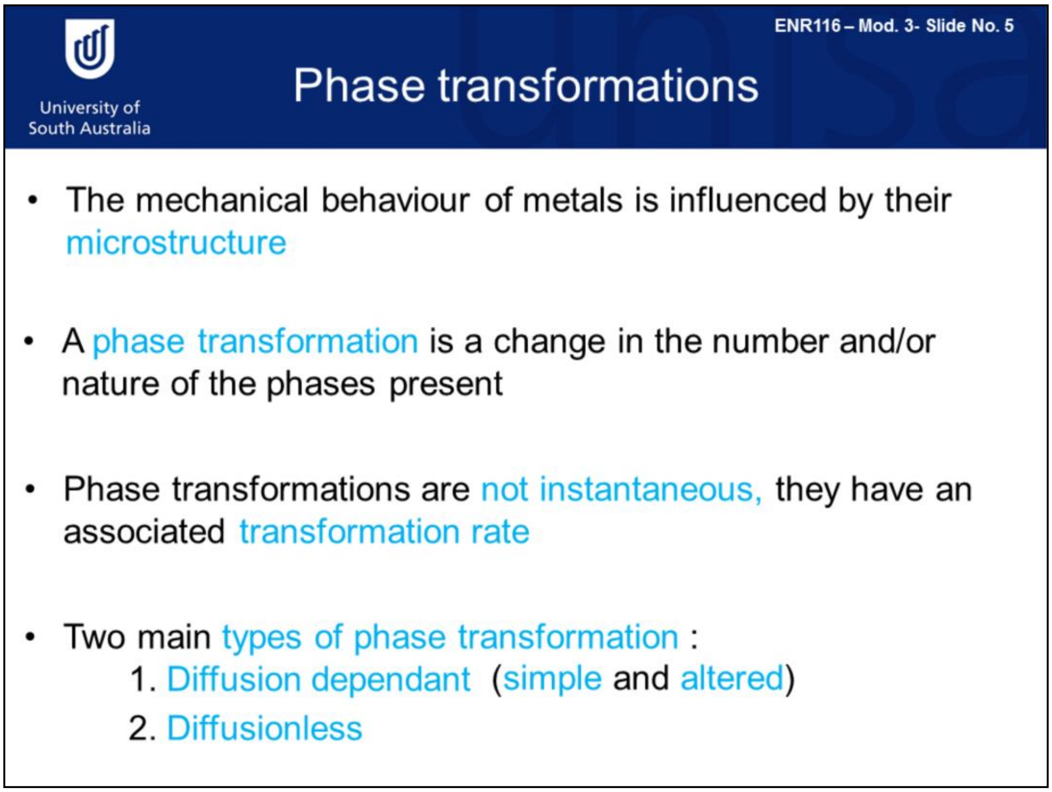
Intended Learning Outcomes

At the end of this section, students will be able to:-

- Understand what phase transformations are and how they occur.
- Understand how the rate of transformation is influenced by both temperature and time.

The intended learning outcomes from this presentation are to understand what phase transformations are and how they occur, and how the rate of transformation is influenced by both time and temperature.



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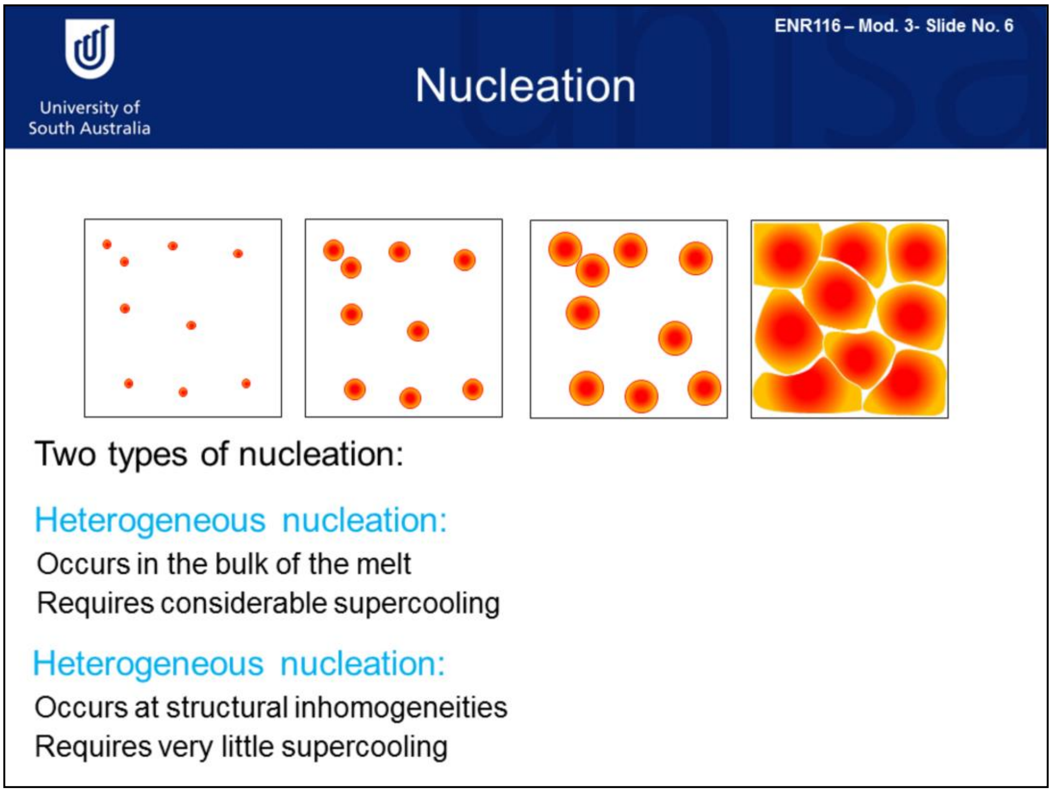
Phase transformations

- The mechanical behaviour of metals is influenced by their microstructure
- A phase transformation is a change in the number and/or nature of the phases present
- Phase transformations are not instantaneous, they have an associated transformation rate
- Two main types of phase transformation :
  1. Diffusion dependant (simple and altered)
  2. Diffusionless

We know from previous lectures that the mechanical behaviour of a metals is influenced by it’s microstructure. The development of these microstructures will usually involves some sort of phase transformation, which we define as a change in the number of the phases and/or their character.

It’s important to realise that the majority of phase transformations do not occur instantaneously, but rather they have an associated transformation rate. We can group phase transformations into two general categories. The first of these are the diffusion dependant transformations, and these can be either simple, which includes single phase processes such as solidification or recrystallization, or altered, where there’s an associated change in the composition and / or the number of phases present. A good example of an altered transformation is the eutectoid transformation of austenite into ferrite and cementite, which was introduced in the last lecture summary.

The second type of phase transformation are the diffusionless processes. These occur rapidly and result in the formation of non equilibrium, metastable phases.



