Metals

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1 10-03-25: — Introduction

Pre-requisites: It's important to understand the **phase transformations** in alloys under developement. We'll also focus on the **quantitative treatments** and most importantly on the **sustainability** of the metals production.

We should already know the atomic structure of metals, crystalline structures, dislocations, boundaries, and other defects. We need to know how to read and understand a phase diagram. Also we need to know the basic principles of thermodynamics and kinetics. Like for example diffusion, concentration gradient, flux and so on.

1.1 Thermodynamics and phase diagrams:

Some terminology:

- Component: element of the periodic table or compound.
- Phase: portion of a system that has uniform physical and chemical characteristics.
- System: mixture of one or more phases.

Some thermodynamic properties:

- Temperature
- Pressure
- Composition

The stability of the system is given from the **Gibbs free energy** G:

$$G = H - TS \tag{1}$$

This is the most useful equation, because we can actually control both T and P. In this course we will assume that the variations of P are small, so we consider it constant.

Thermodynamic quantities are extensive quantities, so they depend on the amount of material. We can define the **molar Gibbs free energy** g as:

$$G_m = \frac{G}{N} \tag{2}$$

In the case it contains more phases, G total will be the sum:

$$G = \sum_{\varphi} N_{\varphi} G^{\varphi} \tag{3}$$

The composition in described as a molar fraction of the total (all expressed in moles):

$$x_{\varphi} = \frac{N_{\varphi}}{N_{tot}} \tag{4}$$

Moreover, the equilibrium is reached when the Gibbs free energy is minimized. This means that we can find it by finding a local minima (metastable) or a global minima (stable):

$$dG = 0, \text{ and } d^2G \geq 0 \tag{5}$$

Interestingly, we never know the actual integral value of G, we always work with differences of it, unless we define a reference state.

Reference state: Don't think is very relevant, but in case you want to investigate further: *Thermodynamics and free energy curves.pptx, slide 7.*

Single component systems (pure metals): We can consider a system made out of a single element, constant pressure. For each phase we can define the Gibbs free energy. But how can I obtain valuable information from this? I can just change T, and rewrite calculating H and S.

$$H = H_{\text{ref}} + \int_{T_{\text{ref}}}^{T} C_p dT, \text{ with } C_p = \left(\frac{\partial H}{\partial T}\right)_P \tag{6}$$

$$S = S_{\text{ref}} + \int_{T_{\text{ref}}}^{T} C_p d\ln T, \text{ with } C_p = \left(\frac{\partial S}{\partial T}\right)_P \tag{7}$$

Where we will need to obtain the values of different c using fitting of real data. So recap: we fit the data obtaining c, then we calculate S and H and then we obtain the amount of G at different T.

These plots have T on the X-axis and C_p on the Y-axis (there's a small digression on the magnetic behaviour of Iron and a big spike in the plot).

If we for example plot the total Gibbs energy and the T, we get that some crystalline structures are more stable than others at different temperatures.

Coordinate system: The plots can be plotted assuming the reference state as the **BCC** at every temperature with pressure 1bar. Remember by the way that each one of the plots with changing temperature, is just a slice, one line of the full diagram phase T and P.

DoF: Remember that the number of degrees of freedom is:

$$\nu = c - f + 2 \tag{8}$$

1.2 Driving force of solidification

By comparing different Gibbs energies at different temperatures of the liquid and solid phase, we obtain the melting point. However, under certain conditions (fast cooling), the solidification happens at a couple hundred degrees lower. The bigger is the difference between the Gibbs energies, the bigger is the driving force (the energy gain) of the transition. The different differences, are obtained from the calculations between solid and liquid phases.

Remember that usually the ΔH is called L as in *Latent heat of fusion.*

1.3 Binary systems

Alloys made of 2 different components. We have two different possibilities:

- Same crystal structure: Homogeneous, because of substitutional solid solution.
- Not same crystal structure: Heterogenous, because both can create substitutional solid solutions inside the other and not mix.

Other cases:

- Interstitial solid solutions

- Different phase, which has a crystal structure that is not A nor B.

Either way, the new plot of rappresentation is a plot that has the Gibbs energy (T and P constant) on the Y-axis and the percentage of composition on the X-axis. At each end of the plot we have a 100% of the given component. The attributes of the mix and the single components is the *'linear interpolation'*, but I guess that in future the true behaviour will not be a straight line.

