2.

TTA / TTT - Diagrams
An essential feature of low alloyed ferrous materials is the crystallographic transformation of the body-centred cubic lattice which is stable at room temperature (\(\alpha\)-iron, ferritic structure) to the face-centred cubic lattice (\(\gamma\)-iron, austenitic structure), Figure 2.1. The temperature, where this transformation occurs, is not constant but depends on factors like alloy content, crystalline structure, tensional status, heating and cooling rate, dwell times, etc..

In order to be able to understand the basic processes it is necessary to have a look at the basic processes occuring in an idealized binary system. Figure 2.2 shows the state of a binary system with complete solubility in the liquid and solid state.

If the melting of the L\(_1\) alloy is cooling down, the first crystals of the composition c\(_1\) are formed with reaching the temperature T\(_1\). These crystals are depicted as mixed crystal \(\alpha\), since they consist of a compound of the components A (80\%) and of B (20\%). Further, a melting with the composition c\(_0\) is present at the temperature T\(_1\). With dropping temperature, the remaining melt is en-
riched with component B, following the course of line Li (liquidus line, up to point 4). In parallel, always new and B richer \( \alpha \)-mixed crystals are forming along the connection line So (solidus line, points 1, 2, 5). The distribution of the components A and B in the solidified structure is homogeneous since concentration differences of the precipitated mixed crystals are balanced by diffusion processes.

The other basic case of complete solubility of two components in the liquid state and of complete insolubility in the solid state shows Figure 2.3. If two components are completely insoluble in the solid state, no mixed crystal will be formed of A and B. The two liquidus lines Li cut in point e which is also designated as the eutectic point. The isotherm \( T_e \) is the eutectic line.

If an alloy of free composition solidifies according to Figure 2.3, the eutectic line must be cut. This is the temperature \( T_e \) of the eutectic transformation:

\[
S \rightarrow A + B \quad (T = T_e = \text{const.})
\]

This means that the melt at a constant temperature \( T_e \) dissociates in A and B. If an alloy of the composition \( L_2 \) solidifies, a purely eutectic structure results. On account of the eutectic reaction, the temperature of the alloy remains constant up to the completed transformation (critical point) (Figure 2.2).

Eutectic structures are normally fine-grained and show a characteristic orientation between the constituents. The alloy \( L_1 \) will consist of a compound of alloy A and eutectic alloy E in the solid state.

You can find further information on transformation behaviour in relevant specialist literature.

The definite use of the principles occurs in the iron-iron carbide diagram. Transformation behaviour of carbon containing iron in the equilibrium condition is described by the
stable phase diagram iron-graphite (Fe-C). In addition to the stable system Fe-C which is specific for an equilibrium-close cooling, there is a metastable phase diagram iron cementite (Fe-Fe$_3$C). During a slow cooling, carbon precipitates as graphite in accord with the stable system Fe-C, while during accelerated cooling, what corresponds to technical conditions, carbon precipitates as cementite in agreement with the metastable system (Fe-Fe$_3$C). Per definition, iron carbide is designated as a structure constituent with cementite although its stoichiometric composition is identical (Fe$_3$C). By definition, cementite and graphite can be present in steel together or the cementite can decompose to iron and graphite during heat treatment of carbon rich alloys. However, it is fundamentally valid that the formation of cementite is encouraged with increasing cooling rate and decreasing carbon content. In a double diagram, the stable system is shown by a dashed, the metastable by a solid line, Figure 2.4.

The metastable phase diagram is limited by the formation of cementite with a carbon content of 6.67 mass%. The strict stoichiometry of the formed carbide phase can be read off at the top X-coordinate of the molar carbon content. In accordance with the carbon content of Fe$_3$C, cementite is formed at a molar content of 25%. The solid solutions in the phase fields are designated by Greek characters. According to convention, the transition points of pure iron are marked with the character A - arrêt (stop point) and distinguished by subjacent indexes. If the transition points are determined by cooling curves, the character r = refroidissement is additionally used. Heat-up curves get the supplement c - chauffage. Important transition points of the commercially more important metastable phase diagram are:

- 1536 °C: solidification temperature (melting point) δ-iron,
- 1392 °C: A$_4$- point γ- iron,
- 911 °C: A$_3$- point non-magnetic α- iron, with carbon containing iron:
- 723 °C: A$_1$- point (perlite point).
The corners of the phase fields are designated by continuous roman capital letters.

As mentioned before, the system iron-iron carbide is a more important phase diagram for technical use and also for welding techniques. The binary system iron-graphite can be stabilized by an addition of silicon so that a precipitation of graphite also occurs with increased solidification velocity. Especially iron cast materials solidify due to their increased silicon contents according to the stable system. In the following, the most important terms and transformations should be explained more closely as a case of the metastable system.

