Turkish J. Eng. Env. Sci.
28 (2004) , 129 – 134.


# Dendritic Solidification in a Copper Nickel Alloy

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Received 06.08.2003

**Abstract**

The distribution of nickel in dendrite arms and in interdendritic regions of copper-10% nickel alloy solidified under production conditions designed to provide 4 different cooling rates was investigated. The results indicate that at different rates of solidification undercooling, diffusion and convection mechanisms affect the microsegregation of nickel and copper in the cast materials to various extents.

**Key words:** Dendritic growth, Solidification microstructure.

## Introduction

Solute redistribution is one of the most important phenomena in the solidification process of multicomponent alloys which determines segregation in the resulting solid materials. Wanqi (2001) points out that problems have been discussed from 4 aspects: (1) solute partition and the partition ratio at the growth interface; (2) solute redistribution in the directional solidification process with a planar interface; (3) solute redistribution in the dendritic solidification process and the resulting micro-segregation; and (4) the formation of macro-segregation and the controlling parameter.

Micro-scale segregation is a common phenomenon in dendritic solidification and is usually considered a solidification defect. The relationship between the solute concentration at the growth interface and the solid fraction has to be determined. In the dendritic solidification process solid diffusion in the liquid is usually sufficient. Solid diffusion in the solid is usually ignored in conventional models.

Casting is one of the main methods of producing shaped metals and alloys. Nucleation and growth are the 2 major mechanisms leading to the final structure of the solidifying metal.

The final grain structure is dependent on the ratio of the temperature gradient in the liquid (G) to the rate of advancement of the solid-liquid interface (R), that is G/R. When the G/R ratio is very high, growth proceeds with plane front solidification. At lower values of G/R a cellular structure is obtained. At still lower values of G/R, a transition from cellular to dendritic growth occurs, with columnar cells branching into dendrites. If the G/R ratio is low enough to start heterogeneous nucleation in the undercooled regions, randomly oriented new growths start to develop. According to Beeley (1982), these grains later transform into dendrites.

Solid composition (Co) in solid solutions also affects the solidification mode and the resultant solidification structure. Sharp and Hellawell (1971) state that with an increased growth rate and higher solute content, the solid-liquid growth changes from cellular mode, which grows in the heat flow direction, to a branched dendritic mode, which grows preferentially on certain crystallographic axes.

The importance of dendritic growth in castings is best described in Kondic's words: 'The dendritic type of growth is so frequently encountered under normal conditions of crystallisation of metals and alloys that not only was it the first to be observed, but until recently it was thought to be the only type of metal crystal growth morphology on the microscopic and macroscopic scale' (1968).

The origin of dendritic growth in solid solutions is the rejection of the solute element by the growing solid. The rejected solute accumulates at the solid-liquid interface and lowers the local freezing temperature. Thus constitutional undercooling arises from a change not only in temperature but also in composition. Any protuberance which forms on the unstable solid-liquid interface finds itself in the undercooled liquid and therefore survives without remelting. For most alloys it is impracticable to avoid constitutional undercooling, and so according to Doherty *et al.* (1973) dendritic solidification occurs during the production of almost all alloys.

The basic dendritic solidification model consists of a fully solid zone near the surface of the casting , a fully liquid zone at the centre , and in between, a liquid-solid mushy zone where dendrites form and grow. Convection creates temperature fluctuations throughout the molten metal and may increase the temperature around the growing dendrites. Due to higher solute content and lower radius of curvature, the melting point of a secondary arm is lowest nearest its root. Flemings (1968) reports that these arms melt off and become separated from the growing dendrite. The detached arms are carried away by convection to initiate growth of randomly oriented new grains

The structure within a grain consists of a large number of dendrite arms which grow from the same initial growth point and have identical crystallographic orientation. Thus each grain is accepted as containing a single dendrite. The main stems are called the primary dendrite arms. In columnar grains the primary dendrite arms are roughly parallel to the heat flow direction. Arms branching out from the primary arms are termed secondary arms. The effects of solidification conditions on dendritic structure are best measured using dendrite arm spacing parameters. Perpendicular distances between primary, secondary and higher order branches provide these arm spacings. Bolling and Fainstein-Pedraza (1974) found that the dendrites formed as needles and grew as free dendrites or in specific arrays. A coarsening mechanism determines the final dendrite arm spacings. Solute composition and convection are thought to have effect on spacings.

