

EFFECT OF COOLING RATE AND GRAIN REFINEMENT ON THE MICROSEGREGATION IN Al-4.8 wt.% Cu ALLOY

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Abstract: Microsegregation is one of the most important phenomena occurs during solidification. It usually results in formation of some unexpected second phases which generally affect the mechanical properties and specially reduce the workability of casting products. The aim of this research is to study the effect of cooling rate and grain refinement on the microsegregation in Al-4.8 wt.% Cu. For this purpose two series of experiments were designed. In the first set of experiments, the alloy was melted and cooled in three different rates, i.e. 0.04, 0.42, and 1.08 K/s in a DTA furnace. In the second series of experiments, the effect of grain refinement on the microsegregation at a constant cooling rate of 0.19 K/s was investigated. Al-5Ti-1B master alloy was used as grain refiner. Results showed that by increasing the cooling rate the amount of non-equilibrium eutectic phase increases from 5.1 to 7.4 wt.%, and the minimum concentration of solute element in primary phase decreases from 1.51 to 1.05 wt.% Cu. By grain refinement of the alloy, the amount of non-equilibrium eutectic phase decreases from 5.5 to 4.7 wt.%, and the minimum concentration of solute element in the primary phase increases from 0.98 to 1.07 wt.% Cu. So it is concluded that increasing cooling rate in the range of 0.04 to 1.08 K/s, increases and grain refinement reduces the microsegregation.

Keywords: Cooling Rate, Microsegregation, Grain Refinement, Al-5Ti-1B Master Alloy.

1. INTRODUCTION

Generally, it is difficult to get perfect equilibrium situation during solidification of alloys, because the microsegregation by non-equilibrium solidification always occurs except for a few cases [1]. Microsegregation is the chemical inhomogeneity at the scale of a grain size or a dendrite arm, and is a result of non-equilibrium solidification of alloys. It is a hot research topic and both experimental and modelling approaches are employed to investigate the concentration profile along dendrite arms and the type and fractions of the interdendritic phases, because of their great importance for downstream processing and mechanical properties [2–4]. It is clear that back diffusion in the solid is important in the formation of microsegregation, and the diffusion in the liquid is insignificant upon normal casting conditions [1, 5]. The extent of microsegregation in the alloy structure is determined experimentally by measuring one of the followings: (a) amount of non-equilibrium eutectic (NEE), (b) amount of non-equilibrium second phase, (c) minimum solid composition,

(d) composition vs fraction solid profiles. The first theoretical treatment of microsegregation is given by the classical non-equilibrium solidification, or "Scheil", equation, which is based on the assumptions of complete mixing in the liquid but no diffusion in the solid [6–8]. The Scheil equation predicts generally greater microsegregation than that found experimentally. The first quantitative analysis of microsegregation with the solid state diffusion effect was made by Brody and Flemings [9]. Ever since, the subject of microsegregation has been addressed by many researchers including analyses by Clyne and Kurz [10], Solari and Biloni [11], Basaran [12], Kirkwood [4], Roosz [13, 14], Matsumiya [15], and Mortensen [16].

The aim of the present research is to study the effect of cooling rate and grain refinement on the microsegregation in Al-4.8 wt.% Cu. In most studies only the NEE phase content is considered as the criteria for quantification of microsegregation level [2]. But in this study, for quantitative analysis of microsegregation, two criteria were considered: the NEE phase content and the concentration profile in primary phase (α_{Al}). This profile provides complete

microsegregation information, including minimum composition, eutectic fraction, and the distribution of the solute element atoms in the primary phase.

