

Massachusetts Institute of Technology  
Department of Mechanical Engineering  
Cambridge, MA 02139

2.002 Mechanics and Materials II

Laboratory Module No. 5 – Background

**Heat Treatment of Low-alloy Steels:  
Effects on Macroscopic Mechanical Properties.**

## 1 Introduction to Heat Treatment of Carbon Steels

### 1.1 Overview

It is perhaps presumptuous to attempt to give even a cursory synopsis of the vast literature surrounding the heat-treatment of carbon steels. There are at least two levels at which the subject can be approached. One level constitutes a phenomenological description of what thermal histories are applied, along with details such as temperature levels, times of holding at temperature, maximum allowable time limits for executing “rapid” temperature changes, and technical nomenclature associated with the processes. A second, and more ambitious level focusses on fundamental physical processes, equilibrium states of matter under different temperatures, and kinetics of the processes by which one state transforms to another under changes in temperature. The second level is based on fundamentals of thermodynamics, kinetics, and materials science which can not be easily (or effectively) introduced in a brief format such as the present laboratory module. Nonetheless, we will attempt to highlight “major aspects” of the heat-treating carbon steels from both the phenomenological/technological and the scientific/academic points of view.

The first notion of importance is that of *equilibrium state* of a collection of matter. We are familiar with the changes of state of a pure substance like water, as a function of temperature: at sufficiently low temperatures, (below  $0^{\circ}\text{C}$ ), the stable, equilibrium state is a solid (ice), while at ambient pressure and higher temperatures, water is liquid. What may not be as well-appreciated is that the equilibrium crystal microstructure of ice is not constant, but depends on temperature and pressure.<sup>1</sup>

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<sup>1</sup>For a popular literary treatment based (loosely) on these notions, see Kurt Vonnegut’s 1963 *Cat’s Cradle*, in which a madcap scientist brings on the end of the world by isolating a new crystal structure, Ice-9, which is stable at ambient temperatures...

And so it is with the solid states of the substance **pure iron** (Fe):

1. At ambient pressure and (high) temperatures between 1394C and 1534C (the latter of which is the melting temperature of pure Fe), its equilibrium phase is a body-centered cubic (BCC) crystal called  $\delta$ -iron;
2. At temperatures in the range 912C to 1394C, the stable phase is a face-centered cubic (FCC) phase called  $\gamma$ -iron;
3. While at temperature from absolute zero to 912C, the equilibrium phase is a BCC crystal structure called  $\alpha$ -iron.

For our purposes, only the temperature ranges corresponding to stable  $\alpha$  and  $\gamma$  phases are of interest.

When iron is alloyed with carbon (C), in concentrations corresponding to 0.04 wt% to 2.0 wt% (along with other alloying elements which we will ignore for the present) one obtains “**carbon steels**”. In this case the central question is:

**“What happens to the carbon atoms in the crystal structures, and how does this affect mechanical properties of the steel?”**

Broadly speaking, there are two places for the carbon to go:

1. The carbon can “dissolve” in solid solution into the Fe crystal structure. In general, a small atom such as C in solid solution occupies an interstitial position between Fe atoms of the crystal structure, leading to a **single phase solid solution** (Fe crystal with dissolved C):
  - (a) When the C is dissolved into the  $\gamma$  phase of Fe, it is termed **austenite**, a ductile solid solution of C in FCC iron;
  - (b) When the C is dissolved into the  $\alpha$  phase of Fe, it is termed **ferrite**, a ductile solid solution of C in BCC iron.
2. The carbon can form a chemical reaction with the iron, forming a hard crystalline second-phase **iron carbide compound**,  $\text{Fe}_3\text{C}$ , called **cementite**, which precipitates out into spatial regions that are separate from the solid-solution crystal phases.

The equilibrium (or lowest energy) structure of low carbon steels at ambient temperature is two-phase: there are spatial regions occupied by the hard cementite compound ( $\text{Fe}_3\text{C}$ ) distributed within/among ferrite crystals ( $\alpha + \text{Fe}_3\text{C}$ ). Depending on the processing history, the morphology of the two phases can vary. One possibility is for the cementite

to cluster into discrete  $\sim$ micron-sized equi-axed carbide particles distributed within the BCC ferrite grains. A more common morphology is for the ferrite and cementite phases to form locally nano-laminated structures of alternating platelet-like layers; such a microstructure is often called “**pearlite**” because its appearance, under light microscopy, is reminiscent of the iridescent luster of exhibited by “mother of pearl”<sup>2</sup>

A map of the equilibrium phase diagram for the Fe-C system is shown in Figure 1. For example, at 0.4 wt% C, at the temperature of 850C, the equilibrium structure is FCC austenite, while at ambient temperature, the equilibrium structure is a mixture of ferrite and local pearlite structures.