**Experimental Procedure**

The research carried out by Dundar (1983) on a copper-10% nickel alloy shows nearly ideal solid-solution properties. An oxidising flux, Cuprex 100, was placed at the bottom of the crucible. Nickel pellets followed by copper were charged into the crucible. The charge was melted and superheated to 1370 °C with periodic mixing to ensure solution of nickel pellets. A proprietary deoxidising tube (Type MG 6) was plunged into the molten metal. The slag was skimmed off after being thickened with dry silica sand. The molten metal was poured into the preheated sand and chill moulds and covered with exothermic powder. In addition to the sand-cast and chill-cast ingots furnace cooled alloy and semi-continuously cast industrial ingots were prepared to represent the extremes of cooling rates.

For optical microscopy, microsections were polished on emery papers followed by diamond polishing and final polishing on a vibromet apparatus. Etching in ferric chloride solution in HCl was used to develop the microstructures. Successive fine diamond polishes and light etches were applied to reveal the structure better. The problem of producing satisfactory low magnification photographs was encountered due to the cored structures.

**Results**

A furnace-cooled ingot showing the results of a very slow cooling rate revealed 20-25 large grains (Figure 1). Although the alloy is a single-phase material, there is a strong contrast due to the different crystallographic orientations of neighbouring grains. Each grain is a dendrite network. The grains themselves are equiaxed but the dendrite arms within individual grains are aligned in specific directions.

In spite of periodic mixing of the melt some nickel pellets persisted in the solution, leading to a dendritic overstructure on the dendritic matrix (Figure 2). Dendrite arm coarsening is clearly visible in Figures 3 and 4. Faceted growth is also observed in Figure 4. An orientation difference between neighbouring grains of the matrix is revealed in Figure 5.

Characteristics of dendritic solidification are easily detected on the dendrite occupying the main grain of interest. The light areas, that is the dendrite spines, are rich in nickel, whereas the darker areas contain more copper. The primary dendrite arm, which is nearly 2 mm long, has about 20 secondary arms projecting at right angles from its stem. The secondary arm spacing, which is the distance between the centres of adjacent secondary arms, can thus be calculated as nearly 0.1 mm (100 $\mu$m). It is also easy to detect the coarsening mechanism. Secondary arms bulging towards each other are in fact trapping others between, which eventually disappear. Signs of crystal multiplication can also be seen, although it is difficult to say whether there is partial fragmentation of the dendrite arms, since the angle of slicing the specimen could give images which may be misinterpreted.