2. EXPERIMENTAL PROCEDURE

The binary Al-4.8 wt.% Cu alloy was used in this study. To study the effect of cooling rate and grain refinement on the microsegregation, two sets of solidification tests were performed as follows: The first set of experiments was designed to investigate the effect of cooling rate on microsegregation. Specimens with dimensions (D×H) 22×20 mm and ~10 g weight were melted and solidified in a DTA furnace. To create of different cooling rates, three experiments were designed as follows: In the first experiment the sample was cooled inside the furnace (slow cooling rate 0.04 K/s). In the second experiment, in order to increase the cooling rate, the sample was cooled outside the furnace (medium cooling rate 0.42 K/s). In the third experiment, increase of the cooling rate was obtained by compressed air injection into the sample chamber (fast cooling rate 1.08 K/s). High purity argon gas (99.999%) was running throughout the tests to reduce the risk of oxidation of the samples. The cooling rate was calculated by the method proposed by Skin et al. [2], by dividing the total solidification range ($T_L - T_S$) to the local solidification time. The required data for this purpose can be extracted from the thermal analysis results. In the second set of experiments; the effect of grain refinement on microsegregation was studied. To do this, alloy was melted in a graphite crucible by an electric furnace and melt was held at 993 K for 10 min. Commercially available Al-5Ti-1B was used as grain refiner and added to the melt at last stage of melting. For homogenous distribution of the grain refiner in the melt, it was stirred with alumina rod and held in 993 K for 5 min. The melt was then cast in a 373-473 K preheated sand mold and solidified at cooling rate of 0.19 K/s.

In order to study the microstructure, solidified samples were cut and prepared by the convenient metallographic techniques, and then etched with Keller's (10 mL HF, 20 mL HNO₃, 20 mL HCl,

and 50 mL distilled water) and Weck's (3g potassium permanganate, 1g sodium hydroxide and 100 mL water) reagents. Quantitative analysis was used to measure the NEE phase content, grain size and SDAS (secondary dendrite arm spacing) from optical and SEM micrographs by using of "Clemex vision" software. The SDAS and the grain size were calculated using standard linear intercept method. For quantitative analysis of microsegregation in both series of experiments, two criteria were considered: the amount of NEE phase and the concentration profile in primary phase (α Al). The amount of NEE phase was measured by Clemex software using as-polished back-scattered electron (BSE) SEM images; about 8 images were analysed for each specimen. SEM/EDS point analysis was used to investigate the concentration profile in the primary phase. In order to have a statistically significant concentration profile in the solid, around 100 points were analysed for each sample. These data were processed to obtain concentration profiles in the solid based on the method proposed by Gungor [3,17].

The NEE phases content and concentration profile in the primary phase were also calculated by PanDat software and Scheil equation. The PanDat simulation considers limited solid and liquid diffusivity using the realistic solute diffusivities, (PanDat also uses the Scheil model with minor correction such as k_0 , it uses an internal thermodynamic database for calculations) whereas the Scheil model is derived based on the assumptions of no diffusion in the solid and infinite diffusion in the liquid [18]. The Scheil equation is defined in equation (1) where C_s , C_0 , f_s , and k_0 are composition of solid, nominal composition of the alloy, solid fraction, and equilibrium partition coefficient. Equation (1) is that form of the Scheil equation which relates the solid composition to the solid fraction and it can be used to calculate the concentration profile in the primary solid phase. It can be rewritten in the form that is based on the composition and the fraction of liquid (equation (2)) which can be used to calculate the eutectic fraction; composition of liquid replaced by the eutectic composition and then the fraction of

liquid is the eutectic fraction.

$$C_S = C_0 k_0 (1 - f_s)^{-(1-k_0)} \quad (1)$$

$$C_L = C_0 f_L^{-(1-k_0)} \quad (2)$$

3. RESULTS

3. 1. Effects of Cooling Rate

The changes of microstructure were caused mainly by the different cooling rates of the sample. It is well known that the cooling rate plays an important role in the refinement of metal structures [2,19]. The effect of cooling rate on microstructural characteristics is shown in the table 1. By comparing the data in table 1, it can be seen that grain size, SDAS, and local solidification time decreases with increasing cooling rate.