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Nucleation

Two types of nucleation:

Heterogeneous nucleation:

Occurs in the bulk of the melt

Requires considerable supercooling

Heterogeneous nucleation:

Occurs at structural inhomogeneities

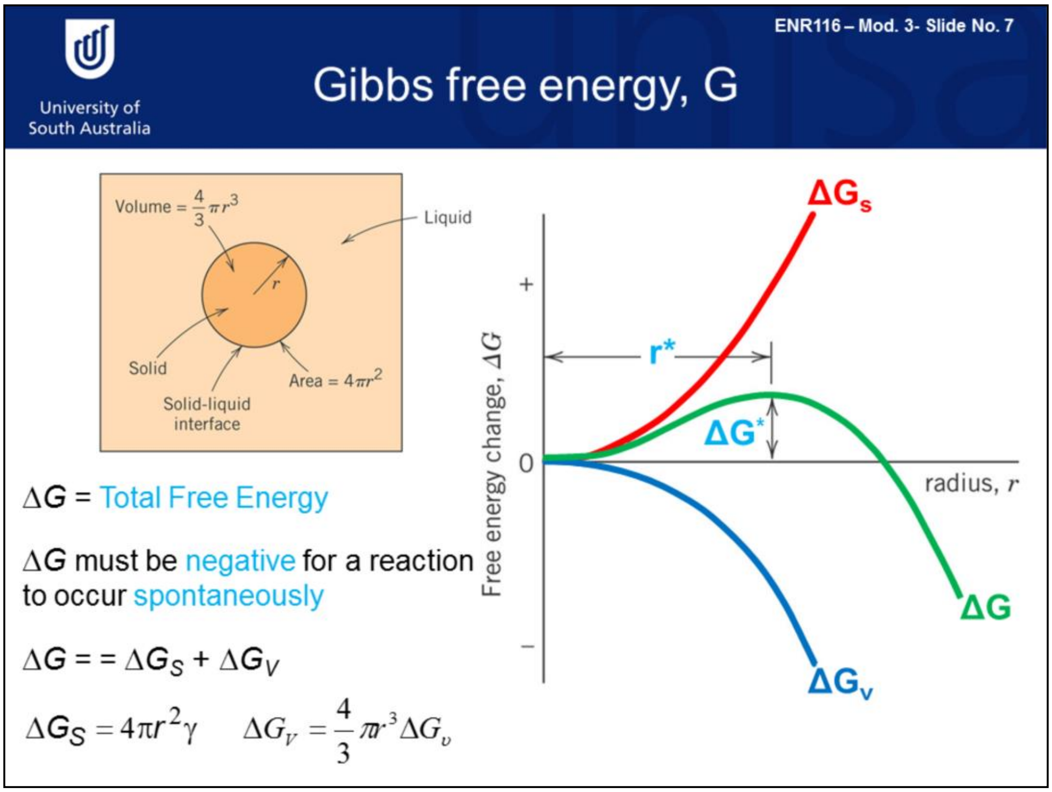
Requires very little supercooling

Now we have defined what a phase transformation is, we’re going to look at how they occur. Typically a phase transformation will occur in two distinct stages, nucleation and growth.

During this first stage – nucleation - very small particles, or nuclei, of the new phase form in the parent phase. These particles will continue to increase in volume until the parent phase disappears or an equilibrium is reached.

There are two types of nucleation, which vary in the nature of the site at which the nuclei form. Homogeneous nucleation occurs uniformly throughout the parent phase, with the nuclei forming within the bulk of the melt. With heterogeneous nucleation, the nuclei form instead at structural inhomogeneitys such as grain boundaries, container surfaces or around impurities.

Of these two types of nucleation, homogeneous nucleation is actually quite rare, and in order to drive it a system must be cooled by as much as 300C below its usual freezing temperature. In contrast, heterogeneous nucleation occurs readily, and requires very little cooling below the normal freezing point of the material to initiate. This process of cooling a system below it’s usual freezing point, without the solid forming, is known as supercooling and is an important concept in the kinetics of phase transformations.



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Gibbs free energy, G

ΔG = Total Free Energy

ΔG must be negative for a reaction to occur spontaneously

$\Delta G = = \Delta G_S + \Delta G_V$

$\Delta G_S = 4\pi r^2 \gamma \qquad \Delta G_V = \frac{4}{3}\pi r^3 \Delta G_v$

Now that we understand the difference between heterogeneous and homogeneous nucleation, we'll take a closer look at some of the factors that drive the formation of nuclei from the melt. As the mathematics of heterogeneous nucleation are quite complicated, for this course we are just going to focus on the simpler case of homogeneous nucleation only.

So, we know that solidification of a pure metal begins via the creation of nuclei in the melt. These nuclei can be modelled as spheres with a radius r, a volume of 4/3 pi r cubed and an area of 4 pi r squared. You can see an illustration of this here.

The driving force for the formation of these nuclei is a reduction in the Gibbs Free energy of the system, which has the symbol delta G. Delta G is a thermodynamic parameter that takes into account both the enthalpy, the internal energy, and the entropy or disorder of the system. A complete analysis of the thermodynamics is really outside the scope of this summary, but for our purposes you do need to know that for a phase transformation to occur, the change in Gibbs energy, delta G, must be negative.

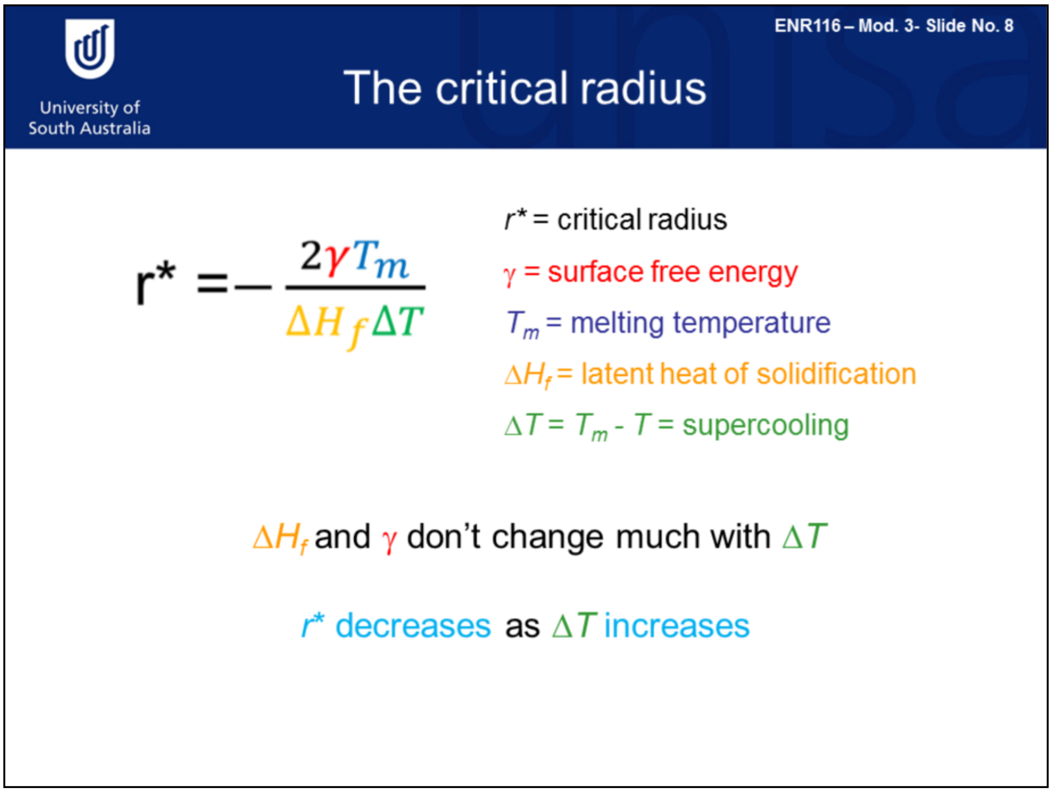
Delta G itself is made up of two components. The first component, delta G s, is the surface free energy contribution. This relates to the energy cost of creating a new solid-liquid interface from the melt. The expression for delta G s includes gamma, the surface free energy and the surface area of the spherical nucleus. As both of these values are positive, the overall contribution to the free energy change from delta G s is therefore also always positive.

