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The Influence of Cold Working and Recrystallization on the Homogenization of As-cast Cu-50 wt.% Ni Alloy

The effects of cold working and recrystallization on the homogenization of a Cu-50 wt.% Ni alloy have been investigated by electron probe microanalysis and other complementary techniques. The occurrence of homogenization has been explained by the synergism of 3 factors: deformation alters interdendritic spacing and diffusion distances, crystalline defects enhance diffusion and microstructure sweeping by grain boundaries during recrystallization assists solute redistribution by grain boundary diffusion.

Die Einflüsse von Kaltverformung und Rekristallisation auf die Homogenisierung einer Cu-50 Gew.-% Ni-Gußlegierung

Die Einflüsse von Kaltverformung und Rekristallisation auf die Homogenisierung einer Cu-50 Gew.-% Ni-Gußlegierung wurden mit Hilfe von Elektronenstrahlmikroanalyse und anderen komplementären Methoden untersucht. Das Auftreten der Homogenisierung wurde durch das Zusammenwirken von drei Faktoren erklärt. Durch die Verformung ändern sich der interdendritische Abstand und die Diffusionswege, Gitterbaufehler beschleunigen die Diffusion, und das Durchlaufen des Gefüges von Korngrenzen während der Rekristallisation vereinfacht die Umverteilung des Mischkristalls mittels Korngrenzendiffusion.

1 Introduction

The conventional solidification of any alloy which shows a finite freezing range produces a dendritic morphology and a solid non homogeneous in composition. The dendritic growth is caused by rejection of solute by the growing solid, which lowers the melting temperature. The undercooled liquid then becomes susceptible to dendritic growth. When small ingots are melted in laboratory, microsegregation or coring can be significantly reduced or even eliminated by diffusion during homogenization heat treatment. For larger industrial ingots the interdendritic spacings and diffusion distances are also larger and segregation elimination is considerably more difficult.

The effect of plastic deformation on homogenization has not been much studied and there is no general agreement on this subject. Weinberg and Buhr [1] studied the homogenization of AISI 4340 steel and concluded that previous deformation had a small effect on its homogenization kinetics. According to these authors, plastic deformation hardly produces a substructure of crystalline defects sufficiently dense and stable to affect diffusion significantly. Cole [2] suggests that plastic deformation by rolling or forging can shorten diffusion distances and therefore promote homogenization. On the other hand, although plastic deformation can reduce diffusion distances in certain directions, it might increase in other directions [3]. Falleiros [4] studied the homogenization of commercially pure aluminum ingots and observed homogeneous areas caused by grain boundary migration. The sweeping of the microstructure by grain boundaries during recrystallization can assist diffusion through the grain boundaries and stimulate solute redistribution. The alloy used by Falleiros had intermetallic particles which intervened with grain boundary migration. In this work, a Cu–Ni alloy of nearly equiatomic composition, without particles, and presenting a high segregation level for conventional casting conditions, was used [5 to 7]. The effect of moderate reductions introduced by cold working and large deformation caused by fine file grinding was studied. Deformation by grinding produces extremely high levels of crystalline defects in the chips which cannot be reached by conventional processes of mechanical forming.

2 Experimental Procedure

The Cu–Ni alloy used in this work contained approximately 50 wt.% Ni and 75 ppm oxygen, and were prepared by

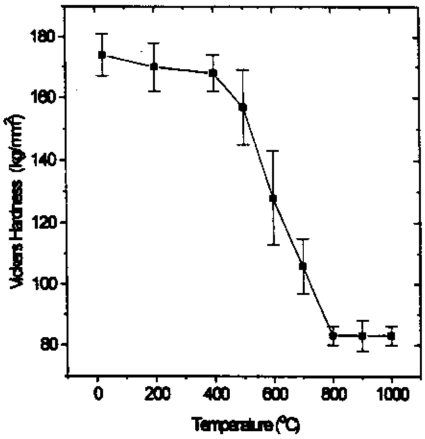


Fig. 1. Temperature dependence of the Vickers microhardness (1 kg load) for an as-cast sample after 33 % reduction in thickness by rolling. The constant time for each temperature was 1 h.

vacuum induction melting of electrolytic copper and nickel, followed by casting in $60 \times 60 \times 180\ \mathrm{mm}^3$ cast iron moulds.

