Phase Transformations in the Fe-Fe_3C System

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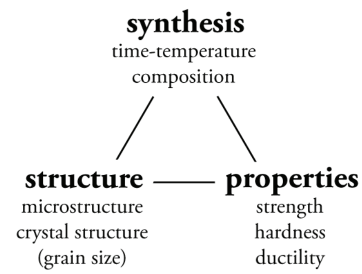
Temperature-induced phase transformations (i.e. nucleation and growth of a new phase) require a finite amount of time to reach completion in a material. The amount that a material has been cooled (a.k.a. undercooling) affects two factors that influence the rate of phase transformation:

- ΔT: the larger the undercooling, the greater the thermodynamic force to drive nucleation of the new phase
- T: the lower the temperature due to undercooling, the slower atoms will be able diffuse and rearrange into new phase regions

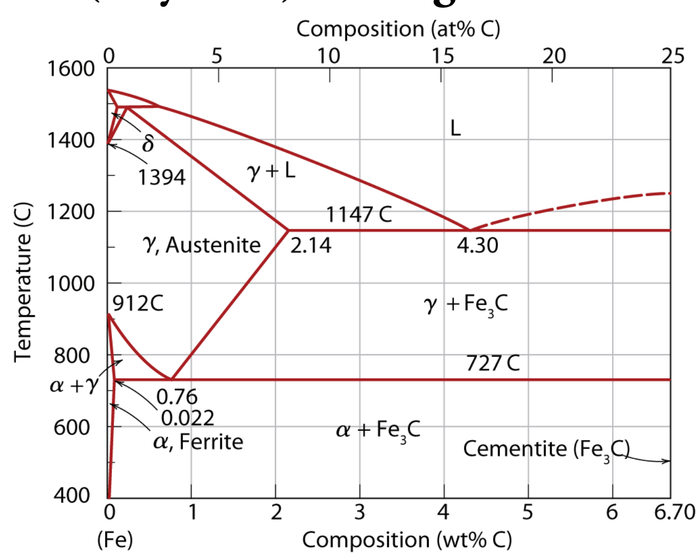
Temperature, time, and composition not only affect the kinetics of phase transformation, but also the eventual microstructure and physical properties of a material. Phase transformation kinetics is a beautiful example of how **synthesis, structure, and properties of a material are all related**!



Steel Synthesis Pathway 1: Equilibrium (very slow) cooling

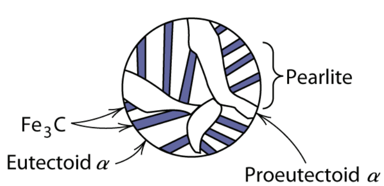
With very slow cooling, atoms will always be able to diffuse to their most thermodynamically stable positions at any temperature. In phase diagrams, the phases and microstructures represented *always* assume equilibrium (very slow) cooling.

Metallurgists make use of the increased solubility of C in the austenite phase and form steels with up to ~2 wt.% C. We will examine phase transformations in this range of compositions.

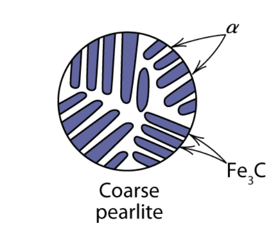


Synthesis–Structure

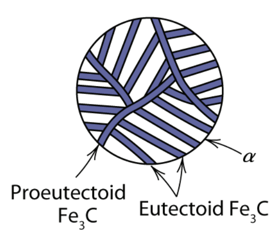
Upon very slow equilibrium cooling, the microstructures for various compositions consist of coarse pearlite and possibly a proeutectoid phase:



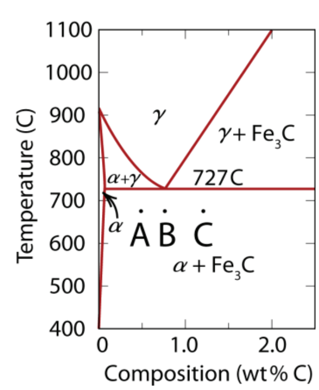
A
(hypoeutectoid wt.%)