Entropy of mixing: Using:

$$S = k_B \ln(\omega_{\text{conf}}) \tag{9}$$

Where we can describe the amount of entropy as the number of different configurations a system can assume. Before mixing we had only 1 configuration of atoms in different position (atoms of the same element are indistinguishible), while after mixing we have different possible configurations and thus a higher entropy. The value of ω is:

$$\omega_{\text{config}} = \frac{(N_A + N_B)!}{N_A! N_B!} \tag{10}$$

With the different N are the number of atoms of different elements:

$$N_A = X_A N_a \tag{11}$$

Sterling's equation: SKIP, it is an approx.: $\ln(N) \sim N \ln(N) - N$. So now we have all the data to calculate the ΔS:

$$\Delta S_{mix} = S_2 = k_B \ln(\omega_{\text{conf}}) = -R(X_A \ln(X_A) + X_B \ln(X_B)) \tag{12}$$

The derivation is often asked at the exam.

2 11-03-25: — Binary systems

The real case is different from the ideal one, in fact, the ΔG_{mix} strongly depends on the temperature, with higher energies we obtain higher differences. Remember that it is always negative in the ideal case. Mixing is always thermodynamically favorable.

But to obtain this type of ideal solution we must use specific alloys, so we need to add complexity to the model, to better simulate real data: Regular Solution Model.

2.1 Regular Solution Model

We first of all assume that the bonding energies do not change with the composition, and P & V remain constant when mixing (this is expressed by the relation: $\Delta U = \Delta H$). We also assume that the the bonding energies between different atoms are fixed:

- A-A bonds with energy ε_{AA}
- B-B bonds with energy ε_{BB}
- A-B bonds with energy ε_{AB}

This simplify a little the calcs, because:

$$\Delta H = \Delta E + \cancel{\Delta (PV)} \tag{13}$$

There are also formulas to get the number of atoms from the number of bonds and viceversa, skipped.

Now follows a demonstration of the calculation of internal energy after mixing, which mainly considers the 2 original values and correlates it to the number of bonds, essentially summating them all over. More information *1 - Thermodynamics and free energy curves2.pdf @ pag.20.*

The final result is this:

$$\Omega = N_a z \varepsilon \tag{14}$$

$$\Delta H_{\text{mix}} = \Omega X_A X_B \tag{15}$$

We can have different combinations of high/low temperature and $\Omega \lesseqgtr 0$. This illustrates how actually the ΔH might not be negative, meaning it is not thermodynamically favorable. The sign depends on wether the bonds between same atoms is tronger or weaker compared to bonds between different atoms. The void zone is called **Miscibility gap**. This gap is always present, even if the ΔH is negative, this is beacause, there always states more favorable (energetically).

2.2 Chemical potential

This tells us how much chemical potential energy a pure element has and how much it lowers whenever creating a solution: usually the solution will have the lowest free energy. This chemical energy is related to the crystal structure, so like the energy contained in the element.

If we mix 2 components which have different crystal structure, the situtation becomes even more complicated, we must consider *'how much a certain component in a certain crystal structure is stable in the OTHER crystal structure'*. We then obtain 2 different curves, each one describing one or the other free energy for every crystal structure considered. Whenever this happens it results more convienient to have BOTH phases together, so both minima. To understand the amount of one phase respect to the other we can use the *'Legge della Leva'*. $\sim$ Rizzi

The tangent line used passes through the 2 minima, and we project our composition down the line. This is applied only inside the miscibility gap, outside it follows the free energy curve.

3 14-03-25: — Recupera appunti

4 17-03-25: — Interfaces in metallurgy

- Free surfaces: between metal and liquid or vapour
- Grain boundaires: between same phase (α/α)
- Interphase Interfaces: between different phase (α/β)

The surface tension is a phenomenon that happens in liquids only (stress free surfaces). In the metals we have the surface energy, which is a measure of the excess energy at the surface of a material compared to its bulk. This also gives information about the energy needed to create one unit of surface. Its like the work needed to increase or decrease the surface.

$$dW_{s(T,P)=\gamma dA} \tag{16}$$

s(T,P) means constant in temperature and preassure. We also have surface / interface stress, which the energy required to deform reversebly a unit on area.

Interfaces: Sharp and diffuse, they can change the atomic configuration in a long or short range. The surface phase changes at every single atomic layer, because the related Gibbs dividing surface changes. This is a mathematical trick to explain the gradient encountered in the interfaces. In general the greater the number of boundaries, greater is the strain resistance, since making the plane atoms slide and encounter boundaries requires more energy to deform.

