# Solidification of a Solid Solution alloy :

When an alloy such as Cu-40% Ni is melted and cooled, solidification requires that both nucleation and growth occurs.

Heterogeneous nucleation permits little or no undercooling, so solidification begins when the liquid reaches the liquidus temperature.

The phase diagram (fig 4), with a tie line drawn at the liquidus temperature, tells us that the first solid to form has a composition of Cu-52% Ni.

Growth of the solid requires that the latent heat of fusion, which evolves as the liquid solidifies, be removed from the solid-liquid interface.

In addition, diffusion must occur so that the compositions of the solid & liquid phases follow the solidus & liquidus curve during cooling.

The latent heat of fusion is removed over a range of temperatures so that the cooling curve shows a change in slope, rather than a flat plateau. (fig 5)

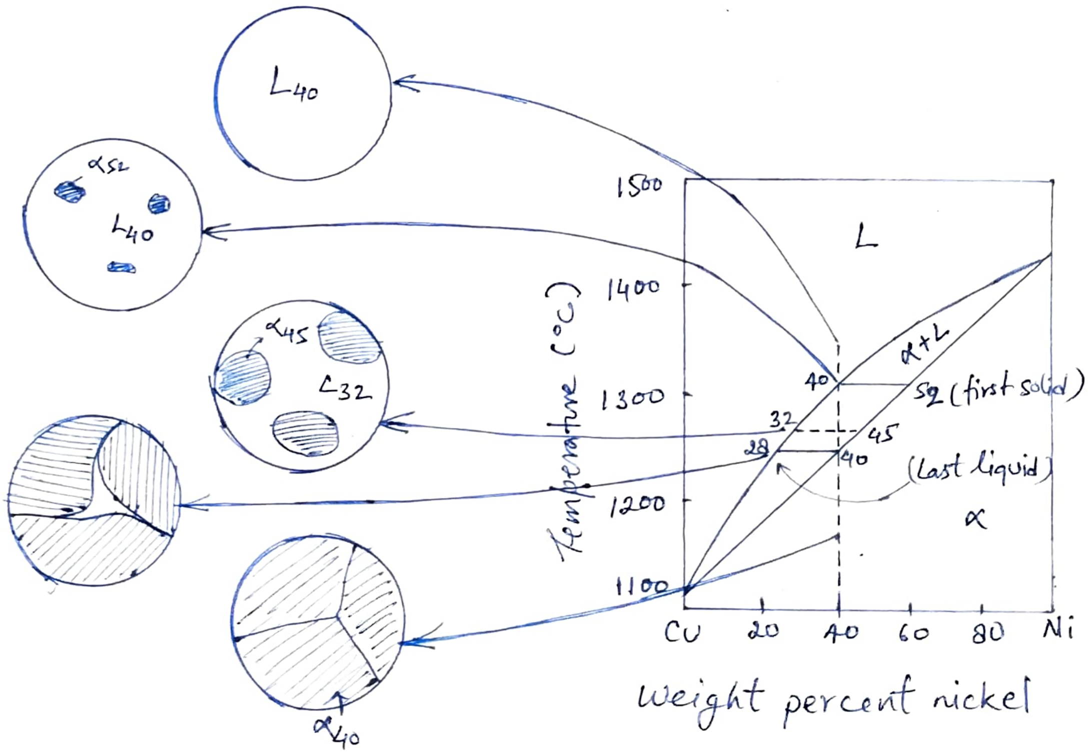


Fig 4 : The change in structure of a Cu-40% Ni alloy during equilibrium solidification. The nickel & copper atoms must diffuse during cooling in order to satisfy the phase diagram & produce a uniform, equilibrium structure.