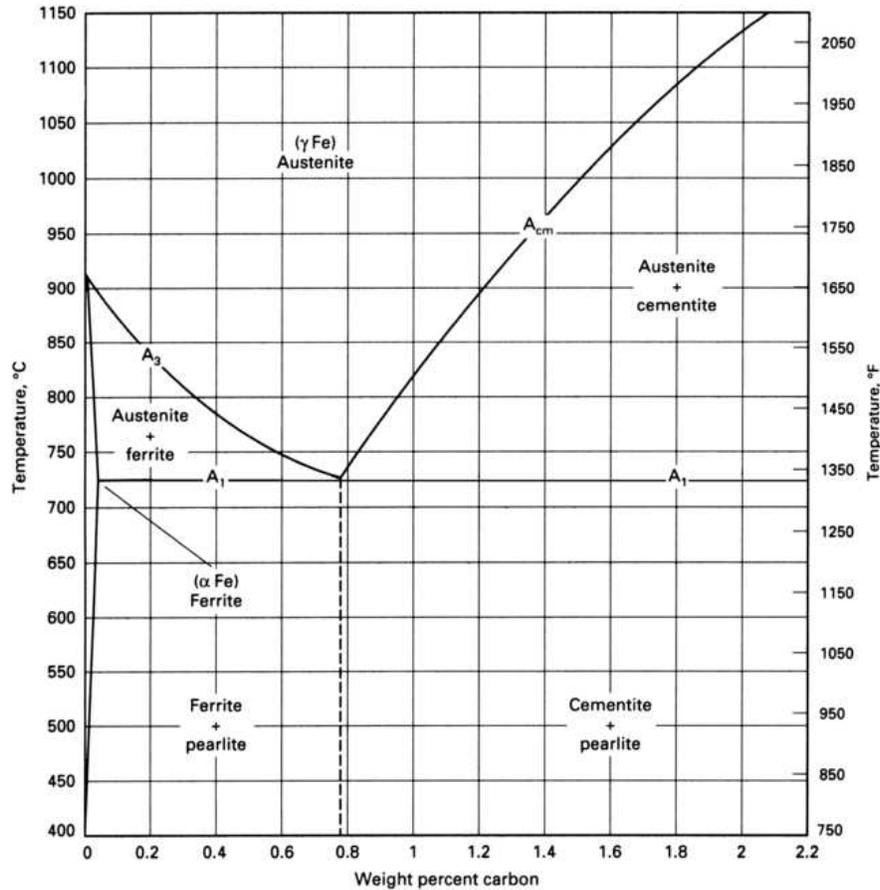


Figure 1: Fe-C equilibrium phase diagram.

<sup>2</sup>“Mother of pearl” is the nacre of certain mollusk species, a laminated bio-composite consisting of layers of hard aragonite crystals connected by biopolymer molecules. The thicknesses of the alternating layers is sub-micron in scale, causing interference with visible light, resulting in different color visibility from different viewpoints. The cementite and ferrite layers within “pearlite” are of similar thickness range.

The most important single fact about the iron-carbon system is that **the solubility of C in FCC  $\gamma$ -iron is very much larger than its solubility in BCC  $\alpha$ -iron**. In other words, it is much more difficult to insert C atoms into the spatially-restricted interstices of the BCC Fe lattice than it is to do so in the more open FCC lattice. It is this essential feature that is exploited in constructing heat-treatment thermal histories that produce special microstructures in carbon steels.

## 1.2 Kinetics aspects: quenching

In the time and temperature histories during which these heat-treatment processes take place, the carbon and the iron atoms, driven by thermodynamic forces, continuously “try” to reorganize themselves into equilibrium (lowest energy) structures. However, the dramatically lowered solubility of C in the BCC ferrite means that, on cooling from FCC austenite, there must be local fluxes of excess C atoms from (what will become) ferrite domains, toward regions that will become cementite, along with counterfluxes of excess Fe atoms from cementite domains toward ferrite regions. A typical mechanism for these fluxes is **atomic diffusion**, a thermally-activated process that dramatically slows down as temperature drops. The short diffusion distances associated with sub-micron-thickness alternating layers of cementite and ferrite accounts for the pearlite morphology.

