Steel is the most important engineering material as it combines strength, ease of fabrication, and a wide range of properties along with relatively low cost. While some are soft and ductile, others can be hardened sufficiently to serve as tools for cutting steel into desired shapes. All steels are primarily alloys of iron and carbon. Plain carbon steels also have small amounts of manganese and silicon, in addition to unavoidable but limited amounts of phosphorus and sulfur. Alloy steels are those that contain specified percentages of other elements, such as nickel, chromium, molybdenum, vanadium and tungsten in their chemical compositions. Manganese also falls into this category when it is specified generally in excess of 1%. Although these alloying elements may be required in steel to achieve special characteristics, carbon is the principal ingredient since the amount present has a pronounced effect on the properties and the selection of suitable heat treatments to attain desired properties.

Because of the importance of carbon content, it is used as a basis for classifying plain carbon steels. When only a small amount of carbon is present, it is called low-carbon, or mild steel. They usually contain less than 0.30% carbon by weight. When the carbon content is between 0.30 and 0.60%, the steel is classified as medium-carbon steel. Steels containing over 0.60% carbon are high-carbon steels, and those with over 0.77% may be called tool steels. The upper carbon limit of steels is about 2%. When more than this amount of carbon is present, the alloy is usually known as cast iron.

A review of the iron-carbon system may be valuable in understanding the solid-state reactions in steel. The phase diagram shown below is plotted only for concentrations less than 6.67% carbon, the composition of Fe₃C, or cementite. The diagram is characterized by three invariant points: a peritectic point at 0.16%C and 2719°F (1493°C), a eutectic point at 4.3%C and 2097°F (1147°C), and a eutectoid point at 0.80%C and 1333°F (723°C). Phase transformations at the peritectic and eutectic points of the system are not essential in studying the behavior of steels during heat treatments. It is the eutectoid region of the phase diagram that is of interest in explaining the transformations and microstructures that form during the thermal cycles.
In steels the microstructural constituents have the names ferrite, pearlite, bainite, martensite, cementite and austenite. Ferrite is the common name for α-iron, which is present at room temperature. It is soft and would commonly be one of the prevalent structures in annealed steel. As the carbon content of steel is increased beyond the solubility limit (0.02% C) on the phase diagram, a constituent called pearlite forms. It is essentially a composite structure consisting of a very hard carbide phase, cementite, and a very soft and ductile ferrite phase. The properties of pearlitic steels are determined by the spacing between the ferrite-cementite lamellae (i.e. steels with coarse and fine pearlite structures). Bainite is also composite of ferrite and cementite, however, unlike pearlite, the ferrite has an acicular morphology and the carbides are discrete particles. Because of these morphological differences, bainite has much different property characteristics than pearlite. In general, bainitic steels have high strength coupled with good toughness, whereas pearlitic steels have high strength with poor toughness. Martensite is a non-equilibrium structure that is formed upon rapid cooling from austenite. It is essentially a supersaturated solid solution of carbon in iron. The amount of carbon in martensite far exceeds that found in ferrite. Because of this, the normal body-centered cubic (bcc) lattice structure is distorted in order to accommodate the carbon atoms. The distorted lattice becomes body-centered tetragonal (bct). Cementite is an intermetallic compound represented by the formula Fe3C, which is very hard and brittle. Austenite is the common name for γ-iron (containing some dissolved carbon), which is one of the solid phases of steel. It does not exist at room temperature in plain-carbon and low-alloy steels, other than as small amounts of retained austenite that did not transform during quenching. This is typically due to the martensite completion (Mₛ) temperature being at or below room temperature when the carbon content exceeds about 0.65 %. Austenite is the high temperature solid phase of steel where many of the heat treating processes require as the starting point from which to make their transformations.
Micrograph showing pearlite (dark) and ferrite (light) in a medium carbon steel

Micrograph showing martensitic structure

Micrograph showing martensite and bainite (feathery appearing structure)
The versatility of steel is attributable in large part to its response to a variety of thermal treatments. They fall into two general categories; 1) those which increase the strength, hardness and toughness by virtue of rapid cooling from above the transformation range, and 2) those which decrease hardness and promote uniformity by slow cooling from above the transformation range. The first category can involve through-hardening by quenching and tempering, or a variety of specialized hardening treatments to enhance hardness of the surface to a controlled depth (Induction hardening, carburizing, nitriding, etc.). The second category includes normalizing and various types of annealing to improve machinability, toughness, cold forming characteristics, or relieve stresses and restore ductility after certain processes.

