Investigation of Influencing Parameters on Zone Melting Refining of Aluminium, Part One Impurities: Iron and Silicon

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Abstract

Zone melting is one of the most important techniques to produce electronic grade materials. It is of good reliability, easy operation, less polluting aspects and has the possibility to produce ultra-pure materials in a considerably higher efficiency than the other refining techniques. However, the refining yield and the final purity depend significantly on the process parameters and properties of the individual material.

Using an industrial sized zone melter and starting material of 2N8-Al made from 4N7-Al doped with the deliberate impurities of Fe (0.09 Wt.%) and Si (0.09 Wt.%), the influences of movement velocity of the induction coil as well as heating induction power on the purification of the above mentioned impurities have been investigated. The results were divided into two parts; first the comparison of removal efficiency for each impurity in relation with their distribution coefficients, and second the effect of process parameters on the refining yield. They showed that after three coil passes, the concentration of both Fe and Si in the first half of the Al-bar was reduced by around 50%, where the refining efficiency of Si is slightly higher than that of Fe under the same experimental conditions. Compared to published equilibrium distribution coefficients (the "effective distribution coefficient" (k_{eff}) of silicon was lower in comparison with iron. Experiments with the lowest movement velocity of 0.8 mm/min, or moderate power of 9 or 9.5 kW represent higher refining efficiency. This zone refining efficiency is defined by the term of zone length, which itself is influenced by an optimum combination of coil movement velocity and electrical power.

1 Introduction

High purity aluminium (5N or 6N) is widely used in special electronics and chemical applications, e.g. thin films and coatings in manufacturing of electronic devices, integrated circuits , or its synthetic products such as aluminium oxide and aluminium nitride to be applied as catalyst and for electronic ceramics [1]. In general, to fulfill the need of high purity or electronic grade materials, a number of methodologies have been investigated, including precipitation, crystallization, electrolysis, vacuum distillation, solvent extraction, and zone melting, etc. [2]. However, precipitation, electrolysis and solvent extraction are mainly considered as pre-refining steps as they are accessible to more contaminating resources. Further refinement (e.g. > 4N- or 5N-purity) will be only achieved in combination with other methods, such as vacuum distillation as well as zone melting [2], the latter particularly is used extensively to produce final ultrapure materials since the early 1950s [3],[4] . The experimental influencing factors while zone melting refining are movement velocity of the heating coil, zone length, the number of passes, and the temperature gradient at the freezing solid/liquid interface. A variety of investigations has been carried out with the focus on optimization of these factors both experimentally as well as simulated. However, the optimizations of these factors are not of general use, as they are strongly dependent on the properties of a particular system, such as equipment specification, ingot diameter, melt viscosity, diffusion- and distribution coefficients of significant impurities [5].

2 The mechanism of zone melting refining of Aluminium

Zone melting refining has essentially the same mechanism as for the purification via unidirectional solidification/segregation. The solution of the impurities in Aluminum is mostly different in liquid or solid state. The ratio of impurities concentration in solid (C_S) to that in liquid (C_L) is defined as equilibrium distribution coefficient k (see Fig. 1(a)), which approximately keeps a constant while temperature changes between liquidus and solidus. This value could be less or more than one for different impurities, showing the level of difficulty for their removal. The zone melting process is operating practically by a slow unidirectional movement of a liquid zone, or a series of liquid zones, along a solid ingot, as shown in Fig. 1(b). When the zone moves, the solid Al ahead of the liquid zone melts at the melting interface of liquid and solid, and the liquid Al solidifies at the freezing interface. Thereby, the impurities at the freezing interface will be continuously rejected to the liquid or to the solid (depending on their distribution coefficients). As a result they become concentrated in one or the other end of Al; hence, the rest of the ingot is partially purified. To achieve a desirable purity level, though, many passes should be occurred.

