TUBITAK Academy Lecturer: Kamran Khodaparasti kkhodaparasti@yahoo.com

International Welding Engineer (IWE)

Module 2: Materials and Their Behavior During Welding 2.4 - Alloys and Phase Diagrams

March 2013- Tehran

References

- \mathbf{r} References:
	- R. E. Smallman, R.J. Bishop, Modern Physical Metallurgy and Materials Engineering ‐ science, process, applications, Sixth edition,1999
	- × ASM HANDBOOKVol.03 (tenth ed.) – Alloy Phase Diagrams
	- ASM Steel‐Metallurgy‐for‐Non‐Metallurgist, ²⁰⁰⁷
	- **College SLV Software**
	- \mathbf{r} Internet documents

2.4 Alloys and Phase Diagrams

Objective:

Understand (in detail)/describe the principles of alloying, the structures of alloys and their representation in phase diagrams.

Scope:

- •Pure metals and alloys
- \bullet Alloying elements
- •**Solidification**
- •Solid solution crystals
- •Structure of alloys
- •Type of structures
- • Hardening mechanisms (cold working, solid solution, dispersion hardening, grain size control, solid state transformation)
- •Intermetallic compounds
- •Ageing
- • Basic types of phase diagrams (non-, fully- and partly soluble components)
- •Fe-C equilibrium diagram
- •Influence of elements on Fe-C diagram
- • Iron-alloys with closed gamma-loop with broadened gamma-area
- •Casting structure
- \bullet Segregation and Coring
- •Mechanical properties
- •Ternary diagrams

Expected Result

- • Describe crystalline lattice distortion due to alloying elements and subsequent structural changes.
- • Explain in detail solidification structure and segregation with relevant examples.
- • Detail mechanisms of precipitation, types of precipitate and their location within the microstructure.
- \bullet Explain in detail the principles of transformation and conditions under which it occurs.
- • Detail the principles of strengthening mechanisms with appropriate examples.
- • Interpret the relationship between microstructure and mechanical properties.
- • Explain in detail the principles of phase diagrams, their construction and use.
- • Interpret the relationship between microstructure and phase diagrams.

Ask a Favor

Alloys

- Also called solid solutions
	- Number of metals dissolve in each other forming solid solutions
- \bullet Mixing of the elements in the solid state in the atomic scale

Alloys (Cont'd)

- Solute atom if much smaller than solvent atom occupies a void space in the parent structure – interstitial alloy is formed - In FCC iron, carbon is an interstitial solute – occupies octahedral voids in the FCC structureFe1.24Å ; C 0.71Å
- If solute & solvent atoms are of comparable sizes solutes occupy solvent positions on regular atomic sites (substitution) ^α-brass – 70% Cu & 30% Zn – FCC – Cu & Zn atoms randomly occupy the atomic sites

Examples

Substitutional alloy

FCC iron 1.24Å; C 0.71Å

Interstitial alloy

Hume Rothery rules & Substitutional Solid Solutions

- \bullet Two metals dissolve extensively when (i) solute & solvent atoms do not differ by more than 15% in diameter(ii) electronegativity differences between the elements must be small
- •Valency & crystal structure of the elements are the same

Examples

- • Ag-Au, Cu-Ni and Ge-Si satisfy the Hume-Rothery conditions very well – hence, form complete solid solutions – i.e. two elements mix in each other in all proportions
- • Starting from pure Ag, the Ag atoms can be continuously replaced by gold atoms in the FCC structure till pure gold is obtained

Alloys (cont'd)

- \bullet Cu – Zn: complete replacement is not possible because Cu is FCC and Zn is HCPForm solid solutions only up to certain extent only
- • At room temperature, up to 35% of Zn can be dissolved in the FCC crystal of Cu because Hume – Rothery conditions are only partially satisfied.
- \bullet But only about 1% of Cu dissolves in the HCP structure of Zn
- • Reason: When Zn dissolves in Cu, an excess of bonding electrons is available($Zn-4s^2$; Cu-4s¹) which is easily accommodated; when Cu dissolves in Zn, deficiency of e- less easily accommodated