Specimens were taken from the as-cast ingots and annealed at 1000 °C for 48 h and at 900 °C for 5 h.

To investigate the effect of cold working on recrystallization, alloy plates being approximately 9 mm thick and 15 mm wide were cut off from the central region of as-cast ingots and moderately cold worked by rolling in five steps with an average reduction in thickness of 35 % per step. All deformation steps were followed by a recrystallization treatment at 900 °C for 1 h. To insure complete recrystallization before the next rolling step, a softening curve was determined (Fig. 1). Severely deformed alloy filings were obtained by grinding the as-cast ingots with a fine file. The heavily deformed filings were sealed in quartz ampoules with zirconium chips, and treated at 600 °C for 1 h.

Nine ingot areas were analysed for macrosegregation by the use of X-ray fluorescence. Microstructural analysis was carried out by optical microscopy, EPMA, XRD, DSC and Vickers hardness measurement. Metallographic specimens were etched with a solution of 100 ml ethanol, 25 ml hydrochloric acid and 6 g ferric chloride. Porosity was evaluated by hydrostatic porosimetry. Microsegregation and homogenization were investigated by EPMA. Copper and nickel contents were determined using a LiF crystal, 25 kV and 5 s counting time. The ZAF method was employed to correct for atomic number, absorption and fluorescence. About 2000 points were analysed by this procedure.

The homogeneity degree was estimated, based on a segregation index I_S, defined as:

$$I_S = \frac{(C_{\max} - C_{\min})}{(C^0_{\max} - C^0_{\min})}$$

in which:

$C_{\max}$ =solute maximum concentration at time t

$C_{\min}$ =solute minimum concentration at time t

$C^0_{\max}$ =solute maximum concentration at initial state

$C^0_{\min}$ =solute minimum concentration at initial state

3 Results and Discussion

3.1 As-cast Alloy

Even though the X-ray fluorescence measurements on nine ingot regions, shown in Table 1, did not indicate severe macrosegregation, samples were always taken from the center and from regions located at half distance between the center and the surface of the ingots.

Table 1. Chemical composition measured by X-ray fluorescence at various ingot locations (wt.%).

	center	half distance between centre and surface	surface	mean
top	44.1	49.1	49.2	47.5 ± 2.9
centre	49.1	48.3	48.4	48.6 ± 0.4
bottom	44.9	49.3	48.3	47.5 ± 2.3
mean	46.0 ± 2.7	48.9 ± 0.5	48.6 ± 0.5	47.9 ± 2.0