SDAS decreases with increasing the cooling rate because of the following reasons: (1) Increasing the cooling rate increases the undercooling. So solidification starts at lower temperatures which leads to higher nucleation and lower growth rates. This situation causes the formation of more grains, so the grain size and consequently the dendrite arms will be finer. (2) Increasing the cooling rate causes the interface of the liquid and solid to move faster, so the ratio of the area to the volume of dendrite arms should increase to facilitate heat extraction. (I have no idea about this) (3) Increase of dendrite thickness is because of coarsening mechanisms which are dendrite arm ripening and coalescence. Both mechanisms are diffusional and need time. But,

when cooling rate increases there is not enough time for these phenomena [19]. This reflects the fact that SDAS and grain size depends on the cooling rate, and more specifically on the solidification time which decreases by increasing cooling rate.

3. 1. 1. Non-Equilibrium Eutectic Phase

The examined alloy solidified under equilibrium conditions should be single-phased. However, due to the microsegregation during solidification caused by incomplete diffusion processes and therefore incomplete mixing and redistribution of alloying components in solid and liquid phases, the liquid phase is enriched in the solute while the solid phase remains diluted. As a result, when the alloy reaches its equilibrium solidus during solidification, some liquid rich in the solute remains in the system. Giving a sufficient degree of microsegregation, the last liquid will solidify at the eutectic temperature thus producing NEE. This phenomenon can be observed even at very slow cooling rates of less than 0.1 K/s [20, 21]. Fig. 1 (a) shows the dendritic microstructure and Fig. 1 (b) with higher magnification shows NEE of the sample solidified at cooling rate of 0.04 K/s. The structure configurations for all samples at different experimental cooling rates were similar which consisted of α -Al dendrites and the interdendritic (α -Al₂Cu) eutectic. Because of microsegregation; isoconcentration contours (coring) are visible. The center of dendrite, corresponds to the darkest area where the solute content is the lowest (Fig. 1-a).

SEM/BSE images for the samples cooled with different cooling rates are shown in Fig. 2. Since the contrast of a BSE/SEM image is mainly due to the difference in mean atomic number, the phase with higher mean atomic number shows up brighter in the BSE/SEM image. Accordingly two types of phases can be distinguished in these micrographs. The dark phase is primary α Al and the white phase is Al₂Cu phase (due to its relatively high Cu concentration) which is precipitated during eutectic reaction and also from the primary α -phase during cooling to room temperature after the end of solidification. The

Table 1. Effect of cooling rate on local solidification time and microstructural characteristics

Cooling rate (K/s)	Local solidification time (s)	SDAS (μ m)	Grain size (μ m)
0.04	2740	324	3430
0.42	264	118	2052
1.08	115	54	1278

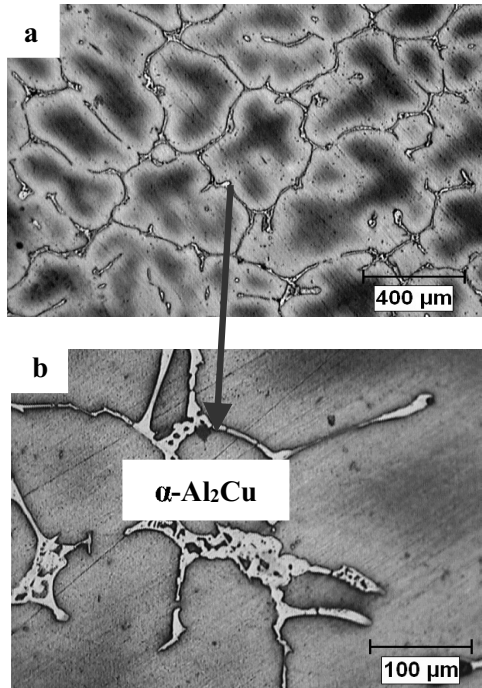


Fig. 1. Optical micrographs of the sample cooled with 0.04 K/s showing coring and the NEE phases. Cu-poor regions look darker (coring) and the NEE phases as bright phase. Sample was etched with Weck's reagent.

