Lecture 8

> *So, grasping hard the stake pointed with fire,*
> *We twirl'd it in his eye; the bubbling blood*
> *Boil'd round about the brand; his pupil sent*
> *A scalding vapour forth that sing'd his brow,*
> *And all his eye-roots crackled in the flame.*
> *As when the smith an hatchet or a large axe*
> *Tempr'ing with skill, plunges the hissing blade*
> *Deep in cold water, (whence the strength of steel)*
> *So hiss'd his eye around the olive-wood.*
>
> The Odyssey of Homer
> Translated by William Cowper

Like most translators Cowper has translated Homer's original word $\beta\alpha\pi\tau\omega$ meaning "dip" (as in "baptize") as "temper." In fact the Poet is describing quenching, not tempering. We will now cover both these in this lecture.

Hardenability is described as the ability of a steel to form martensite upon quenching. This is a very qualitative definition, so it is necessary to develop quantitative measures. Generally this involves heating a standard size and shape of specimen to the fully austenitic state and then after quenching, assessing by metallography or by hardness measurement how far from the surface the steel has transformed to martensite rather than a softer product such as ferrite and pearlite. We should not use TTT diagrams except to discuss isothermal transformation, nevertheless **slide 2** serves to point out that the rate of cooling needs to be fast enough to avoid any "noses" in the TTT diagram, and that this condition may be met near the surface but not at the centre of the piece, since there the cooling rate will be less. If the specimen is in the form of a bar then the depth of hardening will of course depend on the diameter of the bar as indicated in **slide 3**.

Think about what happens when the hot metal is dropped into a quenching medium, be it water, brine, oil or a polymer quench. We distinguish three stages.
1. **Vapour blanket stage**. When the steel meets the quench medium a blanket of vapour is immediately created isolating the piece from the medium so that heat loss is by radiation and rather slow and is governed by the *emissivity* of the steel.
2. **Nucleate boiling**. The vapour blanket collapses and the liquid makes contact with the piece and boils. The onset of this stage can be quickened by using a high boiling point medium, for example a salt solution. This is the stage of the highest cooling rate, but it is relatively short.
3. **Convective cooling** Once the medium stops boiling the system settles down into convective cooling and the cooling rate is governed by the heat transfer coefficient. This stage is the longest and so dominates the final microstructure.

Slide 5 shows these stages in cartoon form by tracking the temperature (in red) and cooling rate (in blue). T_{vp} and T_{cp} are the temperatures at the onset of the vapour and convection phases. You see that the first two are over after about ten seconds and the rate of cooling for the largest part of the quench is dominated by the convective phase. Therefore we focus now on that part of the quench in an attempt to extract a quantitative measure of what is called the *quench severity*.

Recall the theory of heat transfer. The transfer of heat by *conduction*, that is, within the piece, is governed by Fourier's law for the heat flux,

$$q = -k\frac{\partial T}{\partial x} \qquad [\mathrm{J\ s^{-1}\ m^{-2}}]$$

in which k is the *thermal conductivity*; and the heat conduction equation for the temperature variation with time,

$$\dot{T} \equiv \frac{\partial T}{\partial t} = \kappa\frac{\partial^2 T}{\partial x^2}$$

in which κ is the *thermal diffusivity*, both given in one dimension for simplicity. On the other hand the rate of cooling of a body by loss of heat to the outside is approximately described by Newton's law of cooling,

$$q = h\,\Delta T = h \times (\text{temperature of body} - \text{temperature of surroundings})$$

in which h is the *heat transfer coefficient*. Note that in Fourier's law the proportionality coefficient between the heat flux q and the (negative) temperature gradient is the *thermal conductivity* having units of $[\mathrm{J\ s^{-1}\ m^{-1}\ K^{-1}}]$. On the other hand the coefficient in the heat conduction equation is the *thermal diffusivity*, which is the ratio of the thermal conductivity and the heat capacity per unit volume. This then has the units of a conventional transport coefficient, $[\mathrm{m^2\ s^{-1}}]$, as does the diffusivity in Fick's second law and the kinematic viscosity which is the viscosity in $[\mathrm{N\ s^{-1}\ m^{-2}}]$ divided by the mass density.