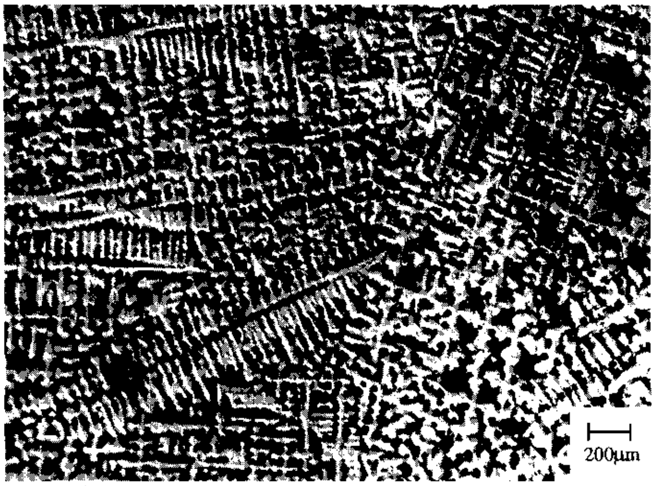


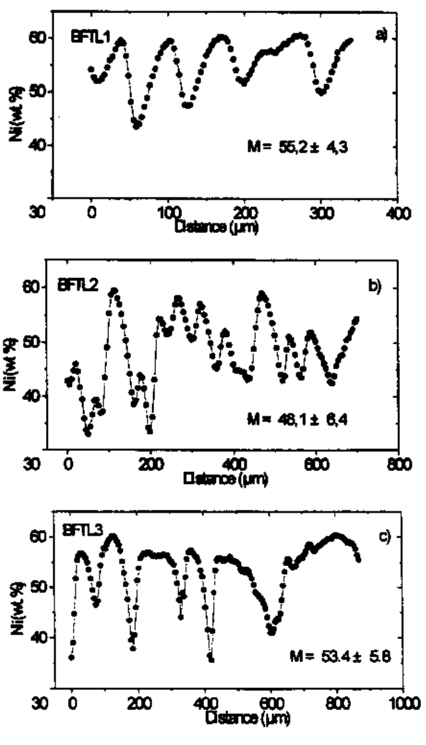
Fig. 2. Optical micrograph of the transversal section of the ingot. Ferric chloride etchant.

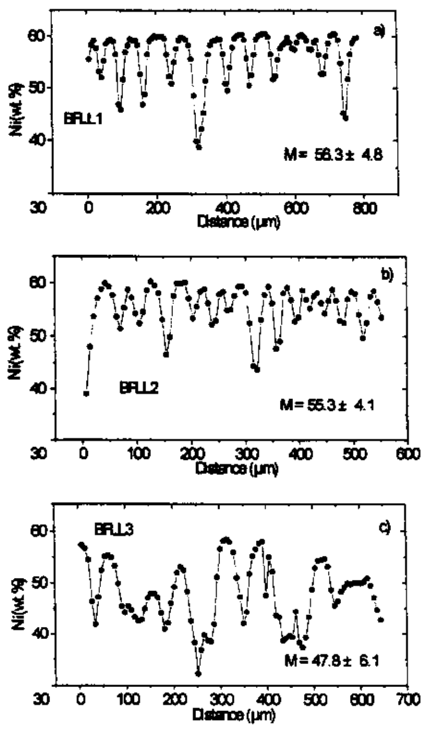
The dendritic structure of an as-cast ingot contained a large number of pores, as shown in Fig. 2. The density of the alloy, determined by XRD, was found to be 8.96 g/cm^3. The pore concentration, determined by hydrostatic density measurements, was about 6 vol. % and was comparable to that obtained by employing quantitative metallography. Average secondary dendritic arm spacing measurements showed substantial scattering and were about 80 µm on the ingot transversal section and about 60 µm on the longitudinal section. Figure 3 presents the nickel concentration corresponding to three different regions on the transversal section of a selected sample. The average and standard deviation values for the set of measurements from a given profile are indicated by M.

Figure 4 shows the variation of composition in dependence on the distance for three regions on the ingot longitudinal section. Profiles along the longitudinal section showed lower minimum and maximum concentration differences than those obtained along the transversal section. Wavelengths along the longitudinal direction were also shorter than those along the transversal direction.