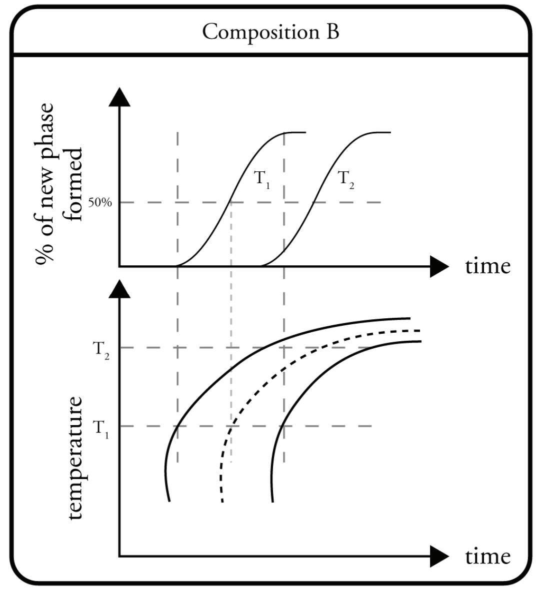
B
(eutectoid wt.%)



C
(hypereutectoid wt.%)



Steel Synthesis Pathway 2: Isothermal heat treatment

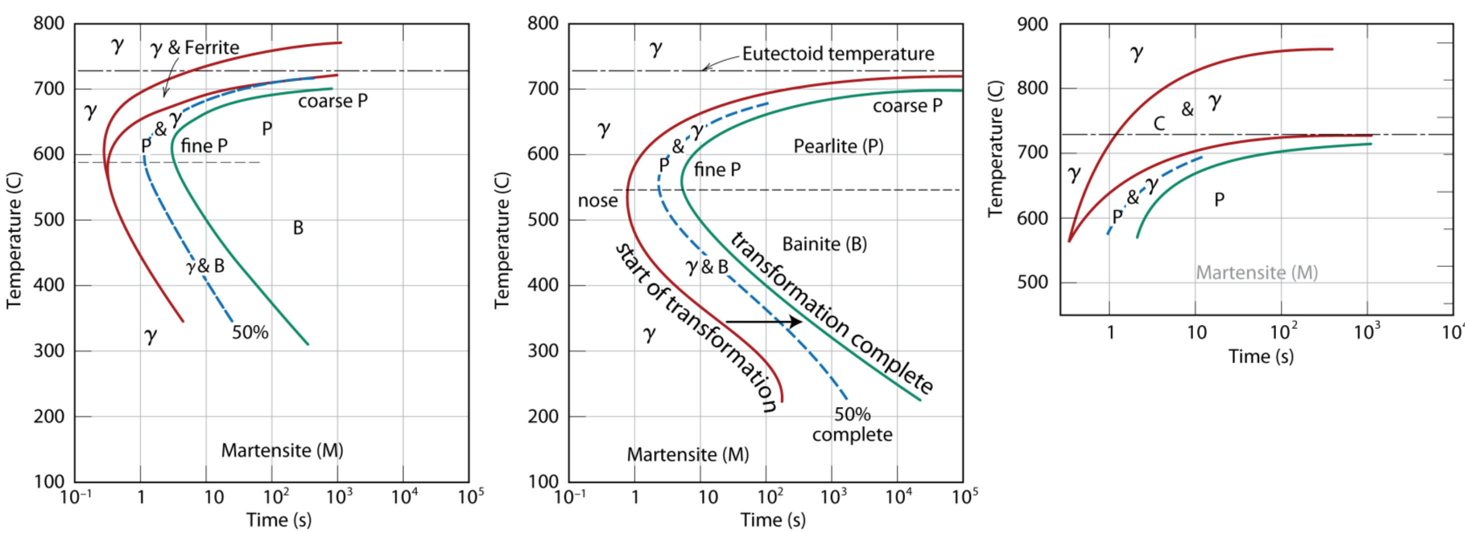


Isothermal heat treatment recipes involve holding a material at one or more temperatures for specified times. The requirement to maintain the material at a uniform, constant temperature restricts the dimensions of a sample to being relatively thin. Isothermal heat treatment often involves rapid cooling and/or quenching (rapidly cooling to room temperature) before and after the holding step; as a result, isothermal heat treatment is usually a non-equilibrium process: there may or may not have enough time for atoms to achieve an equilibrium arrangement, or even for the entire material to undergo phase transformation!

By plotting the time it takes for a material to undergo a complete phase transformation at a particular temperature (S-curves), we can generate isothermal time-temperature-transformation (TTT) diagrams – one for each material composition. As noted above, we will examine synthesis pathways for cooling from a single-phase austenitic (γ) steel.

Synthesis–Structure

A (hypoeutectoid wt.%) | B (eutectoid wt.%) | C (hypereutectoid wt.%)



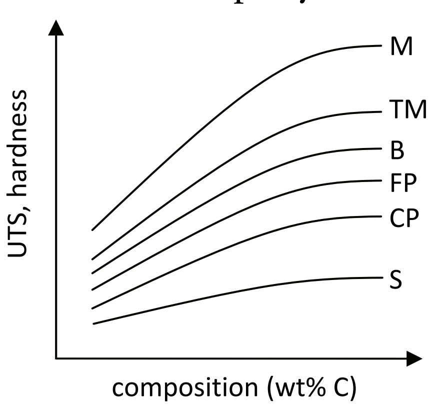
These TTT diagrams describe *non-equilibrium* *<u>isothermal phase transformations of austenite</u>* (γ) that occur below the eutectoid temperature: only γ transforms into other phases. This is especially important if a holding step results in an incomplete transformation; phases that γ transforms into (e.g. pearlite, bainite, martensite) will not transform again with further cooling. *All* austenite will eventually transform into something else upon cooling.