Delta G V is the change in the volume free energy of the system. This value is negative provided the temperature of the system is below the equilibrium solidification temperature.

OK, so lets have a look schematically at how both of these components change with the size of the nuclei. In the diagram here, you can see in red the increase in surface free energy that occurs with an increase in the radius of the nucleus. The contribution is always positive, and increases with the radius. The blue line, here, shows how the volume free energy decreases with an increase in the radius of the nucleus.

By summing these two contributions together we can generate this green data, here, which represents the change in total Gibbs free energy as the nucleus grows. You can see that the line initially increases, then goes through a maximum and then decreases. Physically this means that as the atoms in the liquid cluster together, the free energy initially increases. It’s not a favourable process. However, once the cluster gets to a certain size, to this critical radius, r star, the nucleus will continue to get bigger with an accompanying decrease in free energy. Beyond r star, the process is favourable.

This value here, Delta G*, is the activation free energy; you can think of this as the energy barrier to nucleation.



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The critical radius

$$r^* = -\frac{2\gamma T_m}{\Delta H_f \Delta T}$$

r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_f = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

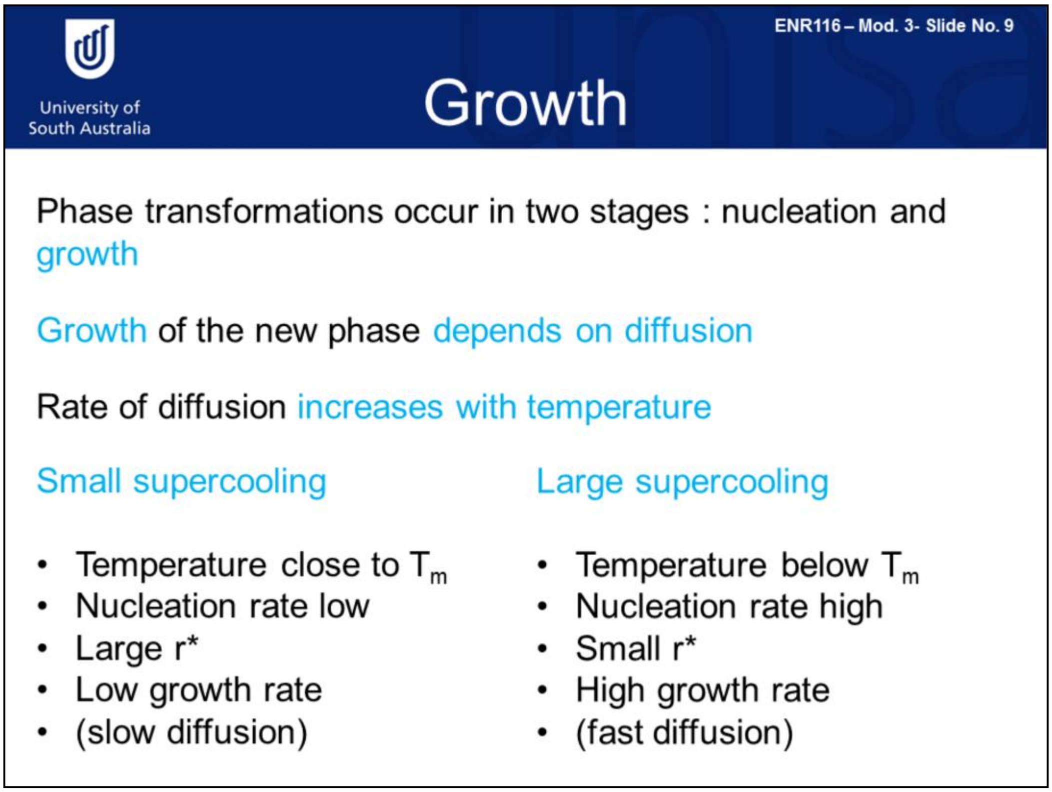
ΔH_f and γ don't change much with ΔT

r^* decreases as ΔT increases

The critical radius is an important parameter in phase kinetics. By further manipulating some of the data in the previous slide, we can generate an expression for the critical radius, r star in terms of gamma, the surface free energy; Tm, the melting temperature, and delta T, the degree of supercooling. Delta H f is the latent heat of fusion, this is a measure of the energy released when a solid is formed from a liquid.

Remember that supercooling is the process of reducing the temperature of a system below it's usual freezing point without a phase transformation occurring. To drive homogeneous nucleation, delta T needs to be quite considerable, typically a few hundred degrees below the nominal freezing point.

The latent heat of solidification and the surface free energy are both relatively insensitive to changes in delta T. However, you can see from the equation that as the degree of supercooling increases, the critical radius decreases. Physically this means that as the degree of supercooling get larger, the size of the crystals in the final piece get smaller. Large supercooling values results in very small , fine crystals, and a small degree of supercooling results in a few large crystals or even a single crystal. We'll look at this effect closer in the next slide.