α -Al₂Cu eutectic phases distributed uniformly but discontinuously in the interdendritic regions. Experimental results of volume fraction of NEE phases for samples cooled with different cooling rates are shown in table 2. According to this table, it is found that amount of the α -Al₂Cu eutectic phases increases with increasing cooling rate. The amount of the α -Al₂Cu eutectic phases also was calculated using the PanDat simulation and Scheil model which are also included in Table 2. According to these calculations, it can be seen that the calculated results are about 20-40% higher than the experimental results. The Scheil equation predicts generally greater microsegregation than that found experimentally. The discrepancy between calculated and experimental microsegregation level arises from back diffusion in the solid and coarsening [3]. Back diffusion always acts to some extent during solidification and effectively reduces the microsegregation or the amount of NEE. Based on the data presented in table 2 it is evident that

Table 2. Effect of cooling rate on the fraction of NEE phase

Cooling rate (K/s)	NEE phase content (wt.%)		
	Image analysis	PanDat	Scheil model
0.04	5.1	8.2	9.1
0.42	5.7	8.2	9.1
1.08	7.4	8.2	9.1

the Scheil model or PanDat Calculations do not give good description of microsegregation [2,3].

3. 1. 2. Concentration Distribution Profile

During the primary dendritic solidification, the liquid concentration increases because of the solute partitioning at the S/L interface, leading to a continuous increase in concentration of the newly-

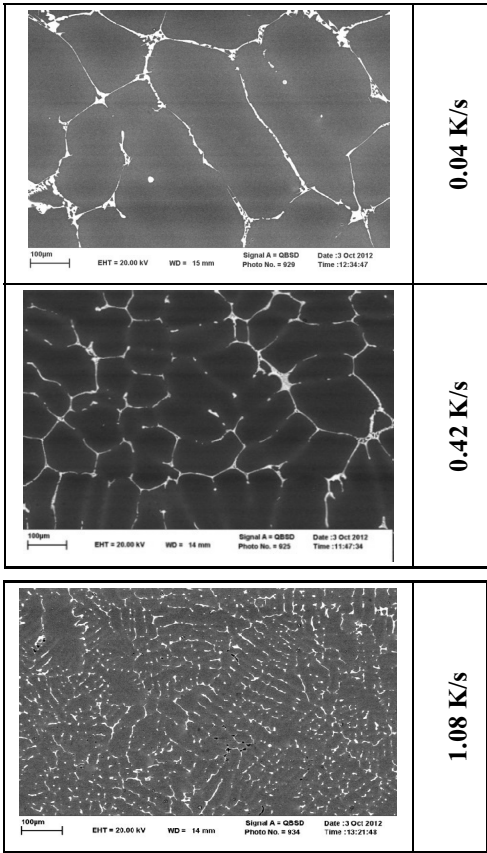


Fig. 2. BSE micrographs of the samples solidified with different cooling rate.

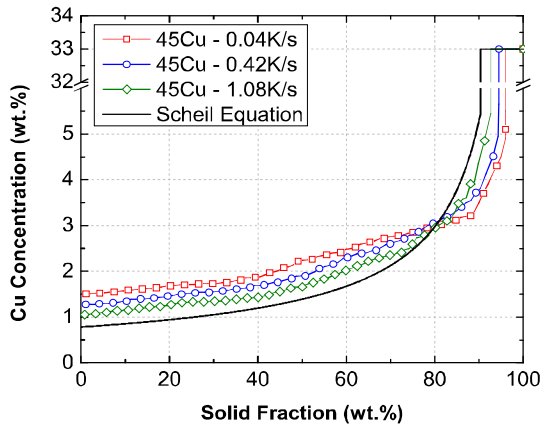


Fig. 3. Concentration profiles for the samples cooled with different cooling rates.

formed solid. Fig. 3 shows the experimentally measured concentration profiles of Cu as a function of the solid fraction at the different cooling rates along with the profile calculated based on the Scheil equation by assuming that $k_0 = 0.17$ and $C_0 = 4.8$ wt.% Cu. According to this figure, the concentration profile at highest cooling rate is closer to the curve calculated by Scheil model and as the cooling rate decreases the concentration profiles shift upward and amount of NEE (as has already been stated) decreases.