Intermetallic Compound

- \bullet 50Cu and 50Zn alloy is an intermediate structure – crystal structure is BCC – different from that of Cu (FCC) and Zn (HCP)
- \bullet If an intermediate structure exists only at a fixed composition, it is called an intermediate compound (e.g. Iron carbide, $Fe₃C$)

Phase (Cont'd)

Component (C)

- \bullet Independent chemical species that comprise the system
- •Oil and water – 2 components
- •Water + alcohol – 2 components

International Welding Engineer | 2.4 - Alloys and Phase Diagrams | Kamran Khodaparasti | 17

2 Phases

Cooling Curve

Phase Diagram

International Welding Engineer | 2.4 - Alloys and Phase Diagrams | Kamran Khodaparasti |

Phase Diagram (Cont'd)

Tie Line

1. A tie line is constructed across the two-phase region at the temperature of the alloy.

2. The intersections of the tie line and the phase boundaries on either side are noted.

3. Perpendiculars are dropped from these intersections to the horizontal composition axis, from which the composition of each of the respective phases is read.

Determination of Phase Compositions

Consider the 35 wt% Ni–65 wt% Cu alloy at 1250C, located at point *B* in • Figure and lying within the ^α ⁺*L* region. Thus, the problem is to determine the composition (in wt% Ni and Cu) for both the α and liquid phases. The tie line has been constructed across the ^α ⁺*L* phase region. The perpendicular from the intersection of the tie line with the liquidus boundary meets the composition axis at 31.5 wt% Ni–68.5 wt% Cu, which is the composition of the liquid phase, $C_{\scriptstyle\! L}$. Likewise, for the solidus–tie line intersection, we find a composition for the solidsolution phase, *C^α* , of 42.5 wt% Ni–57.5 wt% Cu.

Determination of Phase Amounts

- •A procedure that is often called the lever rule
- •Consider again the example, in which at 1250C both α and liquid phases are present for a 35 wt% Ni–65 wt% Cu alloy. The problem is to compute the fraction of each of the α and liquid phases. The tie line has been constructed that was used for the determination of α and *L* phase compositions. Let the overall alloy composition be located along the tie line and denoted as *C*0 , and mass fractions be represented by *WL* and *W^α* for the respective phases. From the lever rule:

$$
W_L = \frac{S}{R+S}
$$
 or, b

y subtracting compositions,

$$
W_L = \frac{C_{\alpha} - C_0}{C_{\alpha} - C_L}
$$

$$
W_L = \frac{42.5 - 35}{42.5 - 31.5} = 0.68
$$

$$
W_{\alpha} = \frac{R}{R+S} \left\| \frac{C_0 - C_L}{C_{\alpha} - C_L} \right\| = \frac{35 - 31.5}{42.5 - 31.5} = 0.32
$$

Eutectoid System

- • Eutectoid involves a solid-solid reaction or represents equilibrium of a system whose components are subjected to allotropic transformation
- •Indicates the decomposition of a solid solution into two other solid phases
- \bullet Peritectic and eutectic are liquid-solid transformations
- •Eutectoid reaction is of the form

Peritectic

Degrees of Freedom (F)

- •It is the number of independent variables
- Gibbs phase rule(1876)
- P+ F = C + E → T & P ---- E = 2
- Pure metal at solidification temperature; C = 1, P = 2 (solid & liquid); reduced phase rule is applied because the vapor of solid is negligible and hence, only T is considered
- F = 1 $-$ 2 + 1 = 0; i.e., invariant or non-variant system

Cont'd

- Alloy of two metals at solidification;
- C = 2, P = 2; F = 2-2+1=1; univariant system;
- \bullet Molten liquid of two metals: C=2;P=1

 $F=2-1+1=2$; bivariant system

Meaning:

F=0, neither P nor T can be varied

F=1, either P or T can be varied

F=2, both P and T can be varied independently within the region

Single Component System (Fe system)