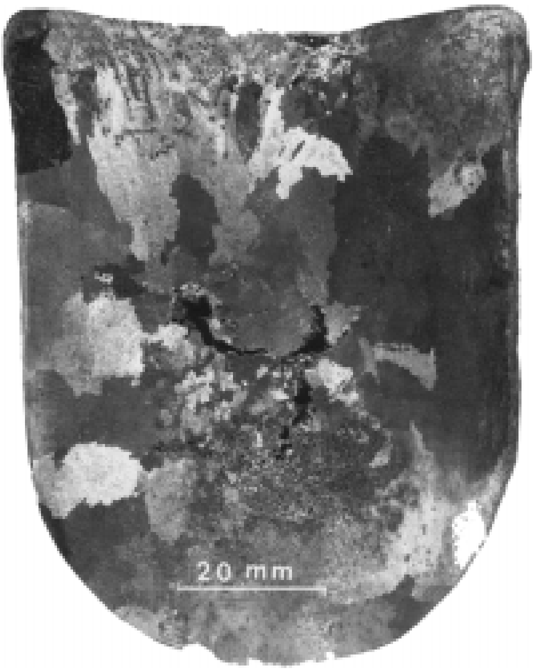


**Figure 1.** Large grains in a furnace-cooled ingot (Scale bar = 20 mm).

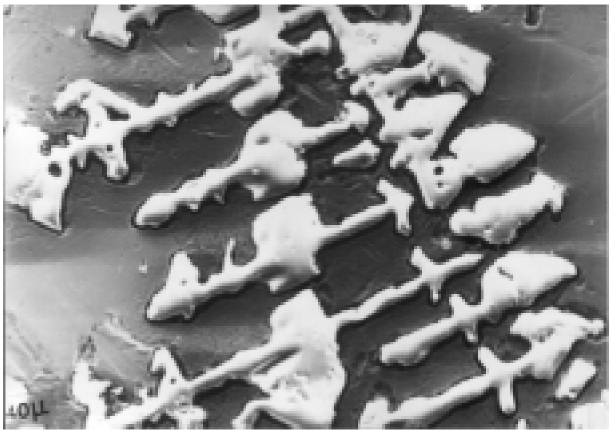

**Figure 2.** Dendritic overstructure (Scale bar = 40 $\mu$m).

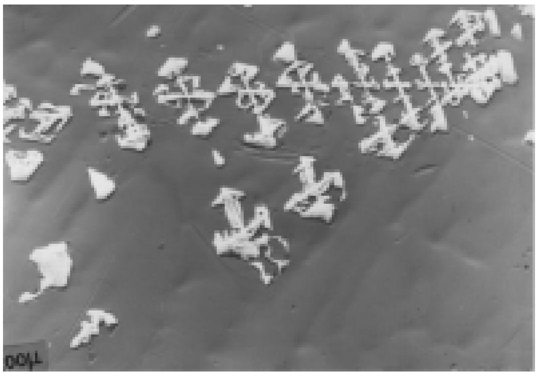

**Figure 3.** Dendrite coarsening in the furnace-cooled ingot (Scale bar = 200 $\mu$m).

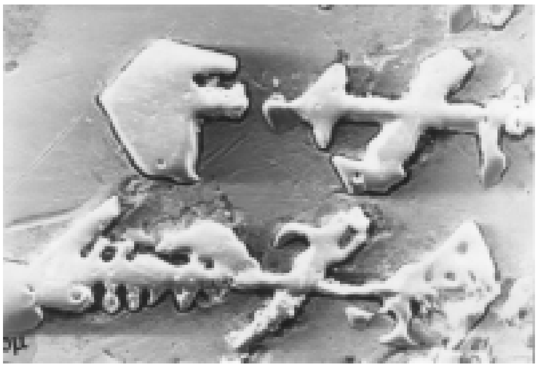

**Figure 4.** Faceted growth in furnace-cooling (Scale bar = 40 $\mu$m).

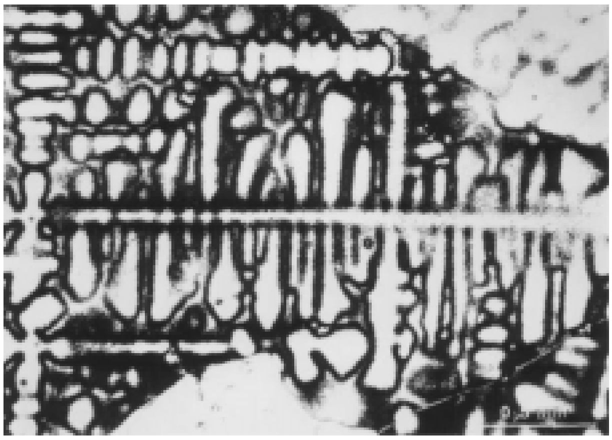

**Figure 5.** Orientation difference in the furnace-cooled ingot (Scale bar = 0.5 mm).

Oblique light was found to assist in showing the cored microstructures of sand castings. Long primary dendrite arms and coarse fragments of single dendrites are the characteristic features of this cooling rate (Figure 6). A group of dendrites originating from the same point is visible too. Secondary and tertiary arm coarsening is another important feature. Grain boundaries are hard to detect but they can be visualised by following the orientation difference of dendrites within neighbouring grains. An average secondary dendrite arm spacing of 0.075 mm (75 $\mu$m) was measured.