At this point, we confront the essential kinetics-limited features of a carbon steel that is *rapidly* cooled from an equilibrium temperature in the austenite regime to a sufficiently low temperature within the equilibrium ferrite plus cementite regime (such a rapid cooling is termed “**quenching**”):

1. Because the temperature dropped so quickly, there was insufficient time for the C and Fe atoms to diffusively rearrange themselves into organized cementite and ferrite domains;
2. Because the temperature at the end of the rapid cooling is now sufficiently low, the diffusional fluxes are now exponentially small, and essentially no further diffusional transport can take place, so that
3. The crystal lattice momentarily finds itself thermodynamically “stuck” in a metastable (higher-than-equilibrium energy) state of still being FCC with high C solid solution content, albeit at a very low temperature compared to the equilibrium phase boundary temperature; such a state is said to be highly “under-cooled”.
4. In a dramatic attempt to lower its energy, the FCC lattice undergoes an extremely rapid diffusionless **martensitic phase transformation** into a BCC-like structure having a supersaturation of C atoms that locally organizes itself in the interstitial sites between Fe atoms within a particular [100] plane; this distorts the cubic BCC lattice dimensions into a BCT (body-centered tetragonal) crystal having one

longer axis (termed the  $c$ -axis), in the direction perpendicular to the [100] plane of excess C concentration, at the same time reducing the remaining two BCC lattice dimensions,  $a$ . The resulting structure is a very hard, highly distorted lattice termed **martensite**. Among different composition steels, as C concentration of the martensite increases, the BCT lattice becomes more distorted (as reflected in the increasing  $c/a$  ratio) and the resulting martensite itself becomes harder. The growth of these martensitic domains typically propagates into elongated lath- or needle-like shapes.

### 1.3 Tempering: a compromise of strength and ductility

Once the martensitic reaction has taken place in response to rapid quenching from a temperature within the equilibrium austenite regime, the steel is extremely hard, but also quite brittle, owing both to high resistance to dislocation motion in the distorted BCT lattice, and to high internal stress within the lattice that can promote local cleavage fracture; these internal stresses are created during quenching due to spatially nonuniform transformation directions of the BCT distortions.

In order to reduce the brittleness of as-quenched martensite, but still retain a substantial fraction of its high yield strength, a final heat-treating step called **tempering** is usually employed. Following a quench, the steel is re-heated to a **tempering temperature** that is well above ambient, but also well within the equilibrium ferrite plus cementite regime, and held for a specified period of time. At these tempering temperatures, the diffusional atomic rearrangement mechanisms again start to act, albeit at very slow rates compared to diffusion at higher temperatures. These diffusional fluxes enable some of the excess C to diffuse from the distorted BCT lattice, and to begin the processes of creation of local ferrite and cementite domains. Since diffusion is thermally-activated, the local relaxations proceed more rapidly at higher tempering temperatures, and conversely, more slowly at lower temperatures. The limited diffusional relaxation of BCT lattice distortion also starts to relieve internal stress generated by quenching. Since the strength of the martensite is greater than that of its tempering-induced decomposition products, the net result of the tempering step is a decrease in overall strength and internal stress with increasing tempering temperature, accompanied by increases in ductility and toughness.

### 1.4 TTT diagram for 4140 steel

We can gain some quantitative insight as to what happens in 4140 steel under a general thermal cooling history from a temperature in the austenite (A) regime by examining its isothermal Time-Temperature-Transformation (TTT) curve, as shown in Fig. 2. The vertical axis is temperature, which is reached rapidly by cooling from an elevated temperature of 850°, and then held constant for indicated periods of time. The horizontal

axis is logarithmic in time, measured from the start of the rapid temperature decrement out of the austenite regime. Marked on the figure are curves denoting the start of the appearance of new structures such as ferrite (F), cementite (C), and martensite(M). For example, if we held at 600°C for a period of an hour or more, we would obtain an equilibrium structure of ferrite and cementite. However, if instead we had cooled rapidly to a temperature below the **martensite start temperature** of  $M_s \doteq 660F$  in less than 2 seconds, we would have a highly undercooled austenite that would start to transforming spontaneously to martensite; by the  $M_{90}$  temperature of 510F, 90% of the austenite has transformed to martensite.

Other time/temperature cooling trajectories would result in other structures; these can be assessed from related time-temperature-transformation curves for **continuous cooling**; we will not address this issue here.

It should be noted that TTT curves for other carbon steels have similar features, but for plain carbon steel lacking alloy elements, the time window for reaching an  $M_s$  temperature becomes exceedingly small (fractions of a second), and in practice it is difficult to achieve sufficiently rapid cooling rates to obtain martensite.