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Growth

Phase transformations occur in two stages : nucleation and growth

Growth of the new phase depends on diffusion

Rate of diffusion increases with temperature

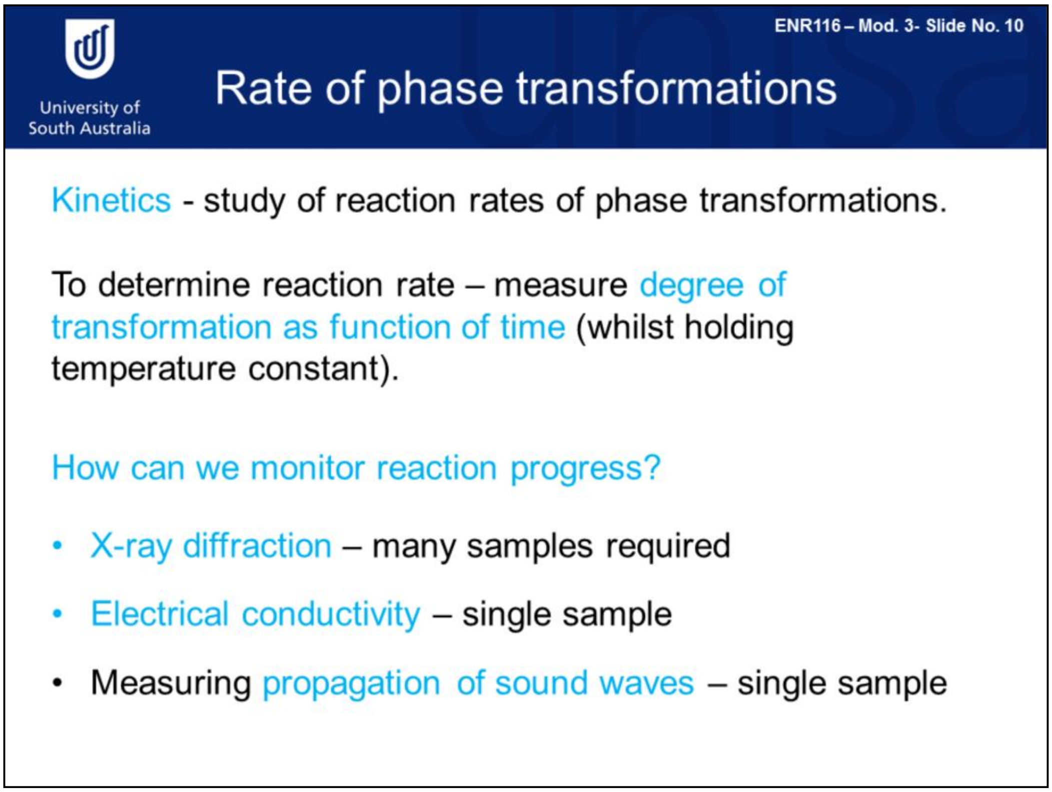
Small supercooling	Large supercooling
Temperature close to T_m	Temperature below T_m
Nucleation rate low	Nucleation rate high
Large r*	Small r*
Low growth rate	High growth rate
(slow diffusion)	(fast diffusion)

So earlier I stated that phase transformations occur in two stages, nucleation and growth. Once a nuclei reaches the critical radius, R star, it becomes a stable nucleus and the process continues with the growth of particles of the new phase.

Growth of the new particles depends on diffusion. The atoms have to move through the parent phase, across a phase boundary and into the new nucleus. You will recall from module 2 that as the temperature of a system is increased, the number of atoms capable of diffusive motion also increases, and therefore the rate of growth increases with an increase in temperature.

So really, when a new phase forms, we have these two processes, nucleation and growth, working simultaneously. When a system is supercooled slightly, the temperature is maintained close to the usual melting point and we have a situation of low nucleation and high growth rates. The relatively high temperature means that we have a few large nuclei, a large value for the critical radius and rapid growth of these. This gives rise to a few large particles, or coarse grains, in the final material.

In contrast, when we have a high degree of supercooling, the temperature is way below the usual melting point and we have high nucleation but low growth rates. The critical radius is correspondingly low but the nuclei grow slowly, so we end up with a number of very small, fine grains in the final piece.



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Rate of phase transformations

Kinetics - study of reaction rates of phase transformations.

To determine reaction rate – measure degree of transformation as function of time (whilst holding temperature constant).

How can we monitor reaction progress?

- X-ray diffraction – many samples required
- Electrical conductivity – single sample
- Measuring propagation of sound waves – single sample

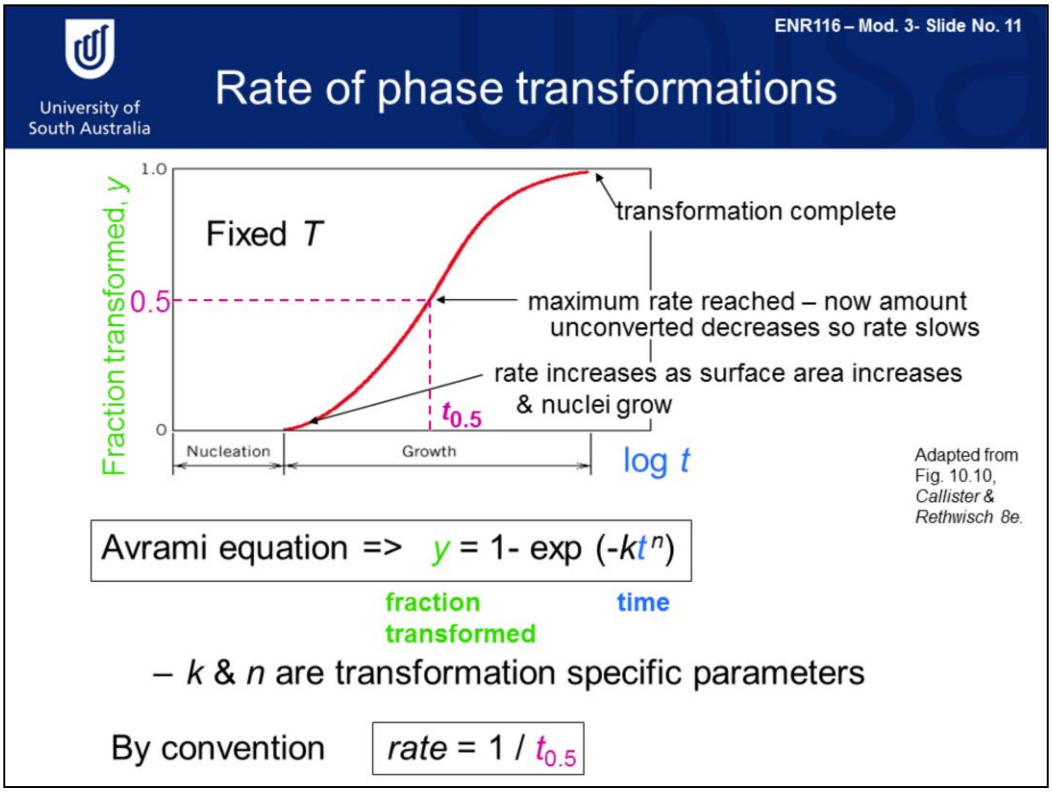
So far in this summary we've talked now a phase transformation occurs, and how the processes of nucleation and growth very depending on the temperature of a system. However, as well as varying with temperature, phase transformations also depend on time. We use the term kinetics when we describe the study of the rates of reactions, and this is what we'll be focusing on for the next few slides.

