Phase-diagram determination

General principles

- An alloy consists of a single phase or of a mixture of phases depending on the composition of the alloy and the temperature.

  Phase diagram: **a plot of temperature vs. composition** → a short map of alloy system

  Investigation of the phase diagram:

- **How X-ray methods can be used in the study of phase diagram of binary systems**

  → Determination of crystal structures of various phases involved

  →Determination of solvus (solid solubility) curves

Powder pattern of alloys → each phase produces its own pattern independently of the presence or absence of any other phase

- If two metal A and B are ***completely soluble*** in the solid state
  →The solid phase α is of the substitutional type→ it varies in composition (but not in crystal structure) from pure A to pure B
  →Effect on powder patterns: shift of the diffraction-line positions in accordance with the change in lattice parameter
- If two metals A and B are only ***partially soluble*** in the solid state (see Fig. 1)
  →The first additions of B to A go into solid solution in the A lattice → expanding or contracting depends on the relative sizes of the A and B atoms and type of the solid solution formed (substitution or interstitial)
  →Finally the solubility limit of B in A is reached→ further addition of B → precipitation of a second phase → B-rich solid solution with the same structure as B

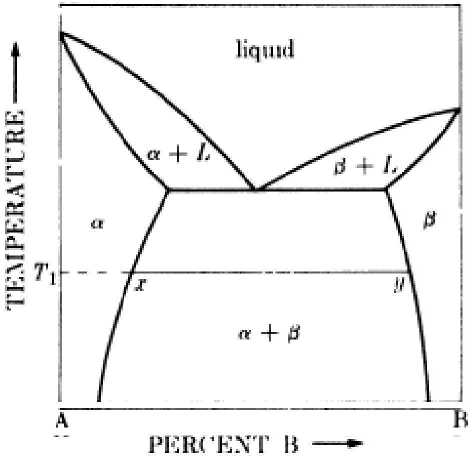

Fig. 1 Phase diagram: partial solid solubility

Single-phase regions: a change in the composition → a change in the lattice parameter

Two-phase regions: a change in the composition of the alloy→ a change in the relative amount of the two phases but no change in their composition→ Powder pattern consists of the superimposed pattern of α of composition x and β of composition y.

Solid solutions

1. **Interstitial**
2. **Substitutional**

1. An **interstitial solid solution** of B in A → when B atom is so small compared to the A atom that it can enter the interstices of the A lattice without causing much distortion

→ Solid solutions formed between a metal and one of the elements, carbon, nitrogen, hydrogen, and boron (all have atoms less than 2 Å in diameter)→ **always accompanied by increase in the volume of the unit cell.**

- The density of an interstitial solid solution is given by the basic density equation

$$\rho = \frac{1.66042 \sum A}{V'}$$

Where $\sum A = n_s A_{s+} n_i A_i$

n_s and n_i are number of solvent and interstitial atoms per unit cell and A_s and A_i are atomic weights of the solvent and interstitial atoms

→ n_s is an integer and independent of the concentration of the interstitial element and that n_i is normally a small fraction of unity.

2. The formation of a ***random substitutional solid solution*** of B and A may be accompanied by either an **increase or a decrease in cell volume**→ depending on weather the B atom is larger or smaller than the A atom.

- The density of a random substitutional solid solution is found from

$$\rho = \frac{1.66042 \sum A}{V'}$$

With $\sum A$ factor being given by

$\sum A = n_{solvent} A_{solvent+} n_{solute} A_{solute}$

Where n again refers to the number of atoms per cell and A to the atomic weight.

But here ($n_{solvent} + n_{solute}$) is a constant integer, equal to the total number of atoms per cell.

- Whether a given solution is interstitial or substitutional may be deduced by determining whether x-ray density calculated according to $\sum A = n_s A_{s+} n_i A_i$ or that calculated according to $\sum A = n_{solvent} A_{solvent+} n_{solute} A_{solute}$ agrees with the directly measured density.

Determination of Solvus curves (disappearing-phase method)

- **Disappearing-phase method**: is based on a determination of the composition at which the β phase just disappear from a series of (α+β) alloys.
  → **"lever law"**: relative proportions of α and β in an alloy of composition z in equilibrium at temperature T_1 is given by the relative lengths of the lines zy and zx (see Fig. 2)

$$\boldsymbol{W_\alpha(z-x)=W_\beta(y-z)}$$

Where W_α and W_β denote the relative weights of α and β if x, y, and z are expressed in weight percent.