3.2 Effect of Deformation by Rolling on Homogenization

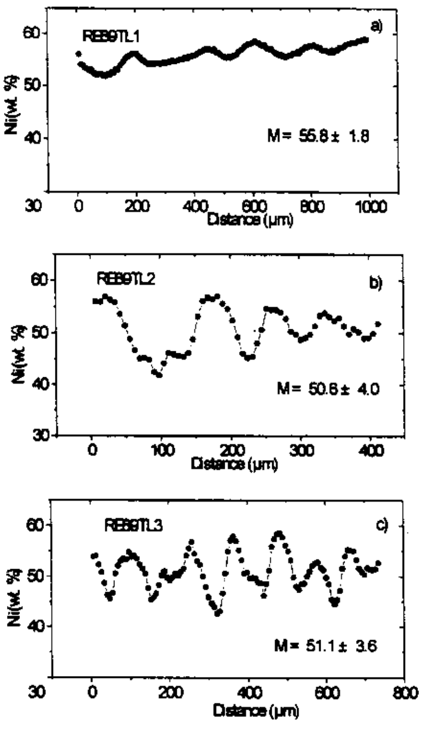
Figure 5 shows nickel concentration profiles corresponding to the transversal section of a sample, subjected to the five-step deformation/recrystallization treatment, and Fig. 6 shows similar data for an as-cast sample annealed at 900 °C for 5 h. Segregation indices obtained from the data of Figs. 5 and 6 were 0.66 and 0.83, respectively, indicating that the deformation/recrystallization treatment effectively contributed to the homogenization of the alloy. There are at least two plausible explanations for the previous observation. First, crystalline defects created during the deformation process promote volume diffusion. Second, as proposed by Falleiros [4], during the process of recrystallization, the sweeping of the microstructure by a migrating grain boundary may enhance solute redistribution, since the diffusivity of the latter along the boundary is faster.



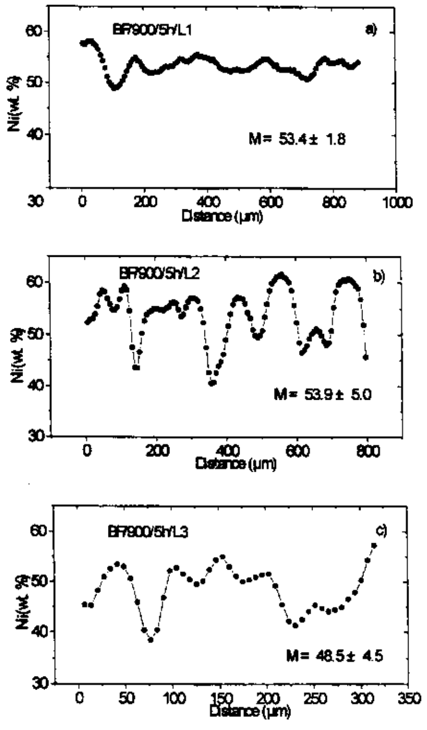


Figs. 3a to c (left). Nickel concentration profiles along the transversal section of an as-cast ingot. (a) EPMA measurement across secondary dendrite arms taken at 3.5 μm intervals; (b) and (c) EPMA measurements taken at 5 μm intervals along randomly selected lines.

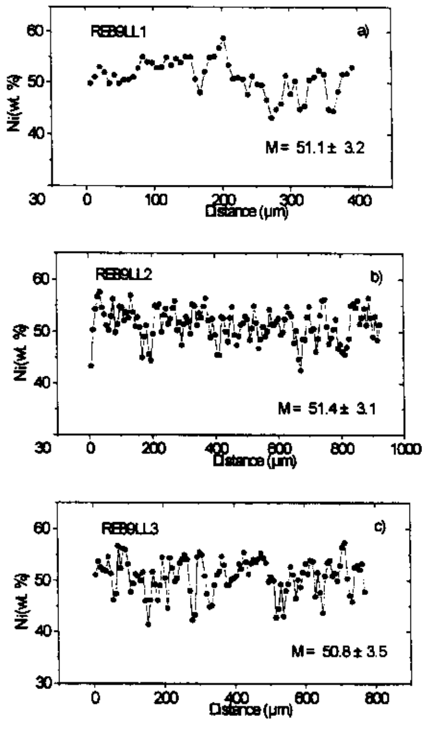
Figs. 4a to c (right). Nickel concentration profiles measured on the longitudinal section of an as-cast ingot. EPMA measurements taken at 7 μm intervals along randomly selected lines.



