The Time-Temperature-Transformation Curve

In this installment of his ‘Back to Basics’ series, the author discusses two new microstructural phases – martensite and bainite.

In the previous column, we discussed the formation of the Iron-Carbon phase diagram. This diagram allowed us to estimate the microstructure under non-equilibrium conditions. In this column, we build on those concepts and discuss the Isothermal Transformation or Time-Temperature-Transformation curves. These curves are very important to start predicting the microstructure for a given alloy.

Transformations of austenite are dependent on the cooling rate. Slow cooling will result in pearlite and ferrite. Fast reactions will result in martensite transformation. However, if the quench rate is too fast, then high residual stress and distortion may occur. This is illustrated in Figure 1.

In this column, we introduce two new microstructural phases: martensite and bainite.

MARTENSITE

Martensite is the name used to designate the hard phase in quenched carbon and alloy steel. Martensite was named after Adolf Martens by Floris Osmond in 1898 [1]. In iron-carbon alloys, austenite transforms to martensite on rapid cooling. It is a non-equilibrium structure. It is a diffusionless transformation. Because of the rapid cooling, diffusion is suppressed and carbon does not partition between ferrite and austenite. The composition of martensite is exactly the same as the parent austenite. Martensite forms a Body-Centered Tetragonal structure (Figure 2).

This is essentially a Body-Centered Cubic structure that has been stretched along a diagonal between two opposite corners of the BCC structure. As the carbon level of the martensite is increased, the stretch of the tetragonal axis also increases. This stretch results in the volume expansion of the steel on fast quenching. As the carbon content is increased, the volume expansion also increases. This volume expansion is the major cause of distortion and warpage in steel parts. If the volume expansion is too large, or occurs at a stress concentration, cracking can occur.

The conversion of austenite to martensite takes place continuously while cooling. The mode of transformation is called athermal transformation (meaning without thermal activation). Martensite transformation starts to transform at the martensite transformation temperature, Ms, and ceases on reaching a given temperature. Only additional cooling can drive the transformation further. The martensite start transformation temperature, Ms, decreases with increasing carbon content, and can be changed with different alloying elements. The martensite finish temperature, Mf, is also a function of carbon content and alloying elements. For most steels above 0.30 percent carbon, the Mf temperature is above room temperature. This can cause significant amounts of retained austenite (austenite present at room temperature) to form. This retained austenite can transform to martensite upon application of lower temperatures, or by sudden shocks. This can contribute to cracking before tempering.

BAINITE

During the late 1920s, during studies of isothermal transformation of austenite, at temperatures above martensite formation, but below martensite transformation, Davenport and Bain [2] discovered a microstructure that etched differently than martensite or pearlite. This microstructure was named Bainite in honor of E.C. Bain.

This microstructure was unique in that it formed under continuous cooling or under isothermal conditions, with a structure that was similar to both martensite and bainite. Pearlite contains a mixture of ferrite and iron carbide, and is diffusion controlled. Martensite is non-lamellar and not diffu-
modern applications, the austenitized part is quenched to transform the austenite to martensite, or occasionally bainite. This is process controlled. Bainite showed both the characteristics of pearlite and martensite, depending on the temperature of formation. Two different morphologies of bainite were observed: upper bainite that formed just below pearlite, and lower bainite which forms at just above the M_s Temperature. It has a similar appearance to tempered martensite, with a feathery appearance (Figure 3). It is very similar to tempered martensite in terms of hardness and toughness. Because of the difficulty in controlling the formation of bainite, it generally has limited applicability, with the exception of austempering. This is a process using molten salts where bainite is formed on isothermal holding at approximately 325°C (620°F). This process is used when a hard and tough structure is needed, in thin sections. Figure 4 shows the morphology of bainite compared to martensite.

To achieve the desired high hardness and strength required for modern applications, the austenitized part is quenched to transform the austenite to martensite, or occasionally bainite. This is usually done by immersion of the part into a liquid such as oil. The steel is rapidly cooled to the temperature of the quenching medium. The quenching medium used depends on the alloy used; the part geometry; and the required strength.

Regardless of the quench medium used, the purpose of quenching is to transform the austenite to martensite, and to avoid the formation of the softer microstructures of ferrite and pearlite. The rate of cooling necessary to harden the part is called the critical cooling rate. It is the minimum cooling rate that will achieve the maximum hardness. If the part is cooled at higher rates than the critical cooling rate, no additional hardness will be achieved, but may cause excessive distortion and possibly cracking. Cooling at slower rates than the critical cooling rate will cause the austenite present to transform into bainite, ferrite and pearlite. This mixed microstructure will lower the hardness of the steel and reduce the toughness of the part.