The best combination of strength and toughness is usually obtained by suitably tempering a quenched microstructure consisting of a minimum of 80% martensite throughout the cross section. Steels of adequate hardenability attain this martensitic structure when liquid quenched from their austenitizing temperatures. Typically, most frequently used steels for quenched and tempered parts contain 0.30 to 0.60% carbon. The hardenability necessary to achieve the desired through hardening is a function of the chemical composition, section size and the quenching parameters. Plain carbon steels with low manganese content can be through-hardened only in very thin sections when a mild quench is used.

The below figures illustrate the structures that form and typical hardness levels that can be expected (in a 0.55% carbon steel) after various transformation processes.

Typical continuous cooling transformation curves showing resulting properties (Ms: martensite start, Mf: martensite finish)
The five main heat treating operations used to alter the structures and modify the properties of steel can be summarized as follows:

**Full Annealing**: is the process of softening steel by a heating and cooling cycle, so that it can be formed or machined easily. It consists of heating cycle above a transformation temperature, a holding period and a controlled slow cooling period (usually in the furnace) so that a coarse pearlitic structure is formed.

**Normalizing**: involves heating to a temperature above the upper critical temperature, followed by cooling in still air. The actual temperature required for this depends on the composition of the steel, but is usually around 1600°F (870°C). The uniformly fine-grained pearlitic structure that normally results enhances the uniformity of mechanical properties, and for certain grades, improves machinability. Notch toughness in particular is much better than that experienced in as-rolled condition. Normalizing is also frequently used as a conditioning treatment prior to quenching and tempering. The purpose is to homogenize the structure and facilitate austenitizing, and improve the steel's response to heat treatment, particularly in grades containing strong carbide-forming elements. Time and temperature play an important part in the austenitizing process. A coarse-grained structure and presence of certain alloying elements greatly increase the time and temperature required for complete solution and diffusion. If steel that has been heated into the austenite range above the upper critical temperature is heated to a higher temperature, no additional phase change occurs. However, the size of the grains increases, which has a marked effect upon the rate of transformation during cooling and, hence, upon the hardening characteristics of steel. The relation between the grain size and properties affected during transformation is listed in the table below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Austenitic Grain Size</th>
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<tbody>
<tr>
<td></td>
<td>Fine</td>
</tr>
<tr>
<td>Depth of hardening</td>
<td>Shallower</td>
</tr>
<tr>
<td>Retained austenite</td>
<td>Less</td>
</tr>
<tr>
<td>Warpage in quenching</td>
<td>Less</td>
</tr>
<tr>
<td>Depth of diffusion in carburizing</td>
<td>Shallower</td>
</tr>
</tbody>
</table>
Hardening: is carried out by quenching, that is cooling it rapidly from a temperature above the transformation temperature. Chemical composition of the steel is the principal factor governing the temperature to which the steel must be heated. For hardening, it is common practice to hold the steel at the desired temperature for 15 minutes per inch of thickness. Holding times are longer for forgings and castings. Steel is then quenched in water or brine for the most rapid cooling, in oil for some alloy steels, and in air for certain higher alloy steels. During quenching austenite transforms to martensite. There are two basic dimensional changes that occur during this phase transformation; one due to the normal thermal contraction from cooling, and the other due to expansion of the metal since there is volume increase associated with the austenite to martensite transformation (approximately 4.3% for a 1% carbon steel). These volumetric changes can produce very high internal stresses leading to quench cracks. In as-quenched condition, the steel is usually very hard and brittle. To regain its ductility, the steel must be tempered.

