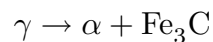


Lecture 6: Ferrous Alloys

Fe–C phase diagram

The vast majority of steels are in the austenitic condition at temperatures in excess of 900 °C. Austenite in iron–carbon alloys tends to decompose into ferrite and cementite (a compound of iron and carbon Fe_3C).

Steels with a carbon concentration less than about 0.8 wt% are hypoeutectoid, those with greater concentrations are hypereutectoid. A steel with exactly 0.8 wt% carbon will tend to decompose into an intimate mixture of cementite and ferrite at 723 °C by a eutectoid reaction (Fig. 1):



A hypoeutectoid steel will first decompose during cooling to ferrite at the austenite grain boundaries; the austenite is consequently enriched in carbon and will eventually form pearlite giving a mixed microstructure of ferrite and pearlite.

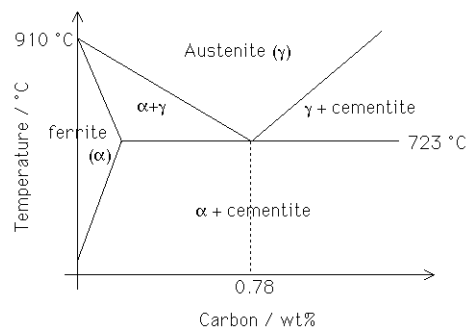


Fig. 1: Iron-carbon equilibrium phase diagram

Martensite in Steel

When austenite is cooled sufficiently rapidly, it transforms into martensite without any change in chemical composition (no diffusion). The transformation begins at a

well-defined temperature called the martensite-start temperature or M_S . The fraction of martensite increases with the undercooling below M_S .

The martensite in steels is supersaturated with carbon. Carbon occupies octahedral interstices in the b.c.c. lattice; these are characterised by three principal axes $a < 0 0 1 >$, $a < 1 1 0 >$ and $a < \bar{1} 1 0 >$. There are three sub-lattices of octahedral holes, along directions parallel to the unit cell edges (Fig. 2).

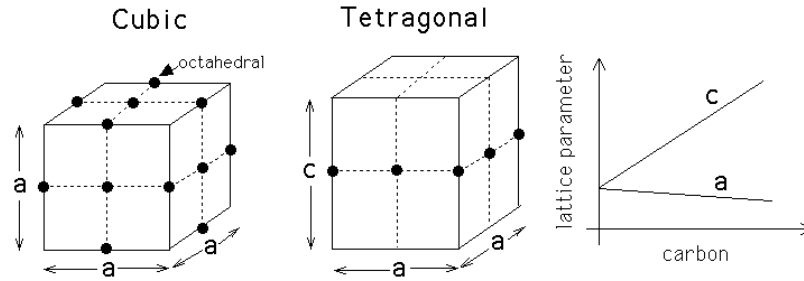


Fig. 2: Tetragonal martensite in some steels.

Each carbon atom causes a tetragonal distortion since the principal axes of the octahedral sites are not equivalent. There is an expansion along $a < 1 0 0 >$ and small contractions along the other two axes. As a consequence, it is favourable for all the carbon atoms to lie on a single sub-lattice of octahedral interstices, giving rise to a body-centred tetragonal structure for the martensite (Fig. 2).

Each carbon atom acts as a strain centre. Because this strain field is tetragonal, it is particularly effective in interfering with dislocation motion since it interacts with both the shear and dilatational components of the stress field of dislocations. This is why carbon hardens martensite much more than it hardens austenite (where the octahedral hole is symmetrical, bounded by $< 1 0 0 >$). Carbon-free martensite is not strong.

Tempering of Martensite

Martensite containing carbon is very strong; this also makes it very brittle. To achieve a compromise between strength and toughness, the martensite is tempered, *i.e.* heat treated at temperatures below that at which austenite can form. The heat treatment causes

1. 200–400 °C. The precipitation of excess carbon at first as a transition carbide $\text{Fe}_{2.4}\text{C}$, which then converts to cementite (Fe_3C). This is accompanied by a significant loss of strength but an improvement in toughness (Fig. 3).
2. 400–500 °C. Recovery with a reduction in dislocation density. Cementite begins to coarsen with further loss in strength.
3. > 500 °C. Recrystallisation of plates into equiaxed grains of ferrite.