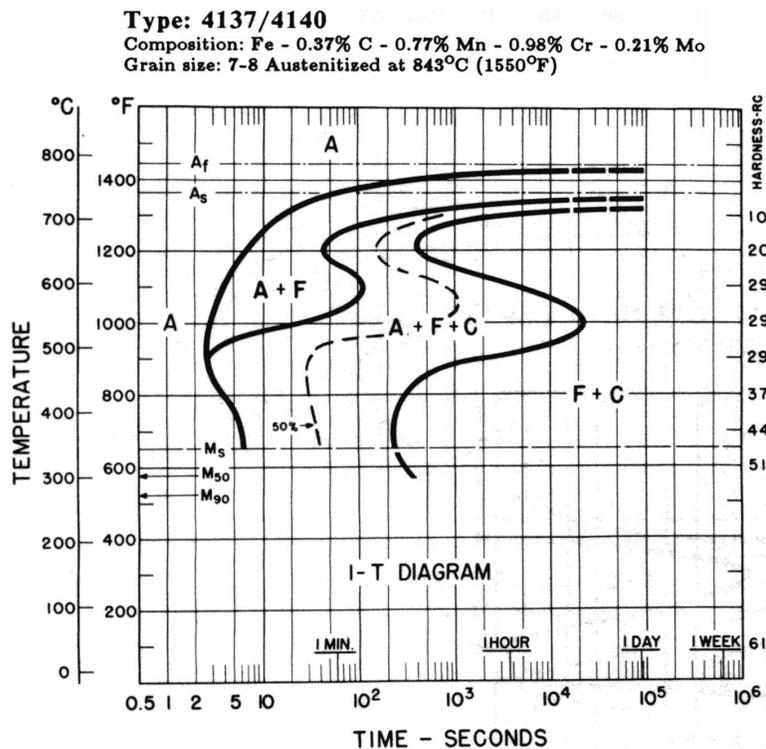


Figure 2: Isothermal Time-Temperature-Transformation (TTT) curve for AISI 4140 low alloy steel.

With this rough “kinetic road map” in mind, we examine some common heat-treatments for 4140 steel.

### 1. Austenitize and Air-Cool:

The thermal history leading to this state is also called **normalizing**. Normalizing of 4140 steel typically consists of the following steps:

- **Austenitize:** put in furnace at 850-875°C in the austenite range, and hold for 1 hour until equilibrium temperature and corresponding solid solution structure have been reached.
- **Air-cool:** remove from furnace and allow to air-cool to room temperature.

**Note: we will not be examining the 4140 steel in this (normalized) heat-treated condition in this lab.**

### 2. Austenitize and Furnace-Cool:

This heat-treatment is sometimes also called **annealing**. Here the steel is subjected to the following temperature histories:

- **Austenitize:** put in furnace at 850-875°C in the austenite range, and hold for 1 hour until equilibrium temperature and corresponding solid solution structure have been reached.
- **Furnace-Cool:** slowly cool in the furnace to  $\approx 350^\circ\text{C}$ , at a rate of  $\approx 50^\circ\text{C/hr}$ , over a period of 10 hours.
- **Air-cool:** remove from furnace and allow to air-cool to room temperature.

The slow cooling across the TTT diagram results in an equilibrium microstructure, as show in Figure 3.

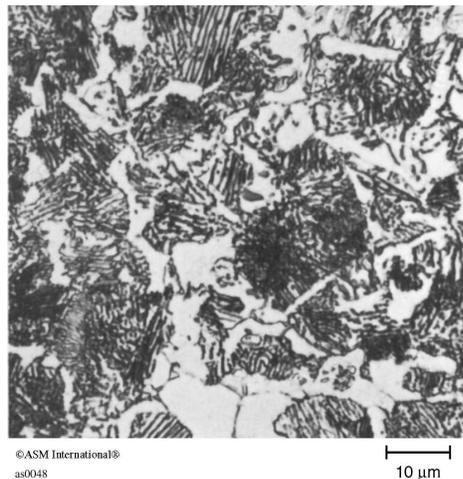


Figure 3: Annealed microstructure of 4140 low alloy steel. Note the alternating layers of the pearlite structures (dark cementite layers adjacent light ferrite layers), plus additional ferrite domains.

### 3. Austenitize and Quench:

- **Austenitize:** put in furnace at 850-875°C in the austenite range, and hold for 1 hour until equilibrium temperature and corresponding solid solution structure have been reached.
- **Quench: Rapidly** remove material from furnace, plunge it into a large reservoir of oil (or water) at room temperature, and **stir vigorously**. In general, water is a more effective quenching medium than oil, resulting in faster temperature change in the steel, and accordingly affecting the extent and nature of the martensite produced.