Grains with smaller angle than 15° are called low-angle grain boundaries. The energy that will build up at the boundaries, is the total energy of all dislocations piled up. There's a strain and tension due to additional atomic planes, which will create a surface (difference of pressure and density). Here's way the low angle boundaries have less energy: there are less dislocations.

When the angle suprasses 15° the energy required flattens, even at higher angles there's the same energy requirement. This is beacuse they are so different that the grains do not try to form a boundary formed by dislocations. They just have some smaller interactions at a long range (couple of atomic distances).

Special cases: It might happen that due to symmetry of the cell orientation, we can get a *Site coincidence*, where it's asif we have a low angle boundary.
Another case is th *Twin boundaries*, where at specific angles we got a coherent (or incoherent) twinning plane where a boundary actually coincise with another plane.

So when dealing with 2 different phases we can actually have the same cases: coherent, semi-coherent and incoherent.

Laplace-Young equations: It describes the effect on interfaces at the equilibrium.

$$\Delta P = \gamma \left(\frac{\partial A}{\partial V} \right)_T \tag{17}$$

This describes also how the temperature changes at different size of particles, this is beacuse of the Gibbs-Thomson effect, which says that small particles have higher free energies (lower melting point).

5 18-03-25: — Phase transformations in solids

They happen among solid phases and they require diffusion. Using thermodynamic we can classify them as:

- First order: Discontinuity in first order derivative, there's latent heat (solidification)
- Second order: Discontinuity in second order derivative, there's a step in specific heat (magnetic transition)

The diffusion transformations involve long range movement of atoms, which can be further divided in heterogeneous (nucleation and growth) and homogeneous (spinodal decomposition(?)). In the end we have Displacive Transformations which involve shift of atoms but over relatively short distances (martensitic transformation).

Classification:

- a) precipitation: small precipitation when the solubility limit is surpassed
- b) eutectoid: a single solid state that transforms into two different solid states upon cooling
- c) ordering reaction: a rearrange without actually changing the metal phase, small increase of internal stability
- d) massive: a reaction so fast that it "skip" intermediate transformations, leading to a clear change from parent phase to stable child phase
- e) polymorphic: same as massive transformation, but for pure elements or single compounds

Nucleation: In ideal case we have a spherical nucleation where the energy to create a small cluster will depend on surface energy and stability in the bulk. There are more informations, but they are all equal to Rizzi's lectures.

6 20-03-25: — Nucleation theory

The important quantities are free energy and surface energy. The nucleation rate depends on two factors:

- Smaller the temperature, the higher the faster the growth.
- Higher the temperature, the higher the number of nucleous.

These two terms combine giving the maximal solidification speed where their product is the highest. Changing the composition, will change this temperature. In heterogeneous nucleation we have the interface of a boundary. So it's more convienient for nucleation to start there, since removing that interface with a lower energy volume is thermodinamically more convienient. It will also depend on the angle, as was shown in previous lessons, where the energy depends on the orientation of the grains. A coherent interface will also be favored, so once again, since creating a new nucleation center costs energy but it's lower than the boundary grains it happens. So it starts almost always following the grain structure (coherent) and then expands chaotically (incoherent).

During the nucleation there's a diffusivity and segregation, since we are on a boundary, there is stress caused by the surface and defects. When the nucleation happens, atoms are favored to move and reorganize themselves. So depending on the heterogeneous phase we will have a diffusion of a single phase from γ to a pure phase α or β.

We can additionally tell that coherent nucleous will be planar, while incoherent will be curved.

Growth rate: $v = \partial x/\partial t$, while the concentration of a certain pure phase will diminsh overtime, until it's completely depleted. Before the nucleation we have an homogeneous solution and concentrations. And after that the regions around the nucleous will loose atoms and accumulate them at the nucleous. We can define it as:

$$J = D\frac{dC}{dx} \tag{18}$$

We can model it using for example a basic model called 'Zener model'. Basically it models a simple diffusion using rectangles and triangles, than it smooths it out by substituting with more complex fuctions and integrating. What this model lacks is a growth stop, it doesn't consider when crystals starts interacting with themselves.

7 24-03-25: — Plate-like growth

$$uh = \nu\lambda \tag{19}$$

Where u is the additional width, h the additional height and ν and λ are bounded to the dinamic of the system. This also depends on how fast we can resupply the depletion zone generated by the nucleation of a new phase.