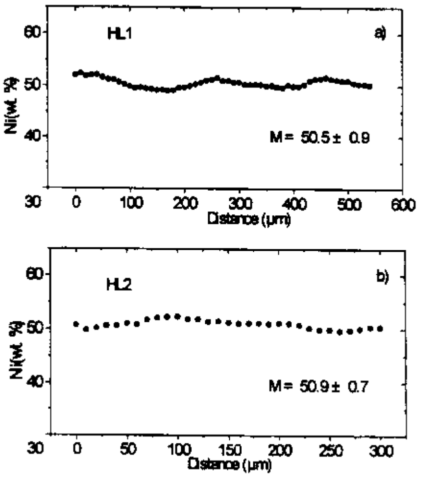
Figs. 5a to c. Nickel concentration profiles corresponding to three different regions on the transversal section of an as-cast sample subjected to 5 cycles of deformation/recrystallization. The total reduction in thickness was about 89 %. The points are spaced by 7 μm.



Figs. 6a to c. Nickel concentration profiles corresponding to three different regions on the transversal section of an as-cast sample heat treated at 900 °C for 5 h. The points are spaced by 7 μm.



Figs. 7a to c. Nickel concentration profiles corresponding to three different regions on the longitudinal section of an as-cast sample subjected to 5 cycles of deformation/recrystallization. The total reduction in thickness was about 89 %. The points are spaced by 7 μm.



Figs. 8a and b. Nickel concentration profiles for two different regions on the transversal section of an as-cast ingot sample annealed at 1000 °C for 48 h. The spacing between the points is 10 µm.

Nickel concentration profiles along the longitudinal section of the specimen of Fig. 7 yielded a slightly lower microsegregation index of 0.61. Metallographic examination of that section showed a significant reduction in the average secondary dendrite arm spacing with increasing deformation.

In addition to promoting homogenization, deformation by rolling reduced the porosity of the specimen. From an initial value of about 6 % in the as-cast condition, the pore volume decreased to about 3 % after the first cycle and to about 1 % after the second cycle of the cold working/ recrystallization treatment. Some residual porosity, however, was measured even after the fifth cycle of that treatment.

A microsegregation index of 0.12 was measured for an ingot specimen annealed at 1000 °C for 48 h. Concentration profiles for that specimen are presented in Fig. 8. The annealing time required to reduce the microsegregation index to 0.05 can be estimated by means of the equation $t_{0.05} \cong 0.3\lambda^2/D_S$ [9]. The diffusion coefficient is $D_S = 4.7 \times 10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ [8]. If the dendrite arm spacing is assumed to be 80 µm and the homogenization temperature is taken as 1000 °C, then the required annealing time is estimated to be 110 h. This value is in agreement with the current results.

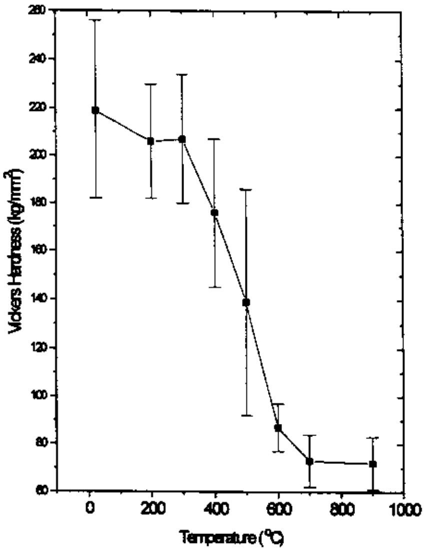
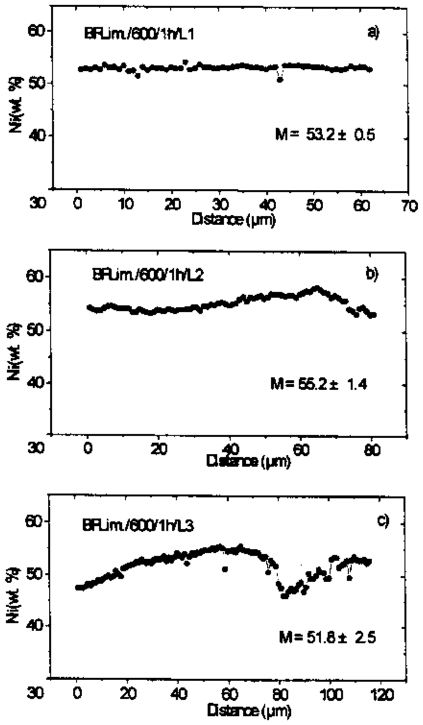