Cont'd

- • The equilibrium crystal form of iron at ambient temperature and pressure is BCC (α-form)
- •On heating to 910^oc, α-form changes over to the FCC (γ) form
- •On heating to 1410^oc, the γ-iron changes over to the BCC (δ) form
- •As the pressure is increased, the α y transition temperature is lowered, whereas the $γ$ $δ$ transition temperature is increased.
- • When a pressure of 15GPa (~150 000 atm) is applied, at room temperature, BCC iron transforms into HCP(ε) phase

Fe-C System

Fe-C Diagram

Microstructure

Microstructure of Steels

Five main constituents:

- •Ferrite
- •Austenite
- •**Cementite**
- •Pearlite
- •**Martensite**

Microstructure of Steels (Cont'd)

Ferrite

Has a body-centred cubic (BCC) crystal structure.It is soft and ductile and imparts these properties to the steel. Often known as α iron.

Austenite

This is the structure of iron at high temperatures (over 912 deg C). Has a face-centre cubic (FCC) crystal structure. Often known as γ iron. Non magnetic

Cementite

A compound of iron and carbon, iron carbide (Fe3C).

Carbon-riched phase It is hard and brittle and its presence in steels causes an increase in hardness and a reduction in ductility and toughness.

Pearlite

Pearlite: Transformation product of austenite to ferrite+cementite under slow cooling rate

Pearlite (Cont'd)

Pearlite (Cont'd)

Pearlite (Cont'd)

Eutectoid Reaction (Pearlite Formation)

•Austenite precipitates **Fe₃C** at Eutectoid Transformation Temperature (727°C).

$$
\gamma \xrightarrow{\text{Cooling}} \alpha + Fe_3C
$$

Heating

• When cooled slowly, forms Pearlite, which is a microcontituent made of ferrite (α) and Cementite (**Fe₃C**), looks like Mother of Pearl.

Hypo-Eutectoid

Microstructure of Hypo-Eutectoid

Hyper-Eutectoid

Microstructure of Hyper-Eutectoid

Martensite

A very hard needle-like structure of iron and carbon.

Only formed by very rapid cooling from the austenitic structure (i.e. above upper critical temperature).

Needs to be modified by tempering before acceptable properties reached.

Increasing the carbon content decreases the amount of ferrite and increases the proportion of pearlite in the structure.

Three plain carbons steels, from left to right: 1018, 1045 and 1095. Increasing the carbon content (from 0.18% to 0.95%) causes the amount of ferrite (light) to decrease and the amount of pearlite (dark, lamellar) to increase.

Reactions

• An eutectic reaction occurs at 1150°C with the eutectic composition at 4.3% carbon

$$
L \xrightarrow{\text{cooling}} Y + Fe_3C
$$

heating

•An eutectoid reaction occurs at 725°c with the eutectoid composition at 0.8% C **cooling**

$$
\gamma \leftarrow \frac{1}{\text{heating}} \alpha + \text{Fe}_3\text{C}
$$

Here, austenite (γ) decomposes into two phases, ferrite (α) and cementite $(Fe₃C)$

Transformations

Transformations (Cont'd)

Eutectic transformation

With Fe-C alloys having between 0.51 and 4.3 % C (point C) y-solid solutions will precipitate along the line B-C from the melt, where both, the residual melt and the y-solid solutions will enrich carbon during solidification. The respective balance of fraction of the phases being at equilibrium at a defined temperature results by applying the lever rule.

Range of concentration $0.51\% \leq C \leq 2.06\%$

If the carbon content is between 0.51 % and 2.06 % (point E) the melt has completely transformed into y-solid solution of the initial composition when reaching the eutectic temperature 1147°C. Further cooling below 1147°C will lead to the precipitation of cementite with carbon contents of the initial composition of over 0.8 % C when reaching the line E-S, since the solution capability of the austenite to solve carbon decreases with the temperature. This cementite is also called secondary cementite since it is the second location of a possible precipitation of cementite. Therefore, in the resulting structure austenite and secondary cementite are one beside the other, or named as phases y-solid solution and $Fe₃C$.

Transformations (Cont'd)

Eutectoid transformation

With Fe-C alloys having C < 0.8 % (point S) the y-solid solution wi transform into α -solid solution when reaching the line G-S.