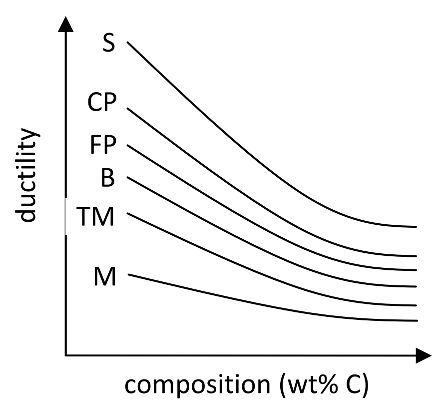
For non-eutectoid compositions and relatively high holding temperatures, a small amount of proeutectoid phase may form before the majority of austenite transforms. The maximum amount of proeutectoid phase that can possibly form can be *approximated* by calculating the microstructure amount from a phase diagram.

Synthesis–Structure continued

Isothermal heat treatment (assume long enough holding time for complete austenitic phase transformation)	**Resulting phases**	**Microstructure formed**	**Sketch**	**Microstructure characteristics**
Hold at ~700°C; quench (to room temp., RT)	α and Fe_3C, possibly proeutectoid	Coarse pearlite (CP); possibly proeutectoid		Wide alternating bands of α and Fe_3C; possible proeutectoid region
Hold at ~600°C; quench	α and Fe_3C, possibly proeutectoid	Fine pearlite (FP); possibly proeutectoid		Narrow alternating bands of α and Fe_3C; possible proeutectoid region
Hold at 300-500°C; quench	α and Fe_3C	Bainite (B)		Needle-like Fe_3C regions in α
Quench immediately to RT	M	Martensite (M)		C is super-saturated in the BCT structure because diffusion rates are too slow to grow a new phase
Quench to RT; reheat to ~400°C for ~1h; cool to RT	α and Fe_3C	Tempered martensite (TM)		Small, finely dispersed grains of cementite (Fe_3C)
Quench to RT; reheat to ~700°C for ~20h; cool to RT	α and Fe_3C	Spheroidite (S)		Relatively large, spaced-out spherical grains of Fe_3C