Transformed fraction f(t,T): Referes to the amount of material that has successfully transformed from the inital phase to the new phase at anu given point in time during the process. It ranges from 0 to 1 where 0 is no transformation and 1 is 100% conversion. Look for *'Theory of transformed fraction f(t,T)'*.

8 31-03-25: — Eutectoid transformation

Using the TTT curve, we can relate the Temperature to the log(T) which gives us the information of when and how long a certain transformation takes. If we have more than one microstructure, they can overlap. This is the case for Bainite and Pearlite for example. If we cool even more, we change the phase (into martensite)

8.1 Bainite

Bainite contains ferrite and cementite.

High Ferrite: The ferrite forms between 2 grains of austenite along the $\perp$ of the grain border (along a direction of the grain), rejecting the carbon.

High Cementite: Generation of cones of ferrite with carbides needle on them.

Civilian / Military: When you find these terms, they are referred on how the atoms move: civilian is like a crowd, chaotic and on average zero. Military is ordered, in a specific order.

8.2 Addition of alloying elements:

TTT curves is shifted to longer times, beacuse alloying materials stabilize some phases:

- Austenite: Mn, Ni, Cu. They lower the eutectoid temperature, slowing the diffusion
- Ferrite: Cr, Mo, Si. They increase the eutectoid temperature, which promotes individual structures (high ferrite) if there's a partition.
- Carbide: Cr, Mo, Mn. If there's no partitioning, these elements 'poison' ferrite nucleation sites with carbides.

In the notes there are various plots showing how 'noses' are formed or removed due to alloying elements.

8.3 CCT

First of all they are shifted to lower temperature than TTT, they indicate how fast you cool your system, the intersection tells you what kind oh phases and microstructures you will encounter.

8.4 Quenching

Discussion of spinodal range, if we mantain the temperature, the solution can diffuse and generate two different regions of different composition, which are more favorable in free energy. They do not change, but they lower the total free energy. This can exagerate until you meet the limits of the miscibility gaps. BUT if the starting concentration is outside the spinodal range, the free energy increases (in the beginning), stopping this process with an energetic barrier (nucleation energy). In the previous case there was no nucleation.

Massive transformation: It is a big jump in free energy, going from a phase β to α for example and than precipitating as usual. The massive part is related to the big change from the 2 initial phases. the transformation occours via migration, but with a very high jump in energy.

9 01-04-25: — Martensitic transformation

9.1 Finishing last lecture

Short range order: We may have ordering solutions, where the alloy arranges itself with a certain order and stechiometry, which can be expressed with long and short range. This of course can range from complete disorder to complete order. We can use the 'short range parameter':

$$s = \frac{P_{AB} - P_{AB}(random)}{P_{AB}(max) - P_{AB}(random)} \tag{20}$$

Where P_{AB} means the number of bonds between $A - B$.

Long range order: Occours only at lower temperatures, ensures a certain order over long distances. Has the following dependecy:

$$L = \frac{r_A - X_A}{1 - X_A} \tag{21}$$

Where r_A is the probability that A is on the right sublattice, namely it is in the correct ideal lattice.

9.2 Martensite

Forms essentially from Austenite (γ) and is usually called Martensite (α') and it's a BCT (Tetragonal).

This transformation happens very quickly, so generally the order is at short range. There are some invariant planes, where the local atoms do not move relatively to the surroundings. What happens is that the crystallographic structure (bain strain) we don't have anymore an invariant plane (due to non-uniform scaling), unless we apply a rotation to increase the lattice correspondance. What happens in reality tho, is that Martensite creates many planes that shear and create many deformations that pile up.

The lateral growth is mainly preferred, here exaplained why 'lens-like' structures form. Further heat treatment can help remove brittleness.

The shape of the lens structures depends on the amount of carbon, and also the habit plane orientation, this is due to the crystalline distorsion of the system.

9.3 Solidification

- Casting: quello che vedi di solito nei reels.
- Welding: classical method, create sheets and then joining them together.
- Additive manufacturing (3D printing): new production method, extremely precise microstructure.

Nucleation: The good news is that we move from a liquid to a solid phase, this means we don't have strain contribution in the formation energy.

10 02-04-25: — Nucleation / Solidification

In pure elements the Solidification tends to be homogeneous along a surface. If it happens that there's a protrusion there are two possible cases:

- Typical case: the protrusion is reassorbed and the surface flattens
- Undercooling: the protrusion is favored and it grows perpendicular to the surface, generating 3D cross structures (Dendrites)

When we have binary alloys or so on, you use the 'regola della leva'.