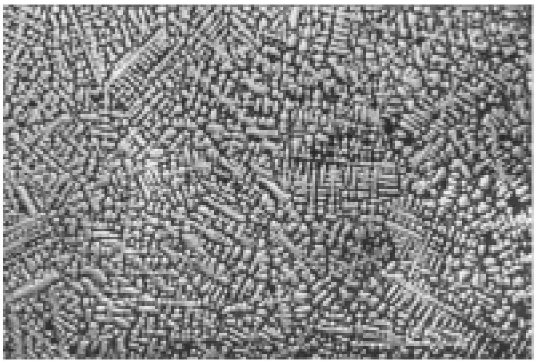

**Figure 6.** Cored microstructure of sand-cast material (Scale bar = 1 mm).

The microstructure of chill castings can be seen in Figure 7 on the composite made up of 36 micrographs. Coring is less significant in this cooling range, and so direct illumination could be employed. A variety of dendrite shapes which can be roughly expressed as X-shaped, T-shaped and twinned dendrites and dendrites originating from one point show most of the basic figures. Fragments of single dendrites are visible all over the structure. Secondary arm spacings in this structure range between 25 and 30 $\mu$m.

A close-up of the composite shows that the dendrite coarsening mechanism is still operative at this higher cooling rate (Figure 8). The disappearance of secondary and tertiary dendrite arms in favour of their more fortunate neighbours causes coarsening of the latter. The grain boundary, limiting the growth of dendrite arms in each direction, is clearly visible too. Secondary dendrite arms, growing from the primary arms and at right angles to them, limit the extension of each other in the grain. The growth of secondary and tertiary arms is favoured at one side of some of the primary arms due to the direction of solidification and the lack of space for growth. The microstructure of a semi-continuously cast hollow bar is shown on a composite in Figure 9.