Severity of microsegregation is defined as the maximum concentration of the solute element divided by the minimum concentration (C_{max}/C_{min}) in the primary phase. As the C_{max} is usually considered the solubility limit at the eutectic temperature, which is constant, the value of C_{min} can then be considered as a criterion for quantification of microsegregation [22]. The lower the C_{min} is the higher the microsegregation will be. The values of C_{min} are reported in Table 3. It can be seen from the table that by increasing the cooling rate, C_{min} decreases which indicates the severity of microsegregation is increased. This is consistent with the previous results of the NEE content.

Cooling rate has two opposite effects on the solidification thermodynamics and kinetics. Effects of cooling rate on the thermodynamics of solidification are very complex and require a detailed thermodynamic analysis of the phase

Table 3. Minimum concentration and non- equilibrium partition coefficient for samples cooled with different cooling rates

Cooling rate (K/s)	C_{min} (wt.%)	k_0
0.04	1.51	0.31
0.42	1.28	0.27
1.08	1.05	0.22

diagram in different cooling rates. To reduce the complexity, in the current research, a constant partition coefficient is used during the whole solidification range. Partition coefficient can be defined by the following equation: $k_0 = C_{min}/C_0$. It should be noted that, these estimates are not in agreement with acceptable theories. The only difference between theoretical and practical estimation in this subject is due to the partition coefficient. However, in practice, mechanisms such as coarsening and back diffusion into solid are effective in the amount of C_{min} . However, when using these concepts, the results of calculation with Scheil equation are much closer to reality. The data obtained from this treatment is also provided in the table 3. It should be noticed that the kinetic effects are stemmed from the diffusion process. Increasing the cooling rate reduces the solidification and hence diffusion time, and at the same time reduces the scale of microstructure, i.e. diffusion distance. The first effect increases and second one decreases the microsegregation level. It is reported that if a large range of cooling rates is used, at first microsegregation increases with increasing cooling rate up to a certain cooling rate (the first effect is dominant) and beyond this critical cooling rate microsegregation decreases with increasing the cooling rate (the latter effect is dominant). Factors affecting the critical cooling rate are not understood yet and therefor different cooling rates have been reported as critical cooling rate [2]. It seems that the cooling rates investigated in the present study are less than the critical rate so the microsegregation increases with increasing cooling rate.

3. 2. Effects of Grain Refinement

Microstructure of the sample with no grain refinement and grain refined sample is shown in Fig. 4. For the case of no-grain refinement sample, the microstructure is consisted of very coarse grains with dendritic morphology. Grain refined sample, on the other hand, have a very fine equiaxed grain structure and no sign of dendrites can be seen in the structure. Generally at large grain sizes the grains are not equiaxed and tend to growth in certain crystallographic directions, but when growth is limited by either thermal or structural factors, equiaxed grain structure can be achieved (as can be seen in the microstructure of the grain refined sample).

The change in morphology may be interpreted in terms of the sever increase in active nucleation sites for α_{Al} grains and/or the high growth restriction factor (GRF) value [23-25]. The segregating power of an element is described by its GRF during solidification. The GRF is a

measure of the growth restricting effect of solute elements on the growing solid/liquid interface. It is defined as $mC_0(k_0-1)$, where m , C_0 , and k_0 are the liquidus slope, nominal composition of the alloy, and partition coefficient, respectively [26]. The value of GRF can be used to determine how important a particular solute addition is on the grain size. GRF value of titanium and copper are 245.6 and 2.8, respectively. Hence, small additions of titanium strongly decrease the grain size, while much larger amounts of copper are required for a similar effect [27]. The importance of dissolved titanium has also been realized by Li et al. [28]. They suggested that the powerful segregation ability of titanium as solute leads to a constitutionally under cooled zone in front of the growing interface within which nucleation can occur on nucleants that are present.