It is important to have a means of determining the rate at which a phase transformation occurs. Most reactions are studied by monitoring the degree of transformation of a sample as a function of time, whilst keeping the temperature of the system as a constant.

So, how can we do this experimentally?

One option is to use X-ray diffraction to monitor sample changes, but in reality the use of x ray diffraction in kinetics are limited as the technique requires a large number of separate samples from various time points in order to get a complete picture of the reaction.

Alternative methods are monitoring changes in electrical conductivity, or the propagation of sound waves across the sample. In both these cases the whole process can be monitored using a single specimen, and so these techniques are used frequently.



Rate of phase transformations

Adapted from Fig. 10.10, *Callister & Rethwisch 8e.*

Avrami equation => $y = 1 - \exp(-kt^n)$

fraction transformed (y) **time** (t)

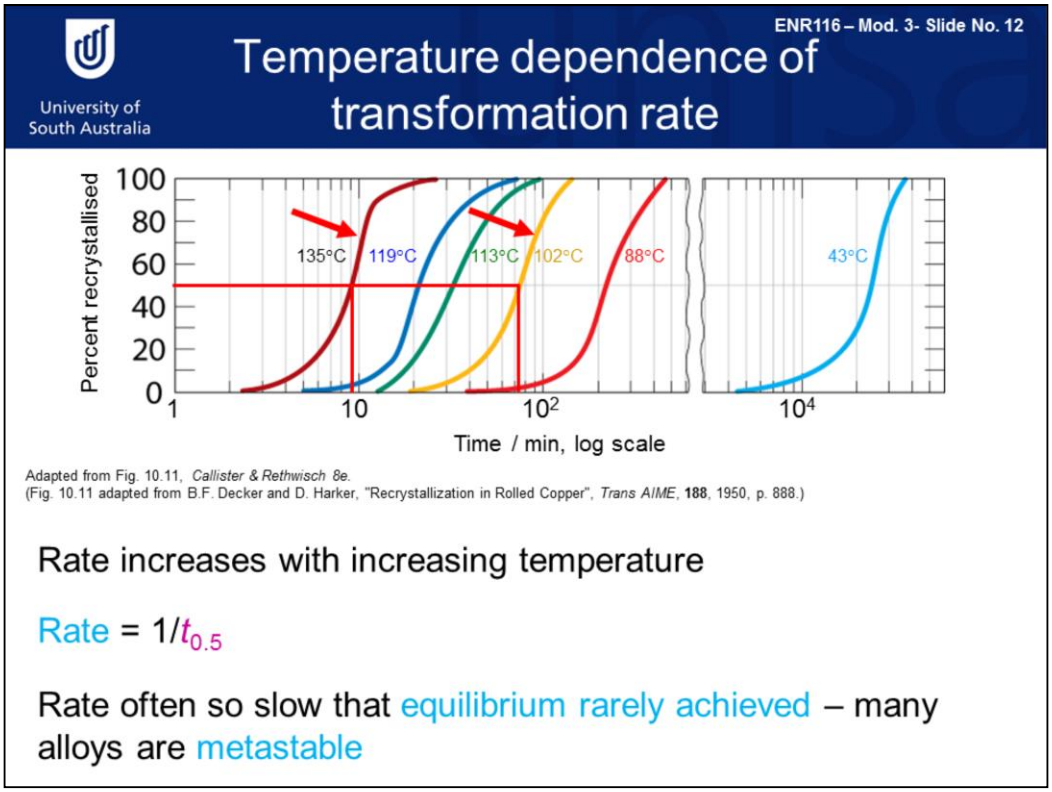
– *k* & *n* are transformation specific parameters

By convention $\boxed{rate = 1 / t_{0.5}}$

This slide shows the typical outcome from a kinetic study of a phase transformation. The data plotted here are the fraction of sample transformed vs the logarithm time, at a fixed temperature. The resulting s shaped curve is typical for a solid state reaction. This behaviour is described by Avrami equation, which states that the fraction transformed is equal to 1 minus the exponential of minus a constant, k, multiplied by the time, t raised to some power, n. K and n are time independent, transformation specific parameters.

You can see from the shape of the plot that at the very beginning of the reaction, the rate is slow as nuclei form and grow. The reaction rate then reaches a maximum in the centre of the curve at a point where the transformation is 50% complete. Beyond this point, the rate again decreases until the reaction reaches either completion or a state of equilibrium.

By convention, the rate of a transformation is taken as 1 over the time required for the reaction to reach halfway to completion, t 0.5. The halfway point is highlighted on screen here, in purple.



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Temperature dependence of transformation rate

Adapted from Fig. 10.11, *Callister & Rethwisch 8e.*
(Fig. 10.11 adapted from B.F. Decker and D. Harker, "Recrystallization in Rolled Copper", *Trans AIME*, **188**, 1950, p. 888.)

Rate increases with increasing temperature

Rate = $1/t_{0.5}$

Rate often so slow that equilibrium rarely achieved – many alloys are metastable

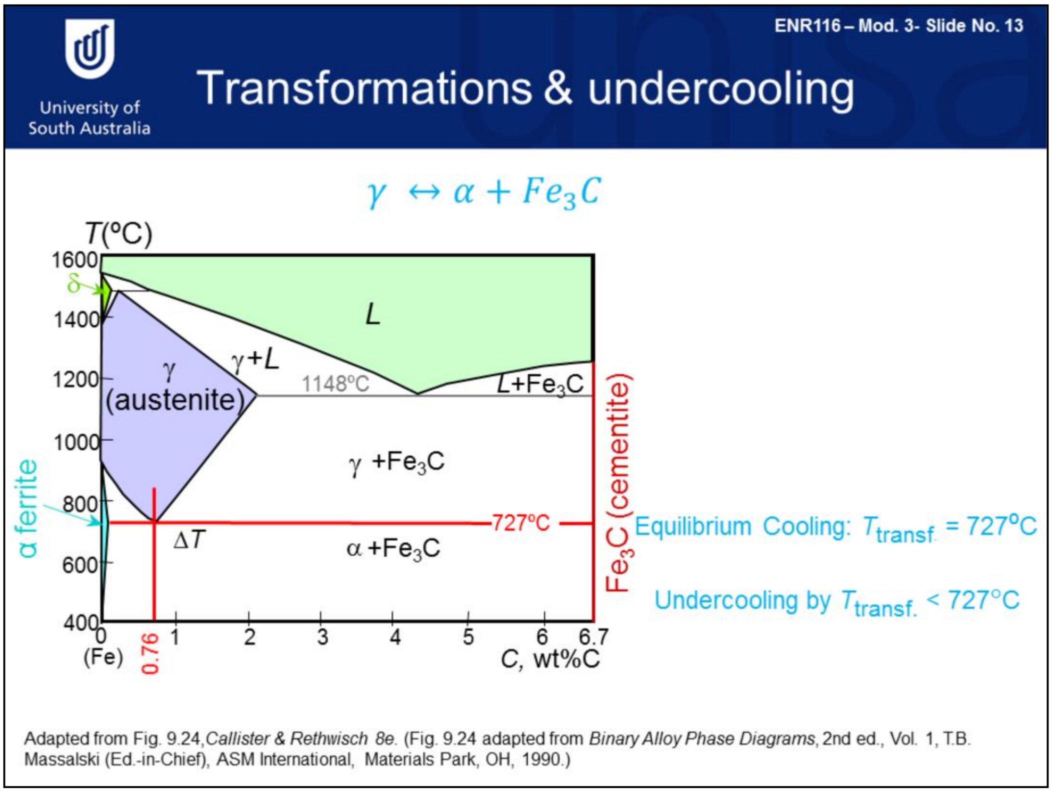
The temperature has a profound influence on the rate of a phase transformation. This figure shows kinetic data for the recrystallisation of copper, over several temperatures.