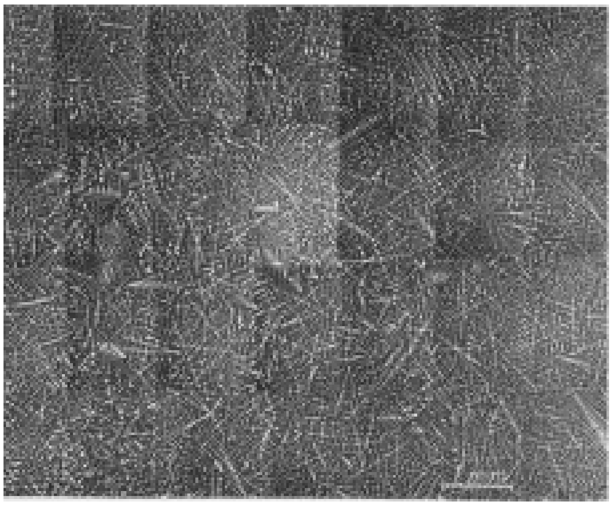

**Figure 7.** Microstructure of chill casting (Scale bar = 1 mm).

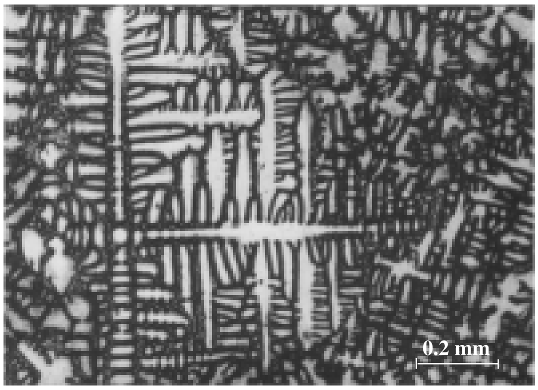


**Figure 8.** A close-up of Figure 7 (Scale bar = 0.2 mm).

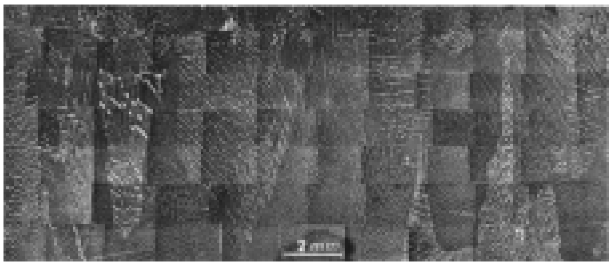


**Figure 9.** Microstructure of semi-continuous casting (Scale bar = 2 mm).

The interior of the bar (top) has a coarser structure due to a comparatively slower rate of heat extraction. The exterior is much finer due to the chilling effect of the running water. Single dendrites dominate the coarser structure whereas large grains of arrays of dendritic elements within them are features of the finer region. Grains with different orientations show different dendritic features. Some of the dendrites grow as unbranched needles; the secondary arms are either primitive or absent. Dendrite fragmentation is minimal. The close-ups of the composite reveal various types of dendritic elements in Figures 10 a,b,c.

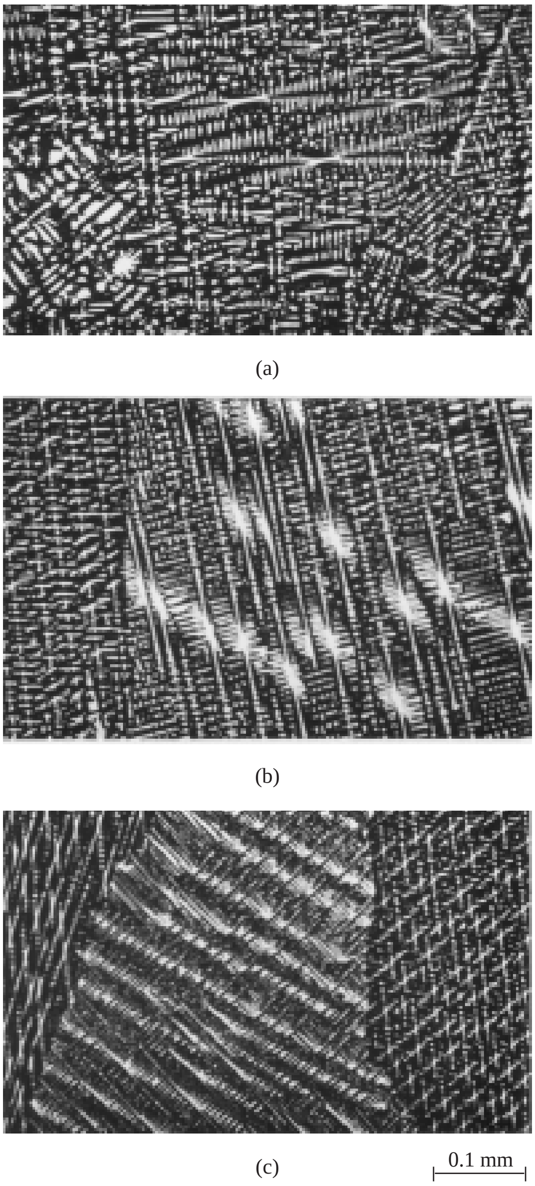


**Figure 10.** Close-ups of semi-continuous casting (Scale bar = 0.1 mm).

Coarsening is apparent only in the slowly cooled region (a). Primary dendrite arms are aligned in specific directions in each grain of the finer part of the structure (b,c). Very sharp changes in crystallographic orientation between neighbouring grains are clearly visible (c). Growth of secondary dendrite arms in some grains is favoured in specific directions (b). Dendrites following the path of similar ones (b,c), thus making a regular pattern, are another feature of this alloy, which solidified much faster than the previous statically cast ingots. Secondary arm spacing of the finer regions is between 8 and 10 $\mu$m.