The coefficient that enters Newton's law of cooling is the convective heat transfer coefficient h. This is the heat flux, (watts per square metre) crossing the surface of the metal into the medium, divided by difference in temperature ΔT between the surface and the medium. It therefore has units of $[\mathrm{J\ m^{-2}\ K^{-1}\ s^{-1}}]$. For the case of a cylindrical bar,

$$h = -\frac{\rho V c_p \dot{T}}{A\Delta T}$$

where ρ is the density of the steel, c_p is its mass specific heat and V and A are volume and surface area. $-\dot{T}$ is the cooling rate.

The conditions during a quench are determined *both* by the rate of conduction from the inside to the surface of the piece *and* by the rate of heat transfer by convection into the quench medium. You are aware that transport phenomena problems (especially involving two competing processes) are greatly clarified by the use of dimensionless

quantities, for example the Reynolds number in viscosity problems which is the ratio of inertial to viscous forces. Where there are both conduction and convection we are interested in the ratio of the heat transfer to the thermal conductivity. To make up a dimensionless number we need a factor L of dimension length. The *Biot number* is[†]

$$\mathrm{Bi} = \frac{hL}{k}$$

(Do not confuse this with the Nusselt number which has the same formula but for which the conduction takes place in the fluid not the solid and so k is the thermal conductivity of the *fluid*). In our case a suitable characteristic length will be half the volume of the bar divided by its surface area: $V/A = 2L$, so that L is roughly a quarter of the radius of the bar.

Now I can define for you the so called Grossman quench severity, $H(T)$, which is a function of temperature. By convention this is defined as the convective heat transfer coefficient divided by twice the thermal conductivity of the steel. It has units of $[\mathrm{m}^{-1}]$,

$$H(T) = \frac{h}{2k}$$
$$= \mathrm{Bi}\,\frac{A}{V}$$

Slides 7 and **8** show data on thermal conductivity and diffusivity in some steels. (1Btu $\approx$ 1kJ—do you know what Btu stands for?) **Slide 9** shows how the H-value varies at the midway and the centre of a bar during a quench as a consequence of its temperature dependence. The table in **slide 10** indicates how we can associate the quench severity with the conditions and the medium of the quench (I assume that the values are in $[\mathrm{inch}^{-1}]$ as in **slide 9**).

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[†] Let me quote to you from the `wikipedia` article on the Biot number. "The physical significance of Biot number can be understood by imagining the heat flow from a small hot metal sphere suddenly immersed in a pool, to the surrounding fluid. The heat flow experiences two resistances: the first within the solid metal (which is influenced by both the size and composition of the sphere), and the second at the surface of the sphere. If the thermal resistance of the fluid/sphere interface exceeds that thermal resistance offered by the interior of the metal sphere, the Biot number will be less than one. For systems where it is much less than one, the interior of the sphere may be presumed always to have the same temperature, although this temperature may be changing, as heat passes into the sphere from the surface. The equation to describe this change in (relatively uniform) temperature inside the object, is simple exponential one described in Newton's law of cooling. In contrast, the metal sphere may be large, causing the characteristic length to increase to the point that the Biot number is larger than one. Now, thermal gradients within the sphere become important, even though the sphere material is a good conductor. Equivalently, if the sphere is made of a thermally insulating (poorly conductive) material, such as wood or styrofoam, the interior resistance to heat flow will exceed that of the fluid/sphere boundary, even with a much smaller sphere. In this case, again, the Biot number will be greater than one."

Continuing our theme of trying to quantify the hardenability, refer back now to **slide 3**. For a bar of a particular diameter, D, the microstructure will probably be fully martensitic on the outside and the fraction of martensite will become less, moving inwards, and there may be no martensite at all at the centre. Let us imagine perfoming this experiment using identical soaking and quenching conditions but using bars of varying diameter. If we section the bar and make a metallographic examination of each bar we can determine the diameter of that bar which has a microstrucutre comprising exactly 50% martensite at its centre. We will call this the *critical diameter*, D_0. This is *still* not a quantitative measure of hardenability that we can convey to other engineers because of course the critical diameter that we get will depend on the severity of quench. So why not invent a quantity called the *ideal diameter*, D_i, that is the critical diameter we would get if we could use an infinite quench severity? Given that after much tedious labour, machining, soaking, quenching, sectioning, polishing and examining bars of different diameters we have a critical diameter for the quench we are using, how can we convert this into an ideal diameter so that we have a repeatable index of the hardenability of our steel? The answer is that we use the table and chart in **slides 10** and **11**. First we estimate the severity of quench in our experiment, then reading off from the chart we choose the line appropriate to our quench and find the ideal diameter corresponding to our critical diameter (again, I'm assuming that the quench severity lines marked off in the chart on **slide 11** are in units of inverse inches and that D and D_i are in centimetres). It is clear that the ideal diameter is larger than the critical diameter because if the quench were infinitely severe then a larger diameter bar will still result in having 50% martensite at its centre.