The mechanical properties obtained in a quenched part are primarily dependent upon the hardenability of the steel as determined by its chemical composition and by the rate at which it is cooled from the austenitizing temperature. Hardenability is a term used to designate that property of steel, which determines the depth, and distribution of a hardness induced by quenching from the austenitizing temperature. Whereas the as-quenched surface hardness is dependent primarily on the carbon content and cooling rate, the depth to which a certain hardness level is maintained with given quenching conditions is a function of its hardenability. Hardenability is largely determined by the percentage of alloying elements present in the steel. Austenite grain size, time and temperature during austenitizing, and prior microstructure also can have significant effects.

A part with a specific mass will cool at a rate determined by its temperature in relation to that of the quenching medium, by the characteristics of that medium, and by the quenching conditions used. Furthermore, the cooling rate developed in a particular facility will depend on the volume of the medium as well as its temperature, specific heat, viscosity, and degree of agitation. Careful selection of quenching medium is essential. Use of a drastic quench may make it possible to develop a given set of properties in a steel however, size and design of the part or the steel composition may be such that the drastic quench will cause quench cracks or severe distortion. Under these conditions, overall economy will be best served by using a quenchant with less cooling capacity and a steel of greater hardenability.

The most common quenching media are water and various mineral oils. In most facilities, water is maintained at a temperature of about 65°F (18°C). As the water temperature increases, or as the amount of agitation during quenching decreases, there is an increasing tendency for an envelope of steam to form around the part. Because this envelope interferes with the flow of water around the part, it reduces the cooling capacity. A brine of 5 to 10% sodium chloride has a lower tendency than plain water to form an envelope, and therefore provides a more effective quench.

Quenching oils providing a wide variety of cooling rates are available. These are characterized by relative stability and chemical inactivity with respect to hot steel, high flash point, and little change in cooling capacity with normal variation in temperature. Regardless of the quenching medium used, it is of utmost importance to temper parts immediately after the quenching operation. Delay in tempering greatly increases the risk of cracking since the part is in a highly stressed condition.

Tempering: sometimes referred to as drawing, consists of reheating a quenched steel to a suitable temperature below the transformation temperature, holding it at temperature for an appropriate time and cooling back to room temperature. Most steels are tempered between 400 and 1100°F (205 and 595°C). As higher temperatures are employed, toughness or shock resistance is increased but the hardness and strength decrease (see below chart). Since freshly quenched martensite is very brittle, tempering is needed to impart ductility to the martensite, usually at a small sacrifice in strength. Microstructural changes accompanying tempering include loss of acicular martensite pattern and the precipitation of tiny carbide particles. The microstructure of quenched and tempered steel is referred to as tempered martensite.
Hardness versus tempering temperature graph for 1050 carbon steel. Note also the effect of chemical composition on the hardness levels achieved after quenching, and upon tempering.

**Stress Relieving:** is the heating of steel to a temperature below the transformation temperature (typically around 1100°F (595°C), as in tempering, but is done primarily to relieve internal stress and thus prevent distortion or cracking during machining or further processing. This operation is sometimes called process annealing.

**Surface protection during heat treating:** when steel is heated in an open furnace in the presence of air and products of combustion, two surface reactions may occur; 1) oxidation, and 2) decarburization. Oxidation of steel is caused by oxygen, carbon dioxide, and/or water vapor and may range from a tight, adherent straw-colored film that forms at a temperature of about 350°F (180°C) to a loose, blue-black oxide scale that forms at a temperature above about 800°F (425°C) with resultant loss of metal. Decarburization or reduction of surface carbon content occurs upon heating steel to temperatures above about 1200°F (650°C) and progresses to greater depths below the surface as a function of time, temperature, and furnace atmosphere.

The problem of oxidation and surface decarburization of steel parts with resultant loss of dimension and lowered surface hardness and strength may be prevented or minimized in several ways:

- Use of protective furnace atmosphere
- Use of vacuum furnaces
- Removal of decarburized surface by machining operations after heat treating
- Application of proprietary stop-off paint or coating before treatment
- Heating parts in a sealed steel box or pot packed in cast iron chips