3. 2. 1. Non-Equilibrium Eutectic Phase

As has already been stated, copper content of the investigated alloy is less than the maximum solubility of copper at eutectic temperature (which is 5.65 wt.% Cu), so it is expected that the alloy should be solidified with a single phase structure (α_{Al}). The structure of the alloy with higher magnification is shown in Fig. 5. It can be seen that the microstructure contains some eutectic phases which implies that the solidification process was non-equilibrium. As it has already been mentioned, the content of the NEE phases can be considered as criteria for quantification of microsegregation; the higher the NEE content, the higher the level of microsegregation is [2]. The results of measurement of NEE content along with the calculated values are listed in Table 4. It is clear that the NEE content for grain refined sample is less than the sample with no-grain refinement. So it can be concluded that the grain refinement reduces the microsegregation level. The main mechanisms which frequently discussed in the literature that affect the microsegregation are back diffusion and coarsening [2, 29, 30]. For both mechanisms the diffusion plays an important role in two ways: diffusion time and diffusion distance. Diffusion time is directly related to solidification time which was not

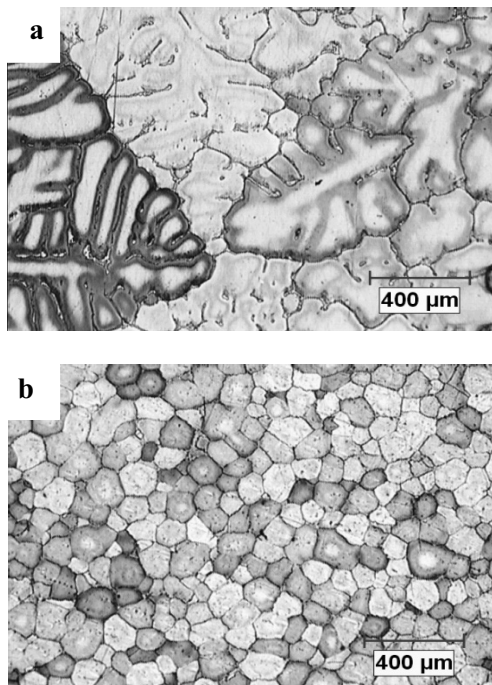


Fig. 4. Microstructure of the samples to study effect of grain refinement on microsegregation, a: no grain refinement and b: grain refined. Samples were etched with Keller reagent.

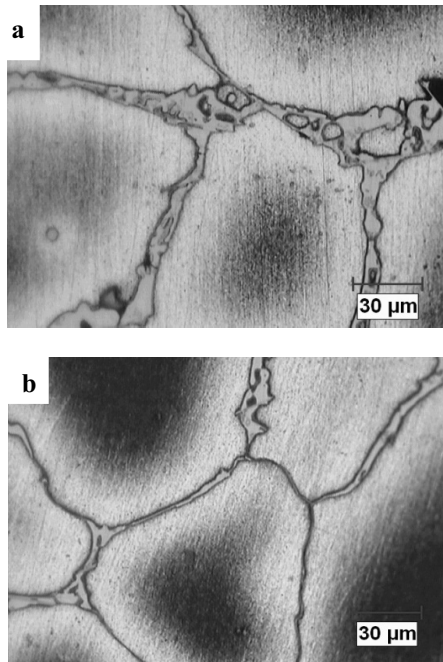


Fig. 5. Eutectic structure, a: no-grain refined, b: grain refined. Samples were etched with Weck's reagent.