Figure 4 shows a micrograph of a water-quenched 4140 steel. The clarity of this digitally-reproduced micrograph leaves much to be desired, so an as-quenched microstructure of a different steel is shown in Fig. 5 for illustrative purposes.

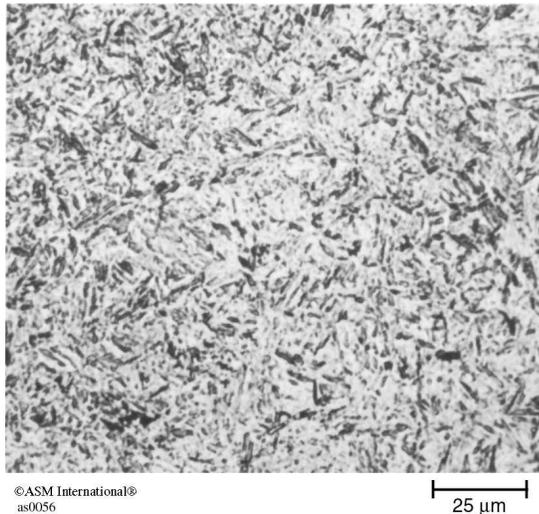


Figure 4: As-quenched microstructure of 4140 low alloy steel (water quench). Note the elongated lath structures

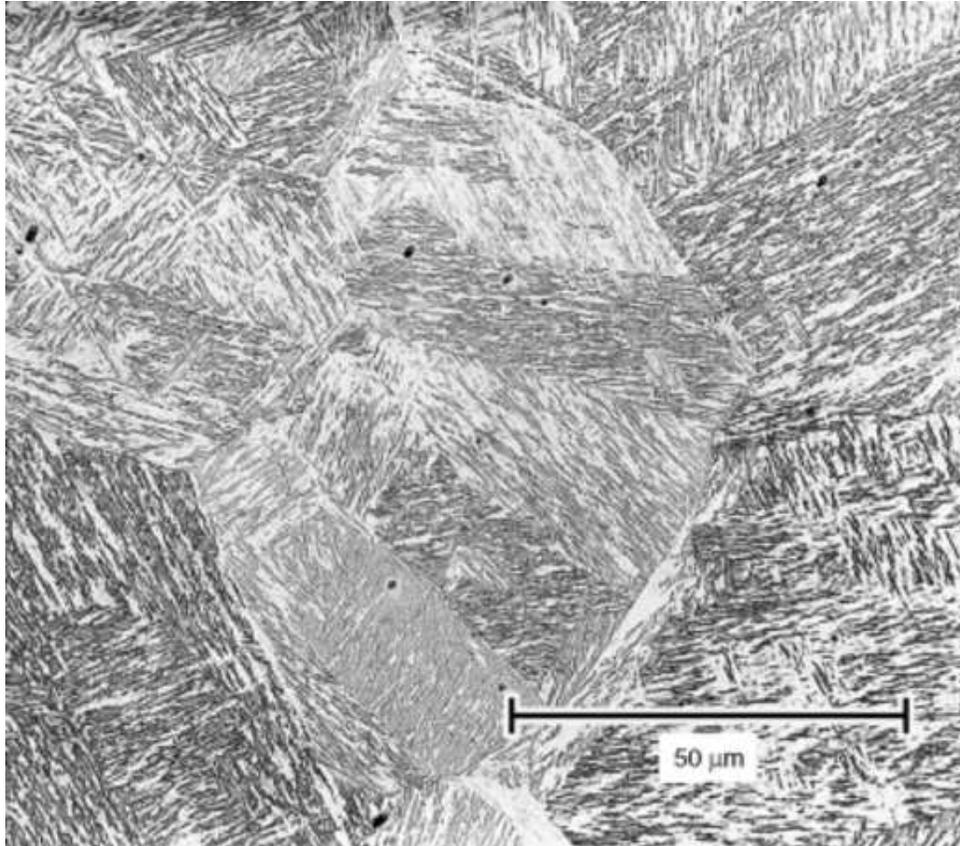


Figure 5: Water-quenched lath martensite in a different steel, shown to better illustrate the elongated lath structures of the martensite.

#### 4. Austenitize, Quench, and Temper:

- **Austenitize:** put in furnace at 845-870°C (1550-1600°F) in the austenite range, and hold for 1 hour until equilibrium temperature has been reached.
- **Quench: Rapidly** remove material from furnace, plunge it into a large reservoir of oil at ambient temperature, and **stir vigorously**.
- **Temper:** Re-heat the steel to to the **tempering temperature** (example: 250C), and hold for approximately 2 hours. Air-cool to room temperature.