As the temperature at which the transformation occurs is increased, the rate of transformation also increases. At 135 degreesC, the dark red data here, rate of reaction is about 10-9. Remember the x axis data here is in a log scale. At 102 degrees, the yellow plot here, the rate decreases massively, to about XX.

This influence of temperature on the rate of transformation is the reason why heat treatments are such an important method in materials processing and in controlling the final microstructure of metal alloys.

As a last point I’d like to note that often the rate of transformation is so slow for many systems that it isn’t really possible to allow a system to reach equilibrium. In order to do this, we would have to cool the system slowly enough so that at each new temperature there was sufficient time for all of the phases to adjust, and reorganise to their equilibrium composition. This just isn’t practical. Therefore, most alloys are actually in a metastable state, where ‘metastable’ is defined as a non equilibrium state that exists indefinitely.

For non equilibrium cooling, the temperature at which a transition occurs is shifted to a lower temperature than that indicated by the equilibrium phase diagram.   This brings us back to the concept of supercooling, or undercooling a system in order to drive a phase transition.



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Transformations & undercooling

$\gamma \leftrightarrow \alpha + Fe_3C$

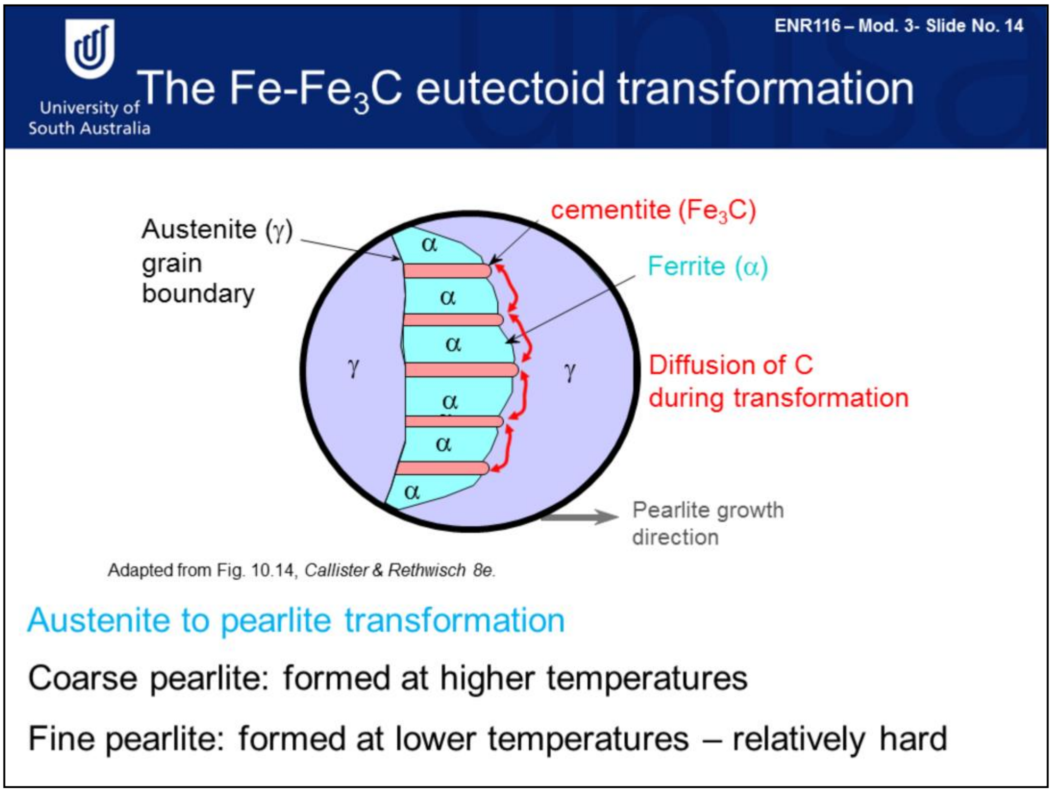
Equilibrium Cooling: $T_{transf.} = 727^{\circ}C$

Undercooling by $T_{transf.} < 727^{\circ}C$

Adapted from Fig. 9.24, *Callister & Rethwisch 8e.* (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

Here’s a practical example. The figure here shows the phase diagram for the iron – iron carbide system, which was discussed in the previous lecture. At the eutectoid composition, 0.76 wt% C, the transformation from austenite to alpha iron (ferrite) and cementite occurs at 727 degrees C.

Now, If we actually held the system at this temperature we would be waiting a very long time for the transformation to finish. For this reason we drive the transformation by ‘undercooling’ the system in order to drive the transformation rate up.



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The Fe-Fe_3C eutectoid transformation