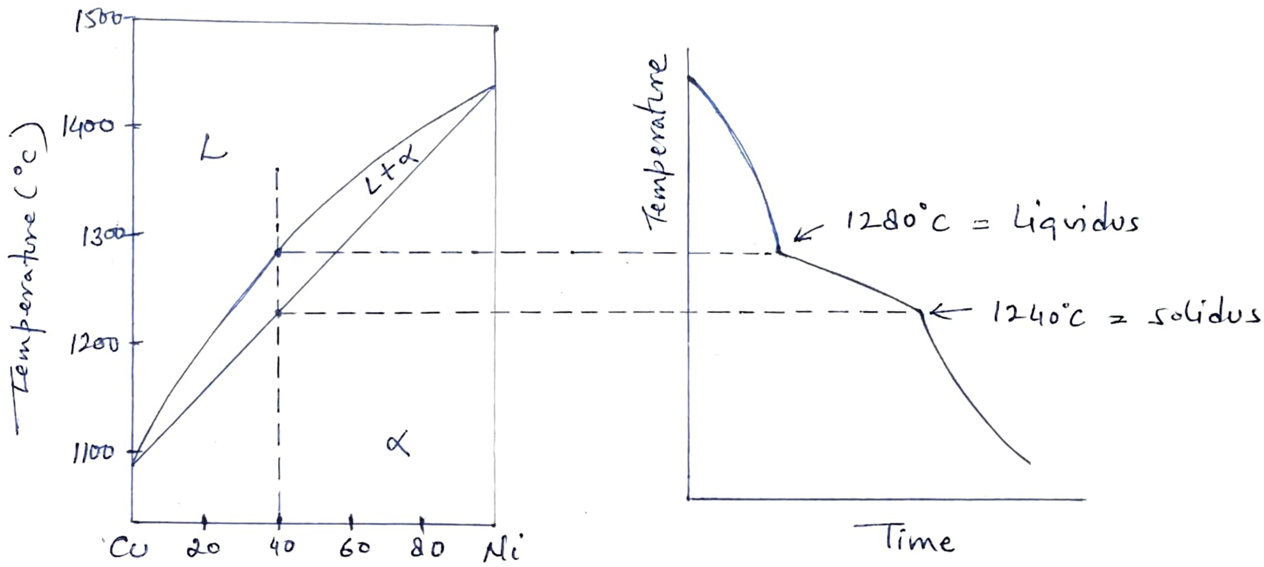


Fig 5: The cooling curve for an isomorphous alloy during solidification. The changes in slope of the cooling curve indicate the liquidus & solidus temperatures, in this case for a Cu-40% Ni alloy.

At the start of freezing, the liquid contains Cu-40% Ni and the first solid contains Cu-52% Ni.

Ni atoms must have diffused to and concentrated at the first solid to form.

But after cooling to ~~1250~~ 1260°C, solidification has advanced and the phase diagram tells us that now all of the liquid must contain 32% Ni and all of the solid must contain 45% Ni.

On cooling from the liquidus to ~~1250~~ 1260°C, some nickel atoms must diffuse from the first solid to the new solid, reducing the nickel in the first solid.

Additional Nickel atoms diffuse from the solidifying liquid to the new solid. Meanwhile copper atoms have concentrated, by diffusion into the remaining liquid.

This process must continue until the last liquid, which contains Cu-28% Ni, solidifies & forms a solid containing Cu-40% Ni.

Just below the solidus, all of the solid must contain a uniform concentration of 40% Ni throughout.

In order to achieve this equilibrium final structure, the cooling rate must be extremely low.

Sufficient time must be permitted for the copper & nickel atoms to diffuse & produce the compositions given by the phase diagrams.

In most practical casting situations, the cooling rate is too rapid to permit equilibrium.

## Nonequilibrium Solidification of Solid Solution alloys :

When cooling is too rapid for atoms to diffuse & produce the equilibrium conditions, unusual structures are produced in the casting. Let's see what happens to our Cu-40% Ni alloy on rapid cooling.

Again the first solid, containing 52% Ni, forms on reaching the liquidus temperature (fig 6).

On cooling to 1260°C, the tie line tells us that the liquid contains 34% Ni & the solid which forms at that temperature contains 46% Ni.

Since diffusion occurs ~~rap~~ rapidly in liquids, we expect the ~~two~~ tie line to accurately predict the liquid composition. However, diffusion in solids is comparatively low.

The first solid that forms still has about 52% Ni, but the new solid contains only 46% Ni. We might find that the average composition of the solid is 51% Ni.

This gives a different nonequilibrium solidus than that given by the phase diagram. As solidification continues, the nonequilibrium solidus line continues to separate from the equilibrium solidus.