**Note:** there are ranges of possible tempering temperatures and hold times; for 4140 steel, the temperature range is approximately from 200 – 650°C, and hold times range from 30 mins to 2 hours. Different tempering temperatures and times lead to differences in the resulting mechanical properties; in general, for a fixed tempering time, ‘lower’ tempering temperatures lead to higher yield strength, but lower toughness and ductility, while ‘higher’ tempering temperatures lead to lower strength, but increased toughness and ductility.

Figure 6 show a micrograph of 4140 that has been oil-quenched, followed by 2 hours of tempering at 600C. Again, the clarity of the micrograph fails to highlight the essential features of tempered martensite, so Fig. 7, a micrograph of a different quenched and tempered steel, is included for illustrative purposes.

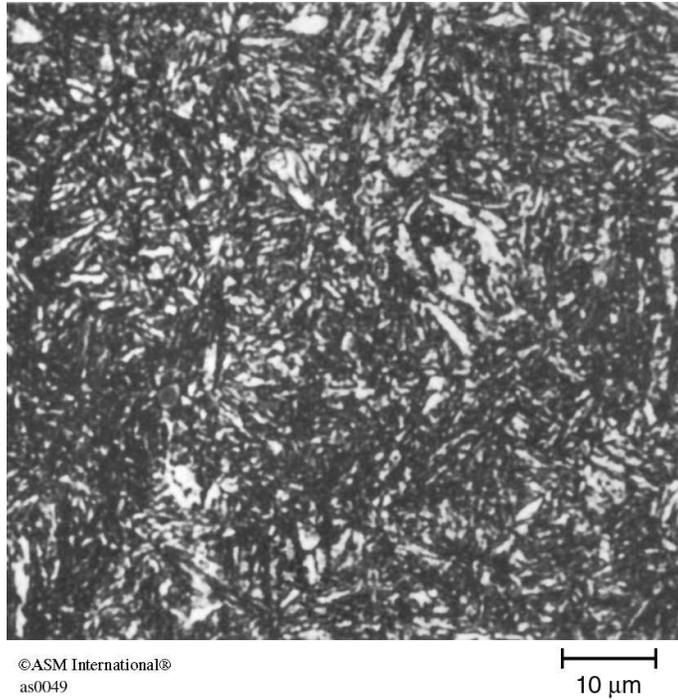


Figure 6: Quenched and tempered microstructure of 4140 low alloy steel (oil quench and tempered at 600C). Note the remnant martensite, as well as zones of ferrite (light).



Figure 7: Quenched and tempered microstructure of a different steel. Note the remnant martensite laths, the small, dark cementite particles, and lighter zones of ferrite.

## 2 Hardness Testing

This common testing mode consists of pressing a pointed diamond or hardened steel ball indenter into the surface of the material to be examined. The further into the material that the “indenter” sinks, the *softer* is the material, and the lower is its plastic flow strength.

The **hardness**,  $H$ , is the applied load,  $F$ , divided by the projected area of the indent into the surface,  $A$ :

$$H \equiv \frac{F}{A} \quad 2.1$$

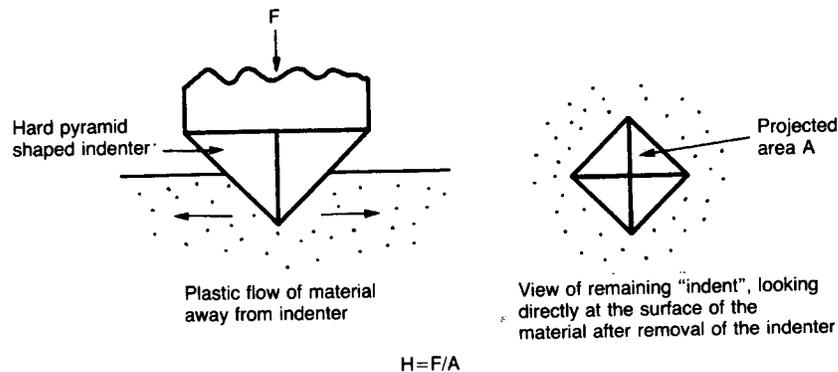


Figure 8: Schematic of a hardness test

For materials which do not appreciably strain-harden, it may be shown that the hardness  $H$  is approximately related to an averaged tensile **flow strength**,  $\sigma_f$  (roughly: an average of  $\sigma_y$  and  $\sigma_{TS}$ ), by

$$\boxed{H \approx 3\sigma_f}. \quad 2.2$$

Thus, the hardness test is a very quick and cheap test for estimating  $\sigma_f$ : there is no need to go to the trouble and expense of making and testing tensile specimens. Hardness testing can be used as a quality assurance test to check if materials meet specifications on  $\sigma_f$ .