Fig. 9. Temperature dependence of the Vickers hardness (0.05 kg load) for as-cast ingot filings. The constant time for each temperature was 1 h.

3.3 Effect of Severe Deformation by Filing on Homogenization

Grinding introduces a massive amount of crystalline defects in ductile metals and alloys. Such defect concentrations cannot be achieved by deformation processes such as rolling, drawing, forging and extrusion. In terms of defect concentration, grinding by filing may represent an intermediate situation between conventional deformation processes and mechanical alloying. During mechanical alloying, there is a significant broadening of XRD peaks, which is followed by amorphous phase formation [10, 11]. In this work, large XRD diffraction peak broadening was observed after step scanning the peak corresponding to the (311) plane with 0.02 degree steps and counting times of 20 s. Figure 9 shows the softening curve corresponding to the alloy filings. The initial hardness was substantially higher than that of the cold worked sample. This is shown by comparing Figs. 1 and 9. Recrystallization of the alloy filings was complete after 1 h at 600 °C or 200 °C below the recrystallization temperature of a cold worked sample.



Figs. 10a to c. Nickel concentration profiles corresponding to as-cast ingot filings annealed at 600 °C for 1 h. The spacing between the points is 1 µm.

Metallographic observation of work hardened alloy filings revealed the presence of several deformation bands. After annealing at 600 °C for 1 h, a fine grained structure similar to the microcrystalline structure obtained by melt spinning was observed. The recrystallization of alloy filings was also investigated by means of differential scanning calorimetry (DSC). The energy release by the alloy filings during recrystallization was much larger than that liberated by copper and its alloys, provided they were deformed by conventional methods [12, 13]. This observation seems to be correct even if the imprecision of the calorimetric method is accounted for and is, therefore, an indication of the high density of crystalline defects in the alloy filings.

The nickel concentration profiles measured on alloy filings after annealing at 600 °C for 1 h are shown in Fig. 10. Homogenization occurred to a large extent and I_S decreased to 0.30.

The occurrence of considerable homogenization at temperatures as low as 600 °C may be explained by the combination of three factors: (i) severe deformation alters characteristic diffusion distances to a great extent; (ii) the contribution of pipe diffusion is significant at high dislocation densities; (iii) during recrystallization, as the migrating grain boundaries sweep the microstructure, they may provide faster diffusion paths for the solute, thus enhancing its redistribution.

4 Conclusions

(i) The ingot which was prepared by conventional means showed a high degree of microsegregation (absolute concentration differences superior to 20 %) and porosity of approximately 6 %.

(ii) Ingot annealing at high temperature for long periods (1000 °C for 48 h) caused a significant decrease in microsegregation ($I_S = 0.12$). Annealing at lower temperatures and for shorter periods (900 °C for 5 h) caused a slight reduction in the microsegregation degree ($I_S = 0.83$).

(iii) Five cycles of moderate deformation by cold rolling (mean thickness reduction of approximately 35 % per cycle) and recrystallization annealing (900 °C for 1 h) resulted in great decrease in porosity and mean grain diameter. However, they caused only a moderate decrease in the microsegregation degree ($I_S = 0.66$), although it was larger of specimens with no deformation.

(iv) Comminution by filing produced high cold working in chips, recrystallization at low temperatures and very fine recrystallized grains. Annealing of chips at a rather low temperature for short time (600 °C for 1 h) caused a comparatively high homogenization degree ($I_S = 0.30$).

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