The Jominy test (below) does not result in a single measure of hardenability although the results contain a wealth of data. On the other hand the Grossman ideal diameter is a measure of hardenability that is independent of the method of quench and hence properly regarded as a materials parameter. For example the effect of different alloy elements may be tested to determine which imparts the greater hardenability. As we have already seen earlier these include molybdenum and boron.

The two principal factors controlling hardenability are prior austenite *grain size* and *composition*. There is a procedure to predict hardenability for a given steel. First use a chart like **slide 12** to read off the *base hardenability*, $D_{i,crit}$, as a function of carbon concentration and grain size. Then there are multiplicative factors to take into account alloying elements using this empirical relation,

$$D_i = D_{i,crit} \times 3.28(\text{wt\%Mo})$$
$$\times 2.21(\text{wt\%Mn}) \times 2.13(\text{wt\%Cr}) \times 1.47(\text{wt\%Ni}) \times 1.40(\text{wt\%Si})$$

Slide 13 shows these individual *hardenability factors*. I don't know why they are not straight lines as required by the empirical formula. The effect of boron is powerful and a further multiplying factor is applied for this as indicated in **slides 15–18**.

It is important for the engineer not to overdo hardenability. For example steels are regarded at not weldable if their "carbon equivalent" exceeds about 0.4wt%. This is because a hard and untempered martensite may be produced in the heat affected zone

that will lead to cracking. The C.E. can be calculated using a formula such as this.

$$\text{Carbon Equivalent} = \text{wt\% C} + \frac{\text{wt\% Mn}}{16} + \frac{\text{wt\% Si}}{43} + \frac{\text{wt\% (Ni + Cr)}}{28} + \frac{\text{wt\% Mo}}{22}$$

The Grossman hardenability is well worth studying because it's easy to appreciate the metallurgical and engineering principles leading to the definition of a materials property that can be communicated between practitioners and steel makers. However the experiments are too time consuming to make this a routine practice for alloy designers and metals testing laboratories. As an alternative it is more common to make a Jominy end quench test. A bar of standard dimensions is annealed and placed in a rig where it is subjected to a jet of water impinging at one end of the bar. The hardness is then measured at intervals along the bar and the surface hardness is plotted as a function of distance from the quenched end. The dimensions are given in **slide 19** and some typical data plotted in **slide 20**. To make contact with the Grossman test there are standard curves that can be produced (**slide 21**) which can be used to relate hardness to the percentage of martensite for a given steel. To complete the connection between the two we need to know how the Jominy quench using a jet of water from one end of a bar relates to a quench in which the bar is fully immersed in a quench medium at a certain quench severity. Again, there are standard curves that can be consulted, such as **slide 22**. The rate of cooling at a chosen distance from the quenched end in the Jominy test is the same as the rate of cooling at the centre of a Grossman bar given by the curve appropriate to the quench severity of the Grossman quench. That is, to find the diameter of bar that would have the same cooling rate at its centre as the cooling rate a certain distance along the Jominy bar, just select the distance along the x-axis and using the curve for the appropriate quench severity in the Grossman test, read off the diameter of bar on the y-axis whose centre will experience the same cooling rate as that part of the Jominy bar.

As you know martensite is generally speaking too hard to be of practical use. Therefore it is tempered after quenching to bring about a balance of strength and toughness by allowing some of the carbon to diffuse out of the supersaturated martensite and produce isothermal products such as bainite or ferrite, containing precipitated iron carbides. Tempering *temperature* is generally more important than tempering *time* in bringing about the desired microstructure. **Slide 24** shows the effects of tempering temperature on a number of mechanical properties of a quenched and tempered steel.