The **Rockwell Hardness Test** is one commonly-used measure of hardness. Instead of separately measuring the force of indentation and the projected area of indent, this test simply measures the depth of indentation under different loads.

The Rockwell Hardness test employs several scales (see Table 1), each associated with a specific indentation load and indenter type. Depending on the expected hardness of the material being measured, the appropriate Rockwell Hardness scale is selected. Here the measure of hardness on appropriate “scales” is empirically correlated with the ultimate tensile strength,  $\sigma_{TS}$ , of metals by performing an exhaustive series of experiments, Table 2. These correlations have been established mainly for martensitic and ferritic steels, and should not be applied to estimate tensile strengths of austenitic steels.

**TABLE 1**  
**COMMONLY-USED ROCKWELL HARDNESS SCALES**

Symbol, HR‘X’ ‘X’ =	Penetrator Diameter if Ball, mm (in)	Load kg	Typical Application
A	Diamond point	60	Tool materials
D	Diamond point	100	Cast irons, sheet steels
C	Diamond point	150	Steels, hard cast irons, Ti alloys
B	1.588 (0.0625)	100	Soft steels, Cu and Al alloys
E	3.175 (0.125)	100	Al and Mg alloys, other soft metals; reinforced polymers
M	6.35 (0.250)	100	Very soft metals; high modulus polymers
R	12.70 (0.500)	60	Very soft metals; low modulus polymers

**TABLE 2.**

**HARDNESS CONVERSION CHART  
(HIGHER HARDNESS)**

Brinell Hardness Tungsten Carbide Ball 3000 kg	Rockwell Hardness			Approximate Tensile Strength	
	A Scale 60kg	B Scale 100kg	C Scale 150kg	(ksi)	(MPa)
-	85.6	-	68.0	-	-
-	85.3	-	67.5	-	-
-	85.0	-	67.0	-	-
767	84.7	-	66.4	-	-
757	84.4	-	65.9	-	-
745	84.1	-	65.3	-	-
733	83.8	-	64.7	-	-
722	83.4	-	64.0	-	-
710	83.0	-	63.3	-	-
698	82.6	-	62.5	-	-
684	82.2	-	61.8	-	-
682	82.2	-	61.7	-	-
670	81.8	-	61.0	-	-
656	81.3	-	60.1	-	-
653	81.2	-	60.0	-	-
647	81.1	-	59.7	-	-
638	80.8	-	59.2	329	2267
630	80.6	-	58.8	324	2232
627	80.5	-	58.7	323	2225
601	79.8	-	57.3	309	2129
578	79.1	-	56.0	297	2046
555	78.4	-	54.7	285	1964
534	77.8	-	53.5	274	1888
514	76.9	-	52.1	263	1812
495	76.3	-	51.0	253	1743

TABLE 2. (Continued)

**HARDNESS CONVERSION CHART  
(INTERMEDIATE HARDNESS)**

Brinell Hardness Tungsten Carbide Ball 3000 kg	Rockwell Hardness			Approximate Tensile Strength	
	A Scale 60kg	B Scale 100kg	C Scale 150kg	(ksi)	(MPa)
477	75.6	-	49.6	243	1674
461	74.9	-	48.5	235	1619
444	74.2	-	47.1	225	1550
429	73.4	-	45.7	217	1495
415	72.8	-	44.5	210	1447
401	72.0	-	43.1	202	1378
388	71.4	-	41.8	195	1343
375	70.6	-	40.4	188	1295
363	70.0	-	39.1	182	1254
352	69.3	-	37.9	176	1213
341	68.7	-	36.6	170	1171
331	68.1	-	35.5	166	1144
321	67.5	-	34.3	160	1102
311	66.9	-	33.1	155	1068
302	66.3	-	32.1	150	1033
293	65.7	-	30.9	145	999
285	65.3	-	29.9	141	971
277	64.6	-	28.8	137	944
269	64.1	-	27.6	133	916
262	63.6	-	26.6	129	889
255	63.0	-	25.4	126	868
248	62.5	-	24.2	122	840
241	61.8	100.0	22.8	118	813