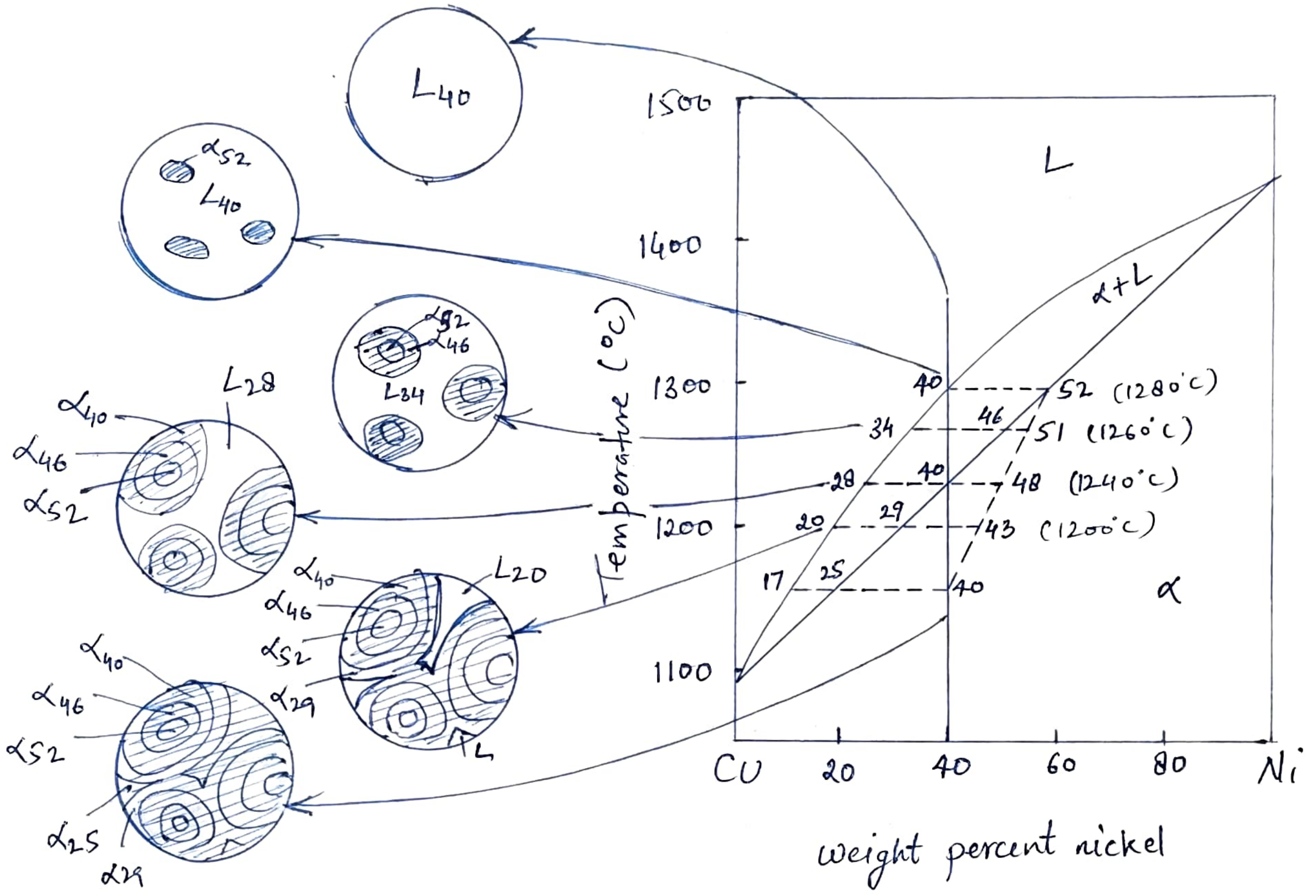


Fig 6: The change in structure of a Cu-40% Ni alloy during nonequilibrium solidification. Insufficient time for diffusion in the solid produces a segregated structures.

When the temperature reaches 1240°C, the equilibrium solidus line, a significant amount of liquid remains.

We could estimate the amount of liquid by performing a lever law calculations, where the ends of the lever are given by the liquidus point and the nonequilibrium solidus point.

The liquid will not completely solidify untill we cool to 1190°C, where the non equilibrium solidus intersects the original composition of 40% Ni.

At that temperature liquid containing 17% Ni solidifies, giving solid containing 25% Ni. The average composition of the solid is 40% Ni, but the composition is not uniform.

The actual location of the nonequilibrium solidus line and the final nonequilibrium solidus temperature depend on the cooling rate. Faster cooling rates cause greater departures from equilibrium.

Ex: Calculate the composition & amount of each phase in a Cu-40% Ni alloy that is present under the nonequilibrium conditions shown in fig 6 at 1300°C, 1280°C, 1260°C, 1240°C & 1150°C. Compare with the equilibrium compositions & amounts of each phase.

Ans:

| Temp | Equilibrium | Non equilibrium |
|---|---|---|
| 1300°C | L: 40% Ni 100% L | L: 40% Ni 100% L |
| 1280°C | L: 40% Ni 100% L<br>α: 52% Ni ~0% α | L: 40% Ni 100% L<br>α: 52% Ni ~0% α |
| 1260°C | L: 34% Ni $\frac{46-40}{46-34} = 50\%$ L<br>α: 46% Ni $\frac{40-34}{46-34} = 50\%$ α | L: 34% Ni $\frac{51-40}{51-34} = 65\%$ L<br>α: 51% Ni $\frac{40-34}{51-34} = 35\%$ α |
| 1240°C | L: 28% Ni 0% L<br>α: 40% Ni 100% α | L: 28% Ni $\frac{48-40}{48-28} = 40\%$ L<br>α: 48% Ni $\frac{40-28}{48-28} = 60\%$ α |
| 1200°C | α: 40% Ni 100% α | L: 20% Ni $\frac{43-40}{43-20} = 13\%$ L<br>α: 43% Ni $\frac{40-20}{43-20} = 87\%$ α |
| 1150°C | α: 40% Ni 100% α | α: 40% Ni 100% α |