Structure–Property





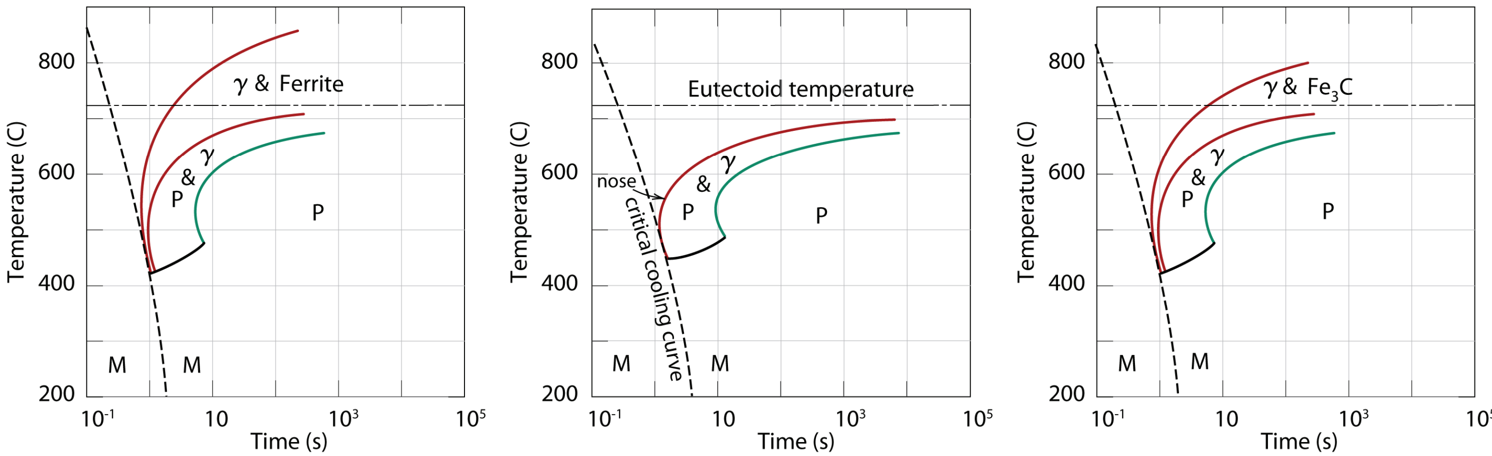
For any steel alloy at a given composition, different heat treatment pathways will result in different microstructures, which in turn can change the steel's mechanical properties by almost an order of magnitude!

Steel Synthesis Pathway 3: Continuous cooling

An often-preferred alternative to isothermal heat treatment is continuous cooling. The material is cooled down at a constant rate (°C/s). Continuous cooling TTT diagrams can also be generated by performing experiments at different cooling rates. Like isothermal heat treatment, most continuous cooling processes are non-equilibrium process *unless* the cooling rate is very slow. The latter case is essentially equilibrium cooling.

Synthesis–Structure

A (hypoeutectoid wt.%) | B (eutectoid wt.%) | C (hypereutectoid wt.%)



Continuous cooling treatment	Resulting phases	Microstructure formed
Very slow cooling	α and Fe_3C, possibly proeutectoid	CP, possibly proeutectoid
Slow cooling	α and Fe_3C, possibly proeutectoid	FP, possibly proeutectoid
Moderate cooling	α Fe_3C, and M, possibly proeutectoid	FP, M, possibly proeutectoid
Cooling faster than the critical cooling rate	M	M

No bainite can be formed with continuous cooling!

Other additives can be added to iron (Ni, Cr, Mo) to drastically reduce the critical cooling rate (~140 °C/s to ~8 °C/s)!

Structure–Properties

The properties of the resulting microstructures are the same as those obtained in isothermal processes.