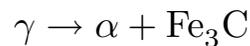


Lecture 10: Ferrous Alloys

Fe–C phase diagram

The vast majority of steels are in the austenitic condition at temperatures in excess of 900 °C. Austenite has a cubic–close packed crystal structure and tends to decompose into ferrite (body–centered cubic) and cementite (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. 51):



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.

Martensite in Steel

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

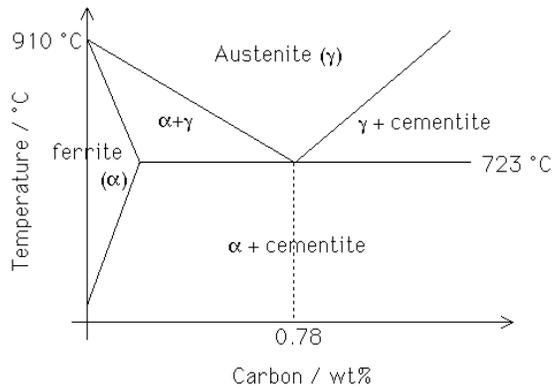


Fig. 51: Iron-carbon equilibrium phase diagram

transformation begins at a 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 $a < 1 \bar{1} 0 >$. There are three sub–lattices of octahedral holes, along directions parallel to the unit cell edges (Fig. 52).

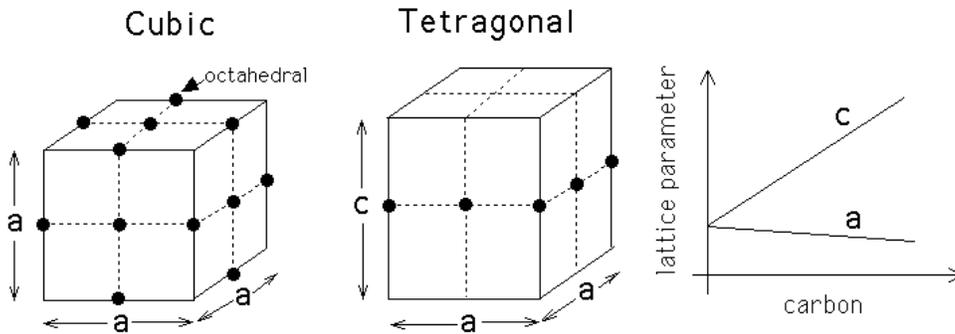


Fig. 52: Tetragonal martensite in some steels.

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-centered tetragonal structure for the martensite (Fig. 52).

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. 53).
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.

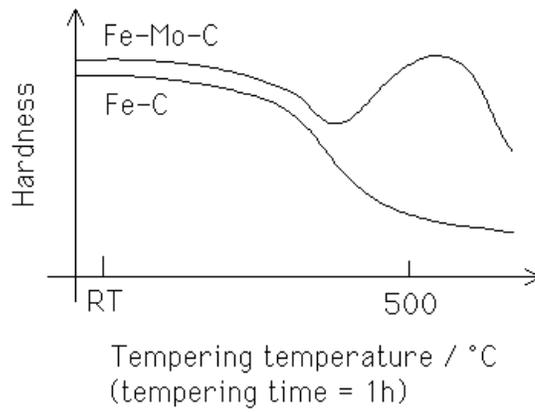


Fig. 53: Hardness changes due to tempering

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, Mo₂C, Cr₂₃C₆ or W₂C, there is an increase in hardening (Fig. 53), *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. 54). The diagram is constructed by rapidly cooling austenite to the specified temperature and measuring the fraction of transformation as a function of time.

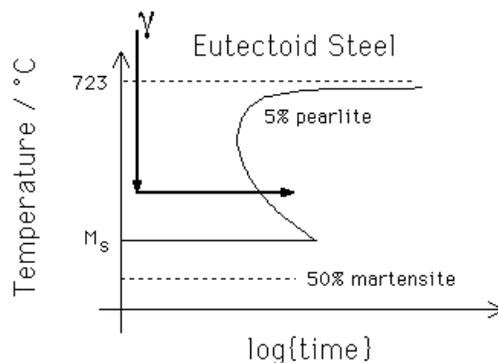


Fig. 54: TTT diagram for eutectoid steel

A real TTT diagram is somewhat more complicated (Fig. 55). Consider for example a hypoeutectoid steel – the first phase to form would be ferrite with transformation becoming possible just below the Ae_3 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 super-

saturated with carbon. The excess carbon rapidly precipitates as fine carbides between the plates of bainite (upper bainite) or within them (lower bainite).

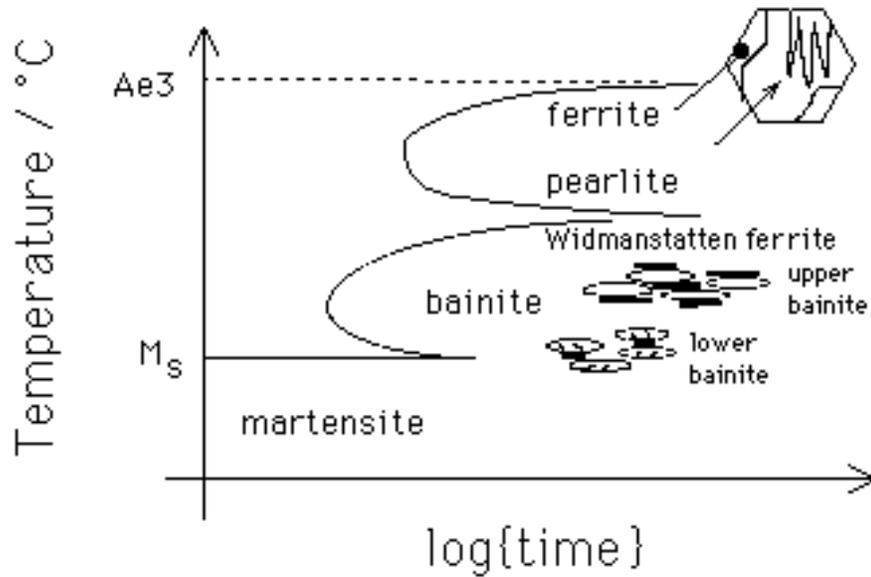


Fig. 55: TTT diagram for hypoeutectoid steel

It is not possible with large components to obtain microstructures by isothermal transformation. However, if the rate of transformation of austenite can be reduced then larger components can be uniformly transformed. A steel in which the austenite transforms relatively slowly is said to possess greater hardenability.

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.

Additional Resources

1. Steels:

www.msm.cam.ac.uk/phase-trans/2005/Fealloys.html