Range of concentration $C < 0.02$ %

Alloys having less than 0.02 % C (point P) are completel transformed into ferrite.

At further cooling cementite will be generated when reaching the line P-Q only since the capability of the α -ferrite to solve carbor decreases from the maximum 0.02 % at 723 °C down to 0.006 % at room temperature. This iron carbide which is also called tertian cementite will predominantly precipitate at the grain boundaries.

%Carbon & Property of Steel

- • In slowly cooled carbon steels, the overall hardness and ductility of the steel are determined by the relative proportions of the soft, ductile ferrite and the hard, brittle cementite
- Cementite content increases with increasing carbon content hardness increases – ductility decreases as we go from low carbon to high carbon steels
- \bullet Rivet should have good deformability and hence a low carbon content
- • Carbon content increased above 1.4% - alloy becomes too brittle to be useful
- \bullet Rail has 0.6% carbon – combines some toughness with some hardness and wear resistance

Introduction

Effect of Carbon

A Graph…

Effect of the Accompanying Elements

 \bullet . The silicon content of a material gives information on the desoxidation state of the material. Steels up to approx. 0.1 % Si are called unkilled and have strong macroscopical segregation zones. These zones have higher contents of C, P, S, thus leading to problems during welding. Steels with Si-contents of about 0.1 to 0.8 % are semi-killed and have no defined segregation zone. These steels have a good suitability for welding. Steels with higher Si contents than approx. 0.8 % are brittle due to these Si-contents and have no good suitability for welding.

- •The manganese content of a steel is apart from the C-content decisive for the strength and the toughness behaviour of a steel. In order to get a usable steel, it must contain at least 0.2 % Mn, in order to bond the residual contents of sulphur to MnS, thus, forming sufficient toughness. Normal building steels contain about 0.4 to 0.6 % Mn.
- • Like silicon manganese has a desoxidising effect so that steels with Mn-contents over approx. 0.6 % can be classified as killed. Higher Mn-contents are to be found in the S355 qualities as well as in the fine grained structural steels where the Mn-contents lie between 1.0 and 1.6 %. With these contents in combination with the C-content the suitability for welding is considerably influenced. Steels of these types have to be preheated to welding starting at a wall thickness of approx. 20 mm. Steels with a higher Mn-content are not used except for the Mn-alloyed austenites, since these steels show a worse toughness behaviour.

- \bullet Phosphorous can be dissolved in the steel at room temperature in small amounts only. With higher contents it is precipitated as Fe3P.
- • In unkilled steels phosphorous segregates very strongly and concentrates in the centre. Phosphorous has an essentially negative effect on the toughness of a steel where the deformation parameters, in particular the notch ductility is reduced. In other words, phosphorous reduces the transition temperature in the notch bar test. Nitrogen and phosphorous together reduce the ageing resistance of a steel. Phosphorous in the steel has a positive influence on the cutting property machinability and the weather resistance of the steel. However, Phosphorous has a negative influence on the suitability of a steel for welding. Starting at a phosphorous content of approx. 0.06 % the steels are not suitable for welding any more. The structural steels applied today contain approx. 0.02 % to 0.035 % of phosphorous.

• Sulphur can only in small amounts be dissolved in steel and can often be regarded as insoluble. Together with iron and oxygen it forms low melting eutectica that in high temperature ranges (over approx. 950°C) lead to the formation of hot cracks and at temperatures about 800°C they are susceptible to brittle fracture (red shortness). Sulphur segregates in unkilled steels and concentrates in the centre. Due to this reason, sulphur is unwanted in steels and from a welding point of view it is the element considerably restricting the suitability of a steel or even making welding impossible. In structural steels the sulphur content is therefore limited to contents lower than 0.06 %, with stainlesssteels the contents are even lower than 0.03 %. However, these low contents must be bound by manganese in order to obtain a usable steel. At high temperatures, manganese forms with sulphur the compound MnS that in the rolled steel can be made visible as a wormlike precipitation in the microsection or becomes visible by means of a large magnification. These precipitations, with stresses in the direction of thickness of the rolling medium, may possibly lead to lamellar tearing**.**