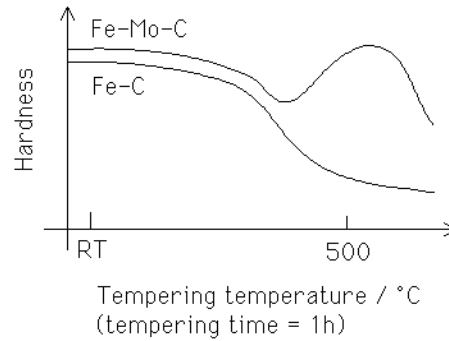


Fig. 3: Hardness changes due to tempering

Secondary hardening

Some steels contain strong carbide forming elements such as V, Mo, Cr or W. These are in substitutional solid solution and do not diffuse much unless the tempering temperature is in excess of about 500 °C. When they precipitate to form carbides such as VC, Mo_2C , Cr_{23}C_6 or W_2C , there is an increase in hardening (Fig. 3), *i.e.* secondary hardening. This is because the carbides are very fine and frequently have coherency strain fields. Microstructures generated by secondary hardening are very stable and form the bulk of the alloys used in the power plant industry where the steam temperature is typically 600 °C.

Time–Temperature–Transformation (TTT) Diagrams

Martensitic transformations are not equilibrium and cannot therefore be represented on an equilibrium phase diagram. However, the M_S temperature can be drawn as a horizontal line on a temperature–versus time plot. If a sample is cooled to a particular temperature and held isothermally, there will be no martensite unless the temperature is below M_S .

Similarly, in a eutectoid steel, pearlite will not form unless austenite is cooled to below the eutectoid temperature. The pearlite transformation involves diffusion and hence will be slow at low temperatures. It will also be slow close to the eutectoid temperature. This can be represented on the $T - t$ plot as a C curve (Fig. 4). The diagram is constructed by rapidly cooling austenite to the specified temperature and measuring the fraction of transformation as a function of time.

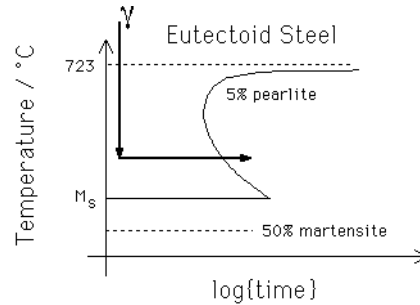


Fig. 4: TTT diagram for eutectoid steel

A real TTT diagram is somewhat more complicated (Fig. 5). Consider for example a hypoeutectoid steel – the first phase to form would be ferrite with transformation becoming possible just below the $Ae3$ temperature.

Widmanstätten ferrite then begins to grow as a displacive transformation in which the interstitial atoms diffuse.

Pearlite forms below the eutectoid temperature. Pearlite is a mixture of cementite and ferrite, each colony being an interpenetrating bicrystal.

At even larger undercoolings we get bainite, which is a displacive transformation like martensite, but unlike martensite does not remain supersaturated with carbon. The excess carbon rapidly precipitates as fine carbides between the plates of bainite (upper bainite) or within them (lower bainite).

We have stated that most solid-state transformations fall into two categories. Displacive transformations involve a coordinated motion of atoms as the parent lattice is deformed into that of the product. There is no diffusion and hence there exists an atomic correspondence between the parent and product phases. A numbered sequence of atoms is maintained in the product phase. Such transformations are called military transformations because there is a disciplined transfer of atoms (Fig. 6); the analogy