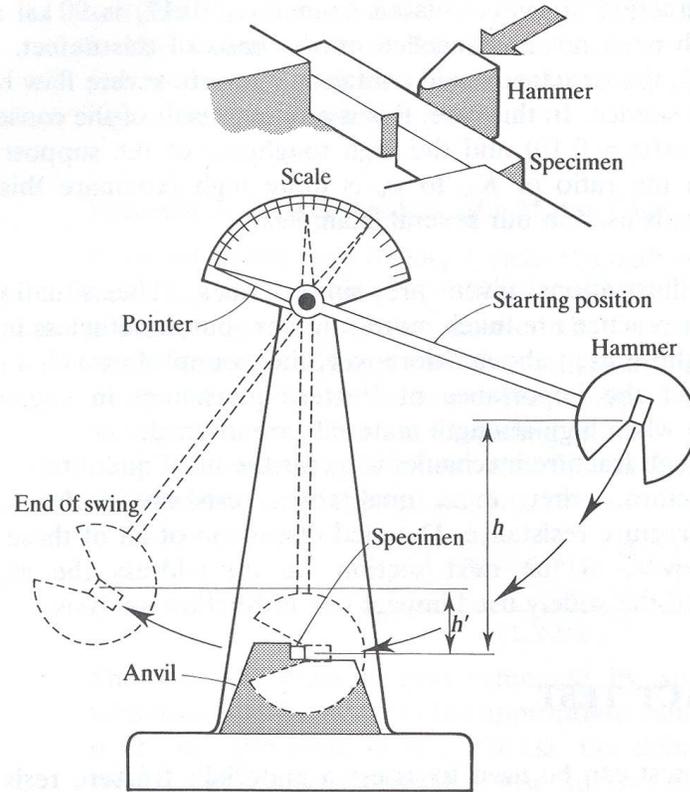
TABLE 2. (Continued)

**HARDNESS CONVERSION CHART  
(LOWER HARDNESS)**

Brinell Hardness Tungsten Carbide Ball 3000 kg	Rockwell Hardness			Approximate Tensile Strength	
	A Scale 60kg	B Scale 100kg	C Scale 150kg	(ksi)	(MPa)
235	61.4	99.0	21.7	115	792
229	60.8	98.2	20.5	111	765
223	-	97.3	20.0	109	751
217	-	96.4	18.0	105	723
212	-	95.5	17.0	102	703
207	-	94.6	16.0	100	689
201	-	93.8	15.0	98	675
197	-	92.8	-	95	655
192	-	91.9	-	93	641
187	-	90.7	-	90	620
183	-	90.0	-	89	613
179	-	89.0	-	87	599
174	-	87.8	-	85	586
170	-	86.8	-	83	572
167	-	86.0	-	81	558
163	-	85.0	-	79	544
156	-	82.9	-	76	523
149	-	80.8	-	73	503
143	-	78.7	-	71	489
137	-	76.4	-	67	461
131	-	74.0	-	65	448
126	-	72.0	-	63	434
121	-	69.8	-	60	413
116	-	67.6	-	58	400
111	-	65.7	-	56	386

### 3 Notched-Bar Impact Tests

Notched-bar impact tests measure the work done (or energy dissipated) while failing a specimen containing a stress concentration – the notch, under high strain-rate loading conditions, at different temperatures. The **Charpy Impact Test** is one common notched-bar impact test. In the Charpy test, a notched bar is subjected to three-point bending under impact loading conditions, Figure 9, and the energy to break the specimen is measured. Both U-notch and V-notch configurations are employed; the V-notch is used more frequently since it provides a more severe stress concentration. In this lab, we will use V-notched bars to assess the effects of differing heat-treatments of 4140 steel on the Charpy Impact Energy.



Geometry of Charpy impact test.

Figure 9: Charpy impact testing machine, and detail of three-point bending specimen and fixture, prior to impact.

The impact loading conditions are achieved by a swinging pendulum, see Figure 9.

1. The pendulum of standard mass is raised above the specimen; the pendulum height (and thus its potential energy) is recorded.
2. The pendulum is then released, the weight swings through and strikes the specimen in three-point bending; the (maximum) pendulum height after breaking the specimen is then recorded.
3. The difference between the initial and final potential energies of the pendulum mass is the energy “lost” in the process of breaking the specimen.

Note that this “loss” of energy represents a simple accounting that encompasses many phenomena, including

1. energy dissipated in the plastic deformation of the specimen,
2. the energy loss in driving the local fracture processes at the notch root,
3. frictional losses as the specimen slides over the supports,
4. kinetic energy acquired by the specimen,
5. acoustic energy lost (you can hear the impact), etc.

Nonetheless, provided standard-sized and -shaped specimens are used, the quantitative differences in impact energy provide important **qualitative** indicators of the expected relative toughness (or brittleness) of the material, in the metallurgical condition tested, during potential service in an engineering product at test temperature, under high loading rates, and in the presence of stress concentration.

Indeed, the Charpy impact test has long been used in both alloy development studies, as well as being incorporated into many materials test specifications.