 \bullet Nitrogen can be dissolved in steel up to a certain amount. At room temperature the solubility, however,is low. With decreasing temperature, however, nitrides are precipitated after a longer time. These precipitations are relatively slow and go on for a time of up to 50 years at room temperature. This type of precipitation that is connected with a considerable embrittlement is also called natural ageing. Higher temperatures and cold deformations as well as certain contents of P, O and C encourage this ageing. By means of annealing embrittlement due to ageing can be removed. The susceptability of a steel for ageing is tested by means of notch-bar samples, 10 % cold-deformed and annealed at 250°C for half an hour. In order to restrict or avoid the ageing process of a steel Ncontents of lower than 0.01 % or alloying with aluminium, niobium or vanadium, thus, bonding the nitrogen to form nitrides is required.

- • Oxygen can be dissolved in steel up to approx. 0.003 %, thus having an embrittling effect. Contents higher than 0.007 % are present as oxides (inclusions). During casting the steel will be boiled connected with the formation of bubbles by CO due to the reaction of the oxygen with the carbon. In order to avoid this reaction, desoxidation media such as Si, Al or Mn is added to the steel. By doing so, killed or fully killed steels will be obtained.
- •Hydrogen leads to embrittlement of the steel. At room temperature 0.0004 ml/100g of iron is soluble. Shapes of appearance of hydrogen induced cracks are fish eyes, micropatches, microcracks and underbead crackings. Susceptible to embrittlement through hydrogen are mainly steels with medium and higher C-contents, as well as weld joints. Fact is that the martensitic structures are more susceptible than ferritic or ferritic pearlitic ones.

Effect of the Alloying Elements

- \bullet Alloying elements in general lead to a shift of the transformation points, the critical cooling speed, the saturation limits of the iron for carbon, the diffusion speed of the carbon in the iron, the magnetisability.
- Some of the alloying elements have a carbide forming effect. These are vanadium, titan, niobium, tantalum, chromium, molybdenum, tungsten and manganese.

Change of Gamma Zone by Alloying Elements

- • An open -area is caused by nickel, cobalt and manganese (formation of austenite).
- A closed -area is caused by chromium, aluminium, titan, silicon, vanadium, molybdenum, phosphorous and tungsten (formation of ferrite).
- A contracted -area is caused by oxygen, sulphur, boron, zirconium, niobium and tantalum

Ternary Phase Diagrams

- • Phase diagrams have also been determined for metallic (as well as ceramic) systems containing more than two components; however, their representation and interpretation may be exceedingly complex. For example, a ternary, or three-component, composition–temperature phase diagram in its entirety is depicted by a three dimensional model. Portrayal of features of the diagram or model in two dimensions is possible but somewhat difficult.
- •See next slide

- How did those names come into beeing? Let's see:
- •The name cementite has something to do with the english word "*cement*", meaning something that binds or glues things together in this context.

In 1885, Osmond and Werth published their "Cell-Theory", in which not only the existence of allotropic forms of iron was proposed (now known as austenite and ferrite), but in which also a new look at carbide formation was given. Their research on high-carbon steels, showed that the matrix consisted of grains or cells of iron, encapsulated by a thin layer of iron carbide. During solidification, iron globules, or cells, are formed first and continue to grow. The remaining melt solidifies as iron carbide. In this way, the carbidephase actually glues or binds the previous formed cells together.

Tips (Cont'd)

- Ferrite is practically self-explaining: *Ferrum* is the Latin root for many modern words around iron and iron compounds. The word ferrum is possibly of Semitic origin
- Austenite was named after Sir William Chandler Roberts-Austen, a British metallurgist (1843–1902).
- Pearlite has its name frorm the pearl-like luster and iridescence of its appearance
- Ledeburite is named after Adolf Ledebur (1837-1916).
- \bullet Martensite was named after Adolf Martens (1850 - 1914).
- \bullet Bainite is named after the American chemist E. C. Bain.
- Sorbite is a compound of iron and carbon intermediate between austenite and pearlite, virtually an extremely minute form of the latter. Sorbite is named after the English geologist Henry Sorby.