## Discussion

Coring is the dominant solidification characteristic of copper-nickel alloys. The degree of undercooling, hinderance of diffusion and convection mechanisms lead to microsegregation of nickel and copper in the structure. The rate of solidification controls the undercooling, diffusion and convection mechanisms to produce dendrites of different arm spacings.

The furnace cooled alloy which solidifies with very little or negligible undercooling facilitates the formation of initial solids with the highest nickel content. Dendrites are nucleated in very small volumes. The balance of copper left in the liquid in such volumes is immediately carried away by diffusion and replaced with nickel diffusing back from the bulk liquid. Dendrites gradually coarsen with further build-up of solid on the skeleton. The copper-enriched liquid approaches the solidus at a similar rate, enabling the interdendritic areas to solidify with the minimum nickel content possible. This microsegregation of regions with maximum and minimum nickel contents leads to strong coring.

The slow rate of solidification of the sand cast alloy also leads to strong coring. The degree of undercooling is still low, producing a dendrite composition close to maximum nickel content. Apart from strong diffusion, convection plays a role in the production of the final structure. Turbulent introduction of the molten metal into the mould cavity initiates fluid motion at the beginning of solidification. Thus the initial solids produced at low undercoolings are distributed throughout the structure. Dendrite arms which form and remelt continuously are carried away by convection to promote solidification in several other regions. As the convection ceases, diffusion eventually takes over the transport of nickel and copper to and from the coarsening dendrites. The solidification period is long enough for the diffusion process to allow the arms to coarsen with the attachment of nickel-rich solids while extending into the surrounding liquid.

The greater undercooling in chill casting decreases the maximum nickel content which can be achieved in the initial dendrites. Diffusion is very limited because of the very short solidification time. A mushy zone is produced in front of the solidifying skin. Convection is the only means of solute and solvent movement. It even separates dendrites from the solidifying skin and carries them through the mushy zone. These dendrites are entrapped in the mushy zone when the latter solidifies as a whole in the last stages of solidification. Thus the maximum and minimum contents do not differ greatly.

Neither diffusion nor convection have enough time to alter the structure of semi-continuously cast material developed after a large undercooling. The solidification can be analysed in 5 short steps between initiation and completion: (a) initial solids form adjacent to the mould wall, leaving a solute-rich area ahead of them, (b) perturbations quickly probe into the solute-rich area, (c) arrays of dendrites extend into the solute-rich area, (d) interdendritic areas which cannot be fed by the bulk liquid at the centre of the billet solidifies, and (e) the final liquid solidifies comparatively slowly to give a coarser structure in the centre.

## Conclusions

The degree of microsegregation in Cu-Ni alloys is significantly influenced by the rate of solidification. Slow rates of solidification result in low undercooling which in turn produces initial dendrite arms rich in nickel content within the bulk liquid. Diffusion and convection mechanisms maintain a uniform composition in the liquid throughout the solidification period by carrying the rejected copper away from the dendrite arms and new supplies of nickel to nickel depleted areas in the adjoining liquid. Dendrite arms coarsen, accompanied by absorption of the transported nickel whilst the liquid to solidify last produces relatively large pools of copper enriched material in the interdendritic regions.

Higher degrees of undercooling resulting from the faster solidification rate obtained in semi-continuously cast material lead to a comparatively lower nickel content in the dendrite centres than in the more slowly solidified material and consequently to a more homogeneous structure. The restriction of diffusion and convection to very short times produces copper-rich areas enveloping the dendrite arms. Dendrite arms probe into these constitutionally supercooled regions, developing long and thin primary arms. Close spacing of the latter hinders the development of secondary arms in the narrow volumes of liquid remaining.

The degree of microsegregation and properties obtained at various locations within the microstructure of chill cast material vary over a range between the sand cast and the semi-continuously cast materials.

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