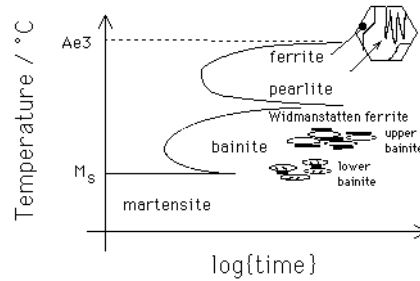


Fig. 5: TTT diagram for hypoeutectoid steel

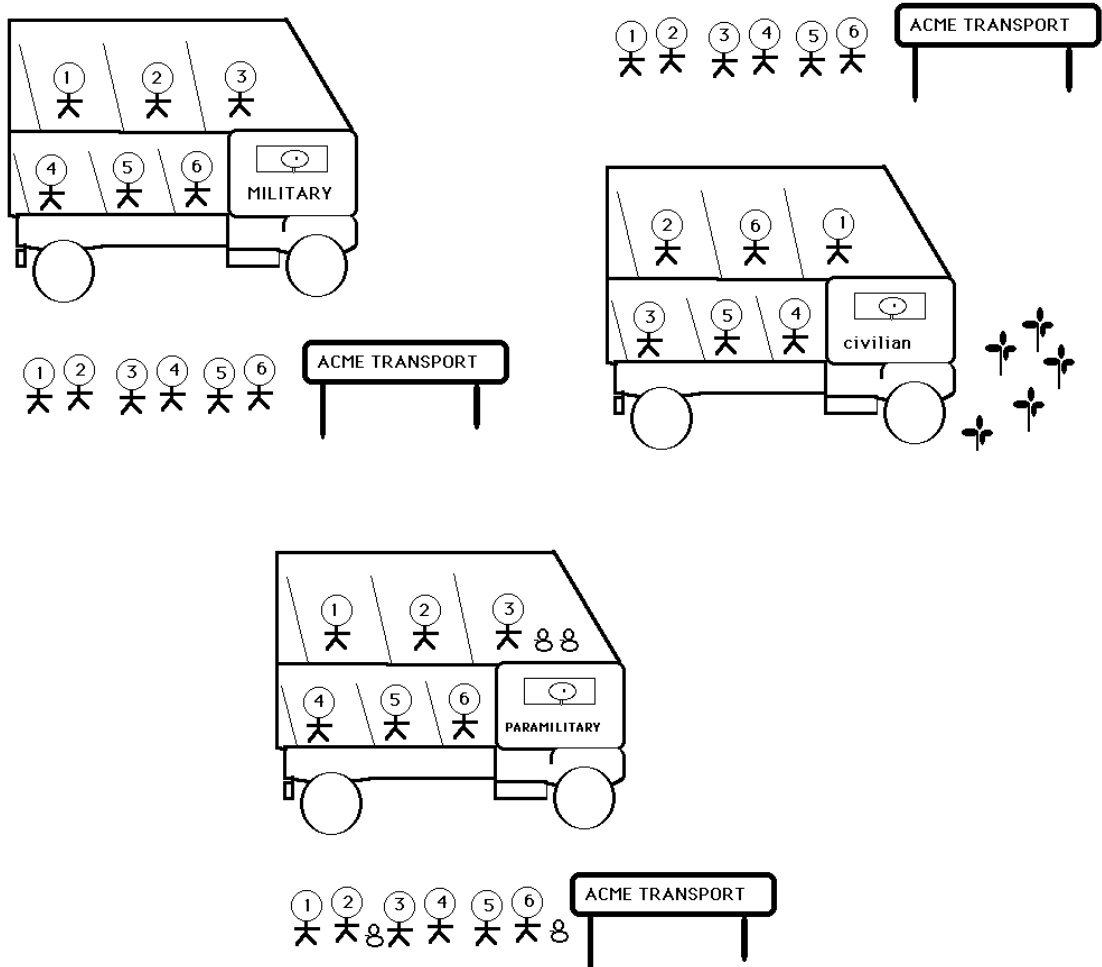
here is that of a highly disciplined queue of soldiers ordered to board a military bus. The number sequence of the bus is identical to that in the queue. The soldiers do not have a choice as to their neighbours (analogous to the solute-trapping phenomenon). The situation is not at equilibrium. It is the diffusion of atoms that leads to the new crystal structure during a reconstructive transformation. The flow of matter is sufficient to avoid strains and solutes may partition between the parent and product phases. The diffusion-driven flow of matter destroys any atomic correspondence between the parent and product phases. This is analogous to a numbered queue of civilians who board the bus in a disorderly manner, so that the the sequence in the queue bears no resemblance to that in the bus.

A paramilitary is a partly disciplined force. A paramilitary transformation is one in which interstitial atoms (which can move rapidly) partition during transformation but the change in crystal structure is achieved by displacive transformation. This is a common mechanism of transformation in Fe-C (Widmanstätten ferrite) and V-H alloys. The interstitials thus achieve equilibrium subject to the constraint that the substitutional atoms do not diffuse.

Hardenability

It is not possible with large components to obtain microstructures isothermally. Hence, the continuous cooling transformation diagrams which we studied in MP6.

The hardenability of a steel depends on the stability of the austenite. Elements like C, Mn, Ni, Mo, and Cr improve the stability and hence retard all transformations. Steels containing these elements can be hardened to a greater depth. By contrast, Al and Co can accelerate the transformation of austenite and hence reduce hardenability.



The effect of alloying elements is two-fold:

1. A thermodynamic effect as the element alters the stability of the austenite.
2. If the element concerned partitions during transformation then it may further retard the reaction because of the need for diffusion. Thus, transformations involving diffusion are retarded to a much larger extent than for example bainite or martensite.