Historical Note

- \bullet The names ferrite, austenite, pearlite, eutectoid, and martensite all were suggested by two men, an American, Henry Marion Howe and a Frenchman, Floris Osmond, in the time period of 1890 - 1903. In the evolution of science the names suggested by researchers often fall by the wayside. An example of this is Howe's suggestion that martensite be called hardenite. It seems unfortunate to this author that Osmond's preference for martensite was eventually adopted, as the term hardenite so aptly describes the outstanding property of the martensite phase.
- The same French scientist, Floris Osmond, who is responsible for the name of martensite is also responsible for the use of the letters "r" and "c" for the shift in the A lines on cooling and heating. At the end of the 19th century, he was the first scientist to use thermocouples to measure the effect of heating and cooling rates. The letter "r" is from the French word for cooling, refroidissement, and the letter "c" is from the French word for heating, chauffage.

Historical Note

 \bullet The first three letters of the Greek alphabet are alpha, beta, and gamma (^α, β, γ), but there is no structure of iron called beta iron. When the structure of iron was being discovered in the late 19th century, the magnetic transition in iron that occurs at 770 °C (1420 °F) caused scientists to theorize a structure of iron they called beta iron, which was later shown not to exist.

Casting Structure

Denderitic Growth

Fig. 3.11 The dendritic growth of metallic crystals from the liquid state. A solid pure metal (D) gives no hint of its dendritic origin since all atoms are identical, but an impure metal (E) carries the impurities between the dendritic arms, thus revealing the initial skeleton.
Weld Metal

International Welding Engineer | 2.4 - Alloys and Phase Diagrams | Kamran Khodaparasti |

Casting Mold

- \bullet Chill zone
- •Columnar zone
- •Equiaxed zone

Defects

Strengthening Methods

- \bullet Heat treatments can change strength and toughness
- • Solid solution can limit the dislocation movement (alloying elements, interstitial, substitutinal)
- \bullet Precipitation hardening
- \bullet Grain size control

Precipitation Hardening

- • Precipitations result, if the solubility of one or more components in a solid solution is reduced depending on the temperature. Therefore, in a binary system A-B, the solubility of the A or B atoms in the respective solid solution can be reduced with decreasing the temperature, thus forming new precipitations in the structure
- •More effective than solid solution
- • Second phase particle can limit the movement of dislocation
- • In Al-4%Cu, by rapid cooling we have supersaturated solution
- • that after specific time, particles of CuAl2 (theta phase) are achieved
- •This is aging process
- • By heating the specimen at 100-150°C, the aging can be accelerated

Grain Size Strengthening

- Grain boundaries are obstacle to dislocation motion, because the orientation of crystal pattern is changed on grain boundaries
- • By reducing the grain size, the number of grain boundaries is increased
- • Numerically, the influence of the intermediate grain diameter d on the yield strength Re can be indicated by the Hall-Petch Relation as follows:

$$
R_e = \sigma_i + k_y \cdot d^{-1/2} \implies R_e \sim \frac{1}{\sqrt{d}} \quad \text{II}
$$

^σi is the frictional stress corresponding to the obstruction of the movement of dislocations within a crystal with unlimited extent; ky is the number of the grain boundary resistance, i.e. it represents the influence of the grain boundary to the movement of dislocations.

Tips

- \bullet With respect to other strengthening method, grain size hardening increases the strength and toughness simultaneously
- •Modern alloys have small grain size

Let's Have a Look at SLV Software(Part 2.4)

International Welding Engineer | 2.4 - Alloys and Phase Diagrams | Kamran Khodaparasti |

Prepared By: Kamran Khodaparasti kkhodaparasti@yahoo.com

International Welding Engineer | 2.4 - Alloys and Phase Diagrams | Kamran Khodaparasti |

First Edition: Fall 2009 First Revision: Winter 2009 Second Revision: Winter 2010 Third Revision: Summer 2012

Khodaparasti**. All rights are reserved by the author. The materials may not be sold commercially, or used in commercial products or services. Comments are welcome at kkhodaparasti@yahoo.com**