Intensity of any diffraction line from the β phase varies from zero at x to a maximum at y→ **This intensity variation used to locate the point x** (see Fig. 2)

- The intensity of a diffraction line depends on atomic scattering factor f (proportional to atomic number Z).

if atomic number of B is considerably less than A →the intensity of the β may be so much lower than α pattern → large amount of β in two–phase mixture will be undetected

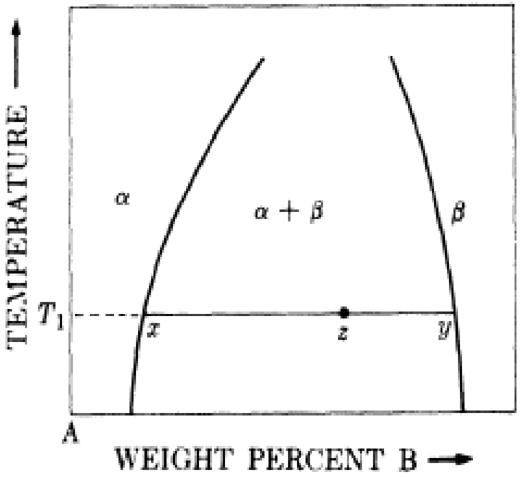

Fig. 2 Level law construction for finding the relative amount of two phases in a two-phase field

Determination of Solvus curves (Parametric method)

- **Parametric method**: is based on observation of the α solid solution itself→ depends on the fact that the lattice parameter of a solid solution generally changes with composition up to the saturation limit, and then remains constant beyond that point (see Fig. 3).
- **Determination of the exact location of the solvus curve:**

→A series of alloys 1 to 7 is brought to equilibrium temperature T_1,

→The lattice parameter of α is measured for each alloy and plotted against alloy composition, resulting in a curve in Fig (3b).

(This curve has two branches)

→An inclined branch *"bc"*, which shows how the parameter of α varies with the composition of α (this branch serves as a sort of master curve for the determination of the whole solvus), and a horizontal branch "*de*", which shows that α phase in alloys 6 and 7 is saturated, because its lattice parameter does not change with change in alloy composition

→The limit of the α field at temperature T_1 is therefore given by the intersection of the two branches of the parameter curve→ x percent B at T_1.

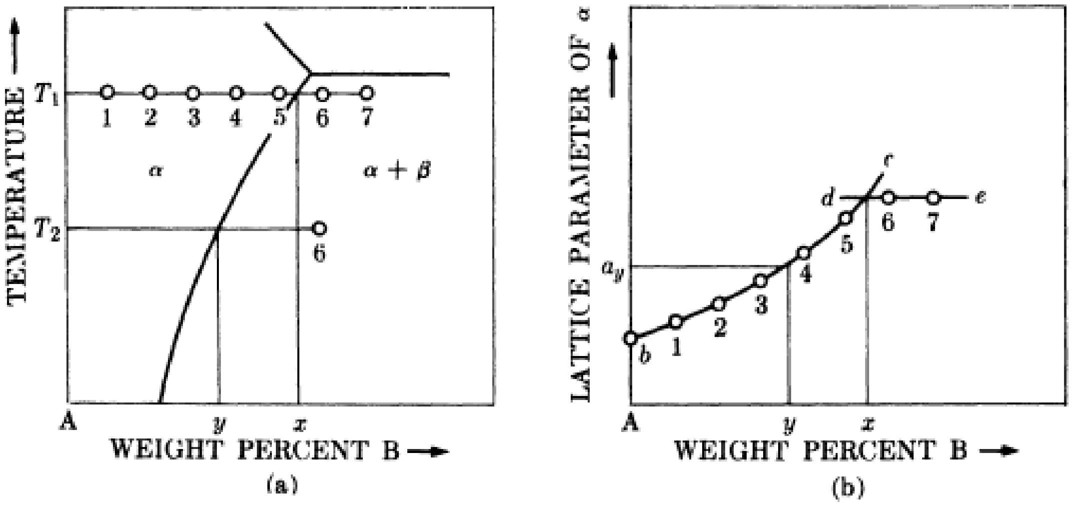

Fig. 3 Parametric method for determining a solvus curve.

→ Once the parameter-composition curve of the solid solution has been estimated only one two-phase alloy is needed to determine the rest of the solvus (see exercise).