Adapted from Fig. 10.14, *Callister & Rethwisch 8e.*

Austenite to pearlite transformation

Coarse pearlite: formed at higher temperatures

Fine pearlite: formed at lower temperatures – relatively hard

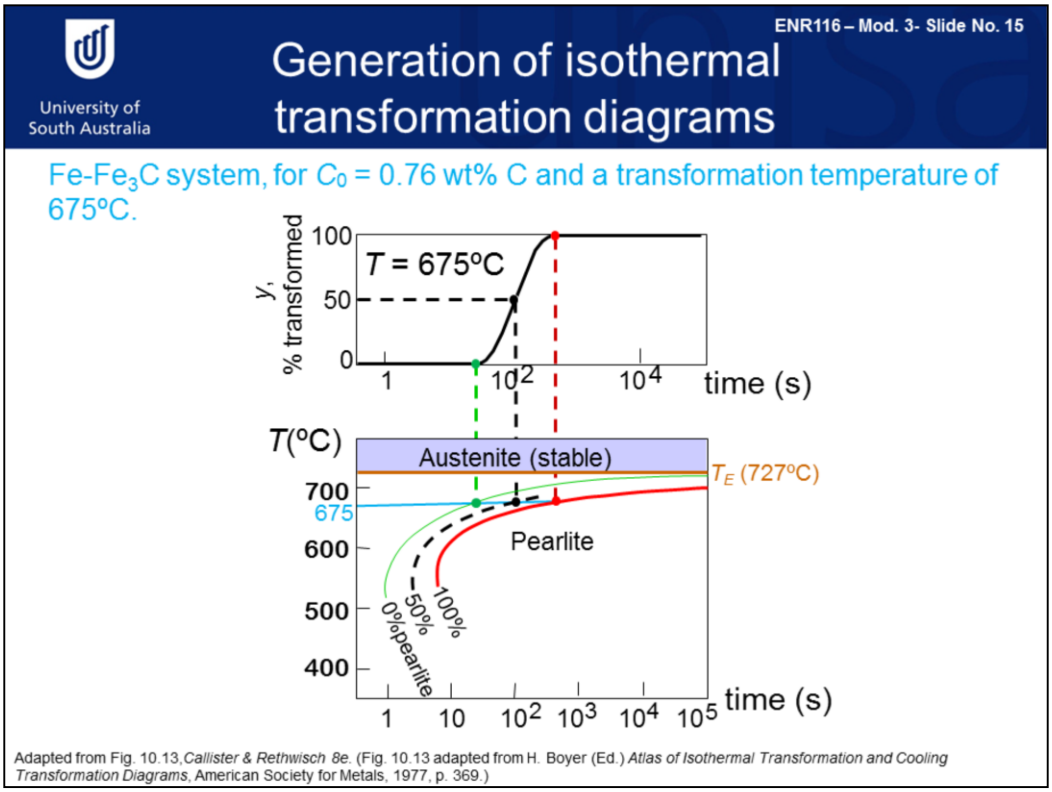
Another practical example of some of the concepts we have discussed in this summary. This illustration shows the transformation of austenite, gamma iron, to pearlite, a microstructure that consists of alternating layers, or lamellae of alpha ferrite and cementite.

During the transformation, carbon atoms diffuse from the ferrite into the carbon rich cementite layers. You can see that illustrated schematically here.

Now, the more we undercool this system, the more rapid the nucleation of the cementite phase rate is and, in the case of pearlite, varying the amount of undercooling actually has quite an influence on the nature of the final microstructure.

If we undercool the system slightly, the diffusion rate of carbon is relatively high and the nucleation of cementite is slow. This results in large grains, and relatively thick layers of both the ferrite and the cementite. This structure is known as coarse pearlite. When the degree of undercooling is greater, the rate of carbon diffusion is slowed but the nucleation is speeded up, and the layers subsequently become thinner. This structure is fine pearlite.

Fine pearlite is considerably harder than coarse pearlite, as a result of the increased boundary area between the layers.



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Generation of isothermal transformation diagrams

Fe-Fe$_3$C system, for C_0 = 0.76 wt% C and a transformation temperature of 675°C.

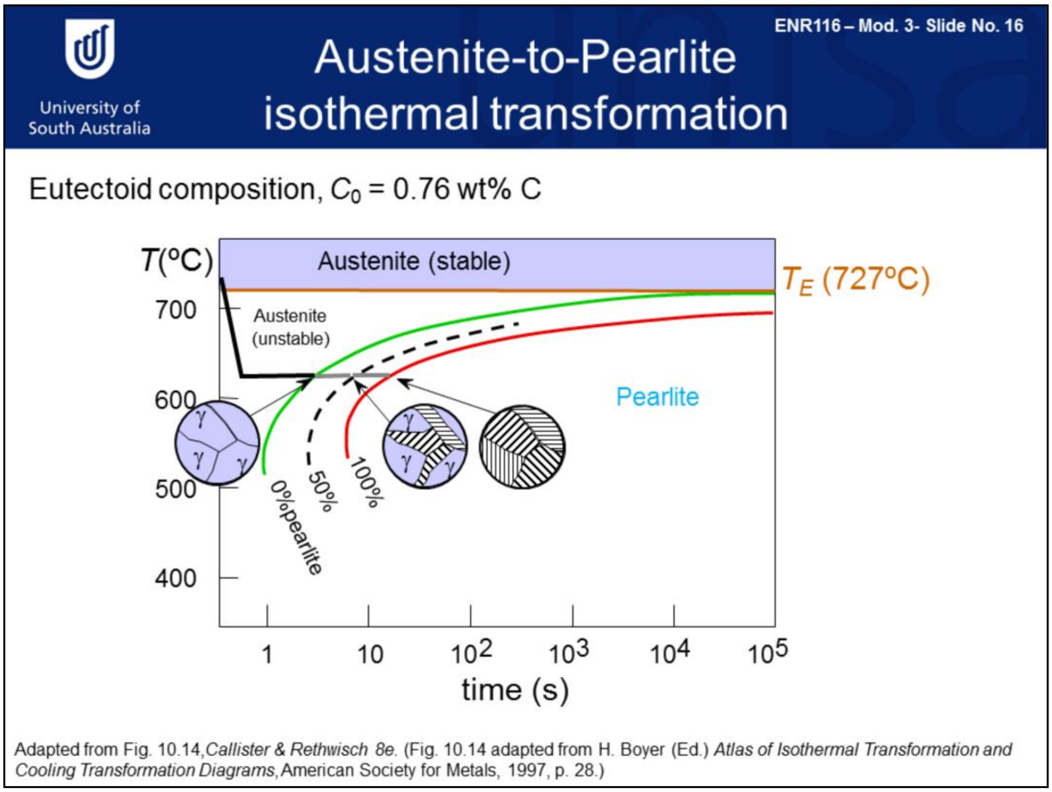
Adapted from Fig. 10.13, *Callister & Rethwisch 8e*. (Fig. 10.13 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 369.)

We're going to finish this lecture summary by introducing a type of diagram known as an isothermal transformation diagram. Isothermal transformation diagrams encompass both the time and temperature dependence of a reaction, in a single plot. They are sometimes called time-temperature-transformation, or TTT graphs.

At the top of this slide you can see a plot of % transformation vs. log time for the iron-iron carbide system, at 675 degrees C.

You can see from this plot the point at which the reaction begins, in green, the 50% completion point, in black, and the end of the reaction, in red.

So lets imagine now that we have a whole series of these plots, across a range of different temperatures. By bringing these data together, we can construct a plot of temperature vs time with lines representing the start, 50% completion and end points. This is a Time Temperature Transformation T graph. Here's the TTT graph for iron- iron carbide. The animation, here, shows how the points on the kinetic plot relate to those on the TTT graph, at 675 degrees C.