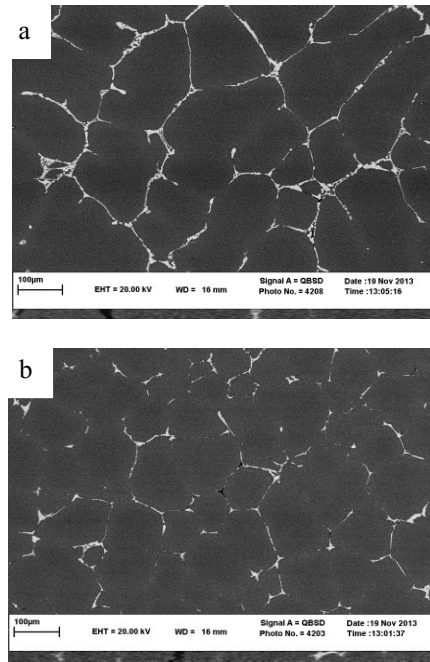


Fig. 6. SEM/BSE micrographs of the samples cooled with 0.19 K/s. a: sample with no-grain refinement and b: grain refined sample.

affected by the grain refinement. So the only effective parameter is diffusion distance which is related to the scale of microstructure. By grain refinement, the diffusion distance reduces and hence the level of microsegregation. Changing the interface morphology from dendritic (for sample with no-grain refinement) to planar (for grain refined sample) also affects the microsegregation level. It is usually believed that the dendritic morphology shows the most microsegregation level [20]. Fig. 6 shows the SEM/BSE images for the samples in the second

NEE (bright phase) decreases with grain refinement.

3. 2. 2. Concentration Distribution Profile

The results of concentration profile in primary α_{Al} phase for the samples in the second set of experiments along with the curve calculated based on the Scheil equation, for comparison, are shown in Fig. 7. It can be seen from the figure that by grain refinement the profile shift upward and the content of the NEE phases decreases. The amount of C_{min} is reported in table 5. It is worth noting that, by grain refinement in alloy, the amount of C_{min} and k_0 increases and consequently degree of microsegregation decreases.

Table 4. Effect of grain refinement on the fractions of non-equilibrium eutectic

Condition	Non- equilibrium eutectic content (wt.%)		
	Image analysis	PanDat	Scheil equation
No-grain refined	5.5	8.2	9.1
Grain refined	4.7	8.2	9.1

set of experiments. It is clear that the content of

Table 5. Minimum concentration and non- equilibrium partiton coefficient for Al-4.8 Cu alloy

Sample condition	C_{min} (wt.%)	k_0	Cooling rate (K/s)
No-grain refinement	0.98	0.20	0.19
Grain refined	1.07	0.22	

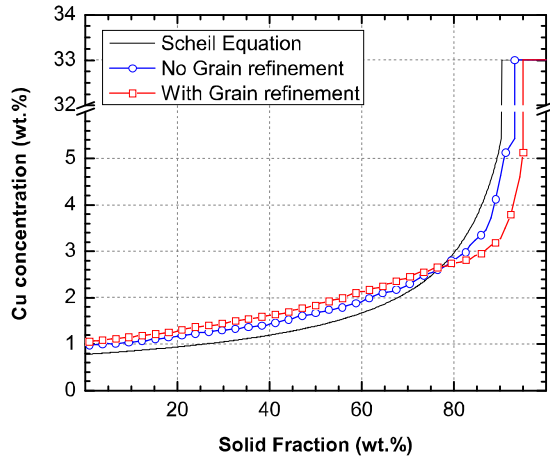


Fig. 7. Concentration profile for the second set of experiments.

4. CONCLUSIONS

In this research effect of cooling rate and grain refinement on the microsegregation in Al- 4.8 wt.% Cu were investigated, and the following conclusions are drawn:

1. In both series of experiments, microstructure shows the same constituents which are primary α Al phase and α -Al₂Cu NEE.
2. By increasing the cooling rate from 0.04 to 1.08 K/s, the amount of NEE phases increases from 5.2 to 7.4 wt.%.
3. Grain refinement reduces the degree of microsegregation by decreasing the NEE content from 5.5 to 4.7 wt.%.
4. The results of concentration profiles measurements shows that by increasing the cooling rate, the value of C_{min} decreases from 1.51 to 1.05 wt.%, but by grain refinement C_{min} increases from 0.98 to 1.07 wt.%.
5. Increasing the cooling rate (in the studied range) increases and grain refinement reduces the microsegregation severity.

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