Four stages in tempering have been identified and I will now describe these. They are summarised in **slide 25**.

Stage 1

Carbon diffuses from room temperature up to 250°C, so for steels with more than 0.3wt% C, martensite is unstable in this temperature range and ε-Fe$_3$C precipitates (**slide 26**). This is hexagonal close packed iron, having C atoms occupying up to 1/3 of the octahedral interstices lying in between the close packed planes. The orientation

relation with the martensite is as follows (see **lecture 7**).

$$(101)_{\alpha'} \parallel (10\bar{1}1)_{\varepsilon}$$
$$(011)_{\alpha'} \parallel (0001)_{\varepsilon}$$
$$[11\bar{1}]_{\alpha'} \parallel [1\bar{2}10]_{\varepsilon}$$

These are nearly coherent precipitates, and are likely to increase hardness by a particle cutting mechanism, see **slide 4**, **lecture 1**. Some ε-Fe_3C precipitates are shown in **Slide 26**).

Stage 2

Principally this is transformation of retained austenite in the temperature range 230–300°C. It is supposed that the transformation products are bainite and cementite.

Stage 3

This stage is characterised by the first appearance of cementite also known as θ-Fe_3C, and by the loss of tetragonality of the martensite. The orthorhombic cementite forms in an orientation relation with the martensite as follows. This is essentially the Bagaryatski relation of **lecture 7** (notes page 3).

$$(211)_{\alpha'} \parallel (001)_{\theta}$$
$$[01\bar{1}]_{\alpha'} \parallel [100]_{\theta}$$
$$[\bar{1}11]_{\alpha'} \parallel [010]_{\theta}$$

This reaction may begin at 100°C, and fully develop at 300°C. Cementite particles are up to 200 nm long and $\sim$15 nm thick. The cementite probably nucleates at the ε-Fe_3C interfaces with martensite (**slide 26**). Cementite eventually consumes the ε-Fe_3C. Cementite may also nucleate on twins which occur in higher carbon martensite, which then grows into colonies of θ-Fe_3C laths (**Slide 27**) having habit planes of $\{112\}_{\alpha'}$ type. Cementite will also nucleate at prior austenite grain boundaries (**Slide 28**) and at martensite lath boundaries. The nuclei grow into thin films which subsequently spheroidise. At the end of stage three the martensite is essentially ferrite, all tetragonality being lost.

Stage 4

This is a stage of cementite coarsening between 300°C and 400°C, followed by spheroidisation at up to 700°C. The resulting microstructure contains equiaxed grains of ferrite and coarse spheroidal cementite (**Slide 29**)

Martensite lath boundaries may remain stable up to about 600°C, but there are rearrangements of the lath boundaries and dislocations within the laths in the range 350–600°C, resulting in a reduced dislocation density and reduction in hardness. This is essentially static recovery.

Slide 30 summarises the hardness reduction in the different stages described for martensites having various carbon contents. The anomalous *increase* in hardness in the initial stages of tempering 0.18% C steel may be attributed to hardening by coherent ε-Fe_3C particles.

Further reading

https://en.wikipedia.org/wiki/Thermal_conduction

R. W. K. Honeycombe, "Steels: Microstructure and Properties," Edward Arnold, 1st Edition, 1981

W. C. Leslie, "Physical Metallurgy of Steels," McGraw-Hill, 1981

https://www.youtube.com/watch?v=qWOaUbTWtVM is a film of the Jominy end quench test.

Chen Zhu, Alfred Cerezo and George D. W. Smith, *Ultramicroscopy*, **109**, 545 (2009)

Problems

8.1 What is meant by the "hardenability" of steel? What is meant by "ideal critical diameter"?

8.2 Describe the Jominy end quench test used to measure the hardenability of a steel.

8.3 State what are the two principal variables that influence hardenability of steel.

8.4 Give an explanation for why boron in parts-per-million concentrations is able to improve hardenability. Why do larger amounts of boron have no further influence on hardenability?

8.5 Give an example of a substitutional impurity element that can be used to improve hardenability. Explain the physical origin of the effect produced.

8.6 What is meant by "tempering"? Why is it normally the practice to temper martensite?

8.7 Describe the four principal stages in the tempering of martensite, including for each stage the temperature range and the resulting microstructure.