The transformation mechanisms explained in the previous sections can be found in the binary system iron-iron carbide almost without exception. There is an eutectic transformation in point C, a peritectic one in point I, and an eutectoidic transformation in point S. With a temperature of 1147 °C and a carbon concentration of 4.3 mass%, the eutectic phase called Le-deburite precipitates from cementite with 6.67% C and saturated γ-solid solutions with 2.06% C. Alloys with less than 4.3 mass% C coming from primary austenite and Le-deburite are called hypoeutectic, with more than 4.3 mass% C coming from primary austenite and Le-deburite are called hypereutectic.

If an alloy solidifies with less than 0.51 mass percent of carbon, a δ-solid solution is formed below the solidus line A-B (δ-ferrite). In accordance with the peritectic transformation at 1493 °C, melt (0.51% C) and δ-ferrite (0.10% C) decompose to a γ-solid solution (austenite).

The transformation of the γ-solid solution takes place at lower temperatures. From γ-iron with C-contents below 0.8% (hypoeutectoidic alloys), a low-carbon α-iron (pre-eutectoidic ferrite) and a fine-lamellar solid solution (perlite) precipitate with falling temperature, which consists of α-solid solution and cementite. With carbon contents above 0.8% (hypereutectoidic alloys) secondary cementite and perlite are formed out of austenite. Below 723 °C, tertiary cementite precipitates out of the α-iron because of falling carbon solubility.
The most important distinguished feature of the three described phases is their lattice structure. $\alpha$- and $\delta$-phases are cubic body-centered (CBC lattice) and $\gamma$-phase is cubic face-centered (CFC lattice), Figure 2.1.

Different carbon solubility of solid solutions also results from lattice structures. The three above mentioned phases dissolve carbon interstitially, i.e. carbon is embedded between the iron atoms. Therefore, this types of solid solutions are also named interstitial solid solution. Although the cubic face-centred lattice of austenite has a higher packing density than the cubic body-centred lattice, the void is bigger to disperse the carbon atom. Hence, an about 100 times higher carbon solubility of austenite (max. 2.06% C) in comparison with the ferritic phase (max. 0.02% C for $\alpha$-iron) is the result. However, diffusion speed in $\gamma$-iron is always at least 100 times slower than in $\alpha$-iron because of the tighter packing of the $\gamma$-lattice.

Although $\alpha$- and $\delta$-iron show the same lattice structure and properties, there is also a difference between these phases. While $\gamma$-iron develops of a direct decomposition of the melt ($S \rightarrow \delta$), $\alpha$-iron forms in the solid phase through an eutectoid transformation of austenite ($\gamma \rightarrow \alpha + Fe_3C$). For the transformation of non- and low-alloyed steels, is the transformation of $\delta$-ferrite of lower importance, although this $\delta$-phase has a special importance for weldability of high alloyed steels.

Unalloyed steels used in industry are multi-component systems of iron and carbon with alloying elements as manganese, chromium, nickel and silicon. Principally the equilibrium diagram Fe-C applies also to such multi-component systems. Figure 2.5 shows a schematic cut through the three phase system Fe-M-C.

During precipitation, mixed carbides of the general composition $M_3C$ develop. In contrast to the binary system Fe-C, is the three
phase system Fe-M-C characterised by a temperature interval in the three-phase field $\alpha + \gamma + M_3C$. The beginning of the transformation of $\alpha + M_3C$ to $\gamma$ is marked by $A_{clb}$, the end by $A_{cle}$. The indices b and e mean the beginning and the end of transformation. The described equilibrium diagrams apply only to low heating and cooling rates. However, higher heating and cooling rates are present during welding, consequently other structure types develop in the heat affected zone (HAZ) and in the weld metal. The structure transformations during heating and cooling are described by transformation diagrams, where a temperature change is not carried out close to the equilibrium, but at different heating and/or cooling rates.

A representation of the transformation processes during isothermal austenitizing shows Figure 2.6. This figure must be read exclusively along the time axis! It can be recognised that several transformations during isothermal austenitizing occur with e.g. 800°C. Inhomogeneous austenite means both, low carbon containing austenite is formed in areas, where ferrite was present before transformation, and carbon-rich austenite is formed in areas during transformation, where carbon was present before transformation. During sufficiently long annealing times, the concentration differences are balanced by diffusion, the border to a ho-
mogeneous austenite is passed. A growing of the austenite grain size (to ASTM and/or in μm) can here simultaneously be observed with longer annealing times.

The influence of heating rate on austenitizing is shown in Figure 2.7. This diagram must only be read along the sloping lines of the same heating rate. For better readability, a time pattern was added to the pattern of the heating curves. To elucidate the grain coarsening during austenitizing, two microstructure photographs are shown, both with different grain size classes to ASTM.