**ISOTHERMAL TRANSFORMATION OR TIME-TEMPERATURE-TRANSFORMATION CURVES**

When steel is austenitized, and then held at a constant temperature below the austenite region (A_s), it will transform to some transformation product like pearlite or bainite. There is an incubation time for nucleation, followed by nucleation and growth. Finally, the reaction will complete, and transformation will end. The course of this transformation can be understood by plotting the amount of austenite transformed against the corresponding elapsed time at constant temperature.

For a given steel, the information given by a series of such curves, each curve determined at a different temperature, can be summarized by a single diagram called a Time-Temperature-Transformation (TTT) curve. This is shown in Figure 5. This diagram shows the time, at a particular temperature, to start to transform and finish transforming to a transformation product such as ferrite, pearlite or bainite. This diagram can be thought of as a map which plots the transformations of austenite as a function of constant temperature and time. This allows estimates to be made regarding how the steel will respond to any mode of cooling from austenite.
Diagrams that describe the transformation of austenite as a function of constant temperature are called Time-Temperature Transformation diagrams. These diagrams are created empirically by taking hundreds of very thin samples and austenitizing the samples. These samples are then quenched into a medium (usually molten salt) at specific temperatures of interest. The samples are individually held isothermally at the desired temperature for various lengths of time. The samples are then quenched in water. Once cool, the samples are metallographically examined and the volume fractions of the microstructure constituents are determined. The results are plotted on a graph showing the progression of transformation as a function of time and temperature.

The TTT diagram is really a simplified diagram of the kinetics of pearlite and bainite formation, and the diffusion-less transformation of martensite. It is a diagram of overlapping curves (Figure 6).

The shape and position of the curves depend on the alloy composition, grain size, and carbon content. Increasing the carbon content tends to retard transformation, pushing the curve to the right. Alloying additions also tend to retard transformation because of a decreased diffusion of carbon in the presence of alloying elements. This also tends to push the curve to the right. Increasing grain size also retards transformation. The combination of chemical composition, grain size, and rate of nucleation results in a greater hardenability, or the ability to harden deeper — not get harder. Comparison of the effect of carbon on the Time-Temperature Transformation diagram is shown in Figure 7. The effect of alloying on the shape of the TTT diagram is shown in Figure 8.

These curves are widely available from many sources [3], and permits estimates of expected microstructures for specific times and temperature. TTT diagrams cover isothermal transformations. As such they are useful for planning heat treatment cycles, however, they cannot be used to accurately predict the course of transformation upon cooling.

There are limitations to the use of TTT diagrams. Heat treating operations are not carried out using isothermal process, but using continuous cooling. As a result, the TTT curves representing the transformation of austenite are not strictly applicable to heat treating operations. The diagrams provide an estimate, but do not provide absolutely accurate microstructure information.

Each diagram is based on a single sample of the alloy. Allowable alloying element variations can result in different results, with the published diagrams based on an average composition. This is particularly true of low-alloy steels with high levels of tramp elements. This is also true of alloys from different countries. In traditional steel making countries, there is a considerable amount of scrap steel that is recycled. This scrap steel comes from many sources, and may contain steels with high values of alloying elements.

This can result in a low alloy steel with small amounts of chromium, molybdenum, or vanadium which can strongly influence the low hardenability of lean alloy steels. Developing countries do not have the large amounts of scrap, and thus create steels that are more like the steels originally developed many years ago, without the influence of trace amounts of alloying elements that increase hardenability.

Many steels are not affected by changes in austenitizing times and temperatures. However, if the steel contains large amounts of carbide-forming elements (chromium, molybdenum, or vanadium), then the effect of temperature may be significant. Increasing the austenitizing temperature increases the amount of carbide in solution. This changes the composition of the austenite, which then results in changes in the decomposition of austenite during cooling. Changing the austenitizing time may also modify the transformation behavior, but this effect is much less.

Knowing these limitations, the use of isothermal Time-Temperature-Transformation curves can be a great aid in planning and controlling the heat treatment of steel.

Should you have any questions regarding this column, or have any suggestions for further columns, please contact the author.

Figure 7: Comparison of the effect of carbon on the TTT curves of plain carbon steel. Left is SAE 1020 steel. Right is SAE 1080 steel. Carbon pushes the nose (or knee) of the TTT curve to the right, retarding kinetics [3].
REFERENCES


ABOUT THE AUTHOR

D. Scott MacKenzie, Ph.D., FASM, is senior research scientist-metallurgy at Houghton International Inc. He is also president of the International Federation of Heat Treatment and Surface Engineering. He can be reached at smackenzie@houghtonintl.com. Go online to www.houghtonintl.com.