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Austenite-to-Pearlite isothermal transformation

Eutectoid composition, C_0 = 0.76 wt% C

Adapted from Fig. 10.14,*Callister & Rethwisch 8e.* (Fig. 10.14 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams,* American Society for Metals, 1997, p. 28.)

Let’s see how a TTT diagram can be used to study and predict the effects of a particular heat treatment on the microstructure of a sample.

Here we have eutectoid composition iron – iron carbide and we have heated the sample to above 727 degree C - so above the melting point - until all of our sample is molten.

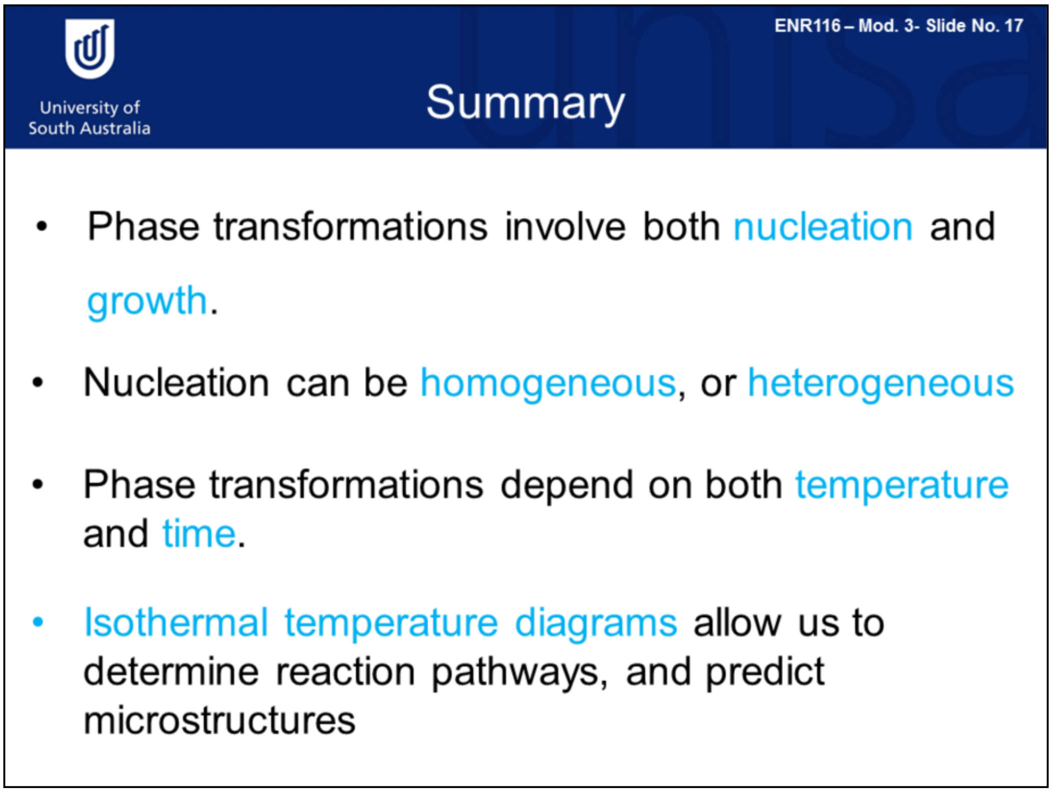
We now rapidly cool the sample, in less than a second, to 625 deg C and hold it at this temp.

To start, all the sample solidifies into austenite.

But, if we stay at 625 degrees C and the time increases, we start to see pearlite form at the austenite grain boundaries.

Eventually if we hold at 625 deg C for long enough, we see that all of the austenite is transformed into pearlite, and this will be our final product.

We can also use TTT diagrams to help decide on the right treatment to use in order to generate a particular desired microstructure. We’ll go through some examples of this in the next lecture.



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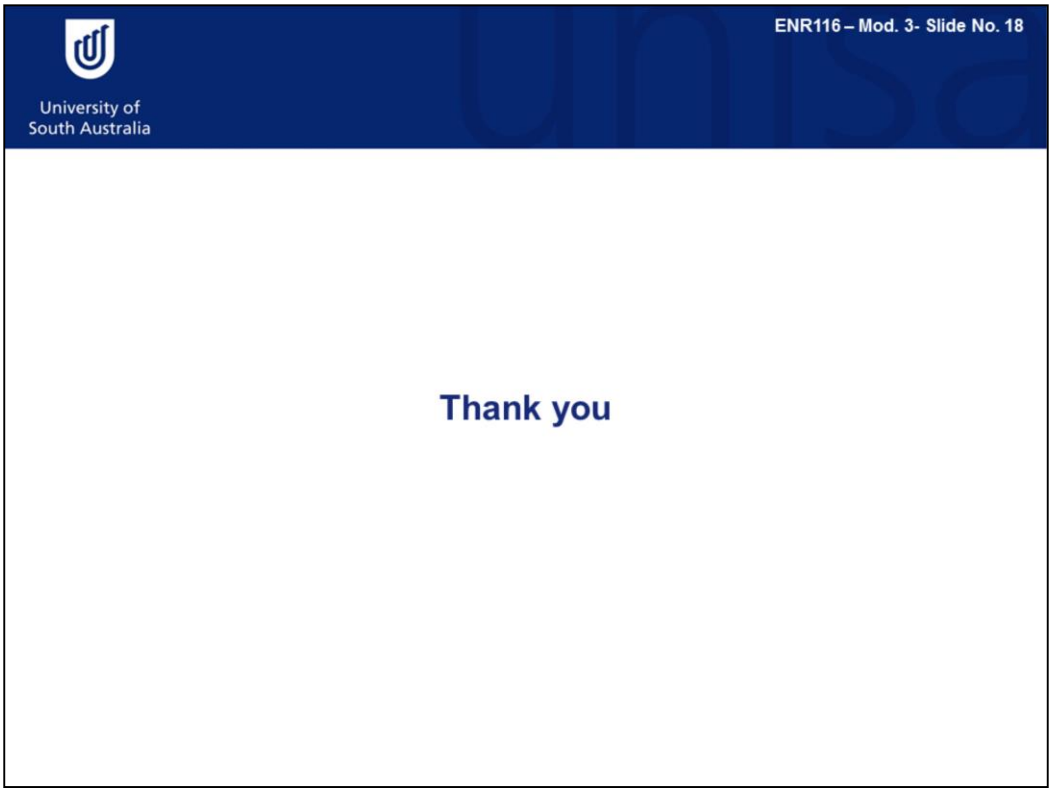
Summary

- Phase transformations involve both nucleation and growth.
- Nucleation can be homogeneous, or heterogeneous
- Phase transformations depend on both temperature and time.
- Isothermal temperature diagrams allow us to determine reaction pathways, and predict microstructures

So to summarise what we have covered in this lecture summary:



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Thank you

If you have any questions or desire further clarification please post a question or comment on the Engineering Materials Discussion Forum.