Figure 2.8 shows the relation between the TTA and the Fe-C diagram. It’s obvious that the Fe-C diagram is only valid for infinite long dwell times and that the TTA diagram applies only for one individual alloy.

Figure 2.9 shows the different time-temperature passes during austenitizing and subsequent cooling down. The heating period is composed of a continuous and an isothermal section.

During cooling down, two different ways of heat control can be distinguished:
1. : During **continuous temperature control** a cooling is carried out with a constant cooling rate out of
the area of the homogeneous and stable austenite down to room temperature.

2. During **isothermal temperature control** a quenching out of the area of the austenite is carried out into the area of the metastable austenite (and/or into the area of martensite), followed by an isothermal holding until all transformation processes are completed. After transformation will be cooled down to room temperature.

Figure 2.10 shows the time-temperature diagram of an isothermal transformation of the mild steel Ck 45. Read such diagrams only along the time-axis! Below the Ac1b line in this figure, there is the area of the metastable austenite, marked with an A. The areas marked with F, P, B, and M represent areas where ferrite, perlite, Bainite and martensite are formed. The lines which limit the area to the left mark the beginning of the formation of the respective structure. The lines which limit the area to the right mark the completion of the formation of the respective structure. Because the ferrite formation is followed by the perlite formation, the completion of the ferrite formation is not determined, but the start of the perlite formation. Transformations to ferrite and perlite, which are diffusion controlled, take place with elevated temperatures, as diffusion is easier. Such structures have a lower hardness and strength, but an increased toughness.

Diffusion is impeded under lower temperature, resulting in formation of bainitic and martensitic structures with hardness and strength values which are much higher than those of ferrite and perlite. The proportion of the formed martensite does not depend on time. During quenching to holding temperature, the corresponding share of martensite is spontaneously formed. The present rest austenite transforms to Bainite with sufficient holding time. The right
2. TTA / TTT – Diagrams

detail of the figure shows the present structure components after completed transformation and the resulting hardness at room temperature.

Figure 2.11 depicts the graphic representation of the TTT diagram, which is more important for welding techniques. This is the TTT diagram for continuous cooling of the steel Ck 15. The diagram must be read along the drawn cooling passes. The lines, which are limiting the individual areas, also depict the beginning and the end of the respective transformation. Close to the cooling curves, the amount of the formed structure is indicated in per cent, at the end of each curve, there is the hardness value of the structure at room temperature.

Figure 2.12 shows the TTT diagram of an alloyed steel containing approximately the same content of carbon as the steel Ck 15. Here you can see that all transformation processes are strongly postponed in relation to the mild steel. A completely martensitic transformation is carried out up to a cooling time of about 1.5 seconds, compared with 0.4 seconds of Ck 15. In addition, the completely diffusion controlled transformation processes of the perlite area are postponed to clearly longer times.

The hypereutectoid steel C 100 behaves completely different, Figure 2.13. With this carbon content, a pre-
eutectoid ferrite formation cannot still be carried out (see also Figure 2.3).

The term of the figures 2.9 to 2.11 "austenitizing temperature" means the temperature, where the workpiece transforms to an austenitic microstructure in the course of a heat treatment. Don’t mix up this temperature with the $A_{CS}$ temperature, where above it there is only pure austenite. In addition you can see that only martensite is formed from the austenite, provided that the cooling rate is sufficiently high, a formation of any other microstructure is completely depressed. With this type of transformation, the steel gains the highest hardness and strength, but loses its toughness, it embrittles. The slowest cooling rate where such a transformation happens, is called critical cooling rate.
Figure 2.14 shows schematically how the TTT diagram is modified by the chemical composition of the steel.

The influence of an increased austenitizing temperature on transformation behaviour shows Figure 2.15. Due to the higher hardening temperature, the grain size of the austenite is higher (see Figure 2.6 and 2.7).

This grain growth leads to an extension of the diffusion lengths which must be passed during the transformation. As a result, the "noses" in the TTT diagram are shifted to longer times. The lower part of the figure shows the proportion of formed martensite and Bainite depending on cooling time. You can see that with higher austenitizing temperature the start of Bainite formation together with the drop of the martensite proportion is clearly shifted to longer times.

As Bainite formation is not so much impeded by the coarse austenite grain as with the completely diffusion controlled processes of ferrite and perlite formation, the maximum Bainite proportion is increased from about 45 to 75%.
Due to the strong influence of the austenitizing temperature to the transformation behaviour of steel, the welding technique uses special diagrams, the so called Welding-TTT-diagrams.

They are recorded following the welding temperature cycle with both, higher austenitizing temperatures (basically between 950 °C and 1350 °C) and shorter austenitizing times. You find two examples in Figures 2.16 and 2.17.

Figure 2.18 proves that the iron-carbon diagram was developed as an equilibrium diagram for infinite long cooling time and that a TTT diagram applies always only for one alloy.