In addition, instead of the equilibrium distribution coefficient (k) the effective distribution coefficient (k_{eff}) is used in practical production, which has a direct effect on refining results. It has a function relation with experimental conditions, defined by [6]:

$$k_{eff} = \frac{k}{k+(1-k)exp\left(^{-V\delta}/_{D}\right)} \tag{1}$$

Where D is the impurity diffusivity in the melt, δ is the thickness of the diffusion boundary layer at the freezing solid/liquid interface and V is the liquid zone travelling velocity.

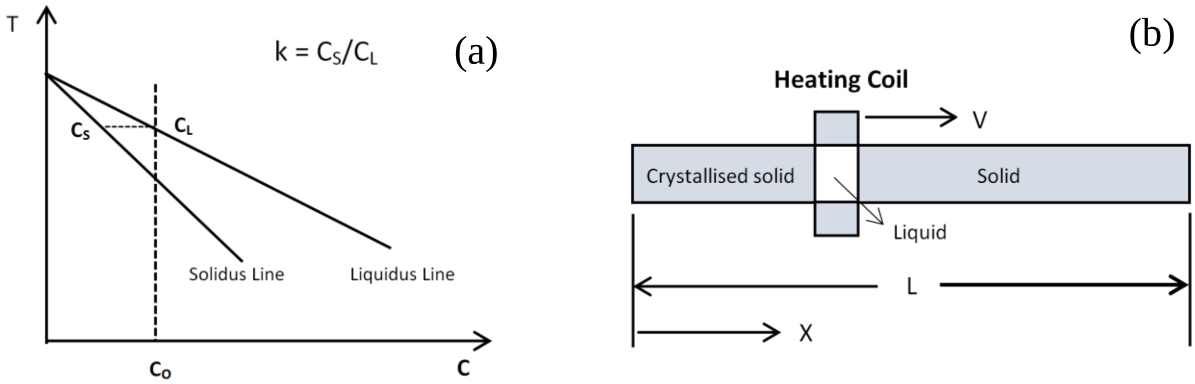

Figure 1: Scheme of part of binary phase diagram (a) and zone melting process (b)

3 Experiments

The starting materials here have been 2N8-Al ingots with the size of 60 cm × 5 cm × 2.4 cm, made from 4N7-Al with the dopant of first series of impurities in this research project - Fe and Si. In table 1 the detailed chemical composition of the starting and doped material has been shown, where each iron and silicon has a content of around 0.09 Wt.%. The Al ingot was then placed in a graphite crucible, located inside a quartz tube, where the system was vacuumed and filled with 350-500 mbar high purity Ar as the protecting gas. While applying an induction power of 15 kW and 10 KHz, the glowing hot coil (see Fig. 2) moved with different velocities and provided a strong mass convection in the liquid. The operational process parameters have been illustrated in table 2. After accomplishment of the process, the Aluminium ingot got a wedge-shape, showing that the mass of Al increased at the top of the bar and decreased at the tail (see Fig. 3). This phenomenon, which is possibly due to the density changes and volume increasing of the material after melting, can normally not be avoided but compensated by using a slight slope on the crucible. The ingot after refining was cut into several pieces by every 5 cm along the axial directions from top to tail, as shown in Fig. 4 and be sent to chemical analysis through spark spectrometry. As the mass of aluminium declines dramatically at the tail of the ingot, making this part a great challenge to be prepared as a sample for analysing, the concentration distribution profiles in the results do not include this area of the ingot.

Table 1: Chemical analysis of casted pure Al bars

Impurity content	Fe	Si	Ni	Zn	Ti	Pb	subtotal of others	Al
Concentration (%)	0.089	0.087	0.006	0.0026	0.0019	0.0028	<0.0061	99.81

Figure 2: Zone melting equipment at IME and its moving glowing hot zone

Table 2: Experimental conditions of zone melting refining of Al

Sample	Velocity (mm/min)	Power (kW)	Passes
1	0.8	10	3
2	1.2	10	3
3	1.6	10	3
4	1.2	8.5	3
5	1.2	9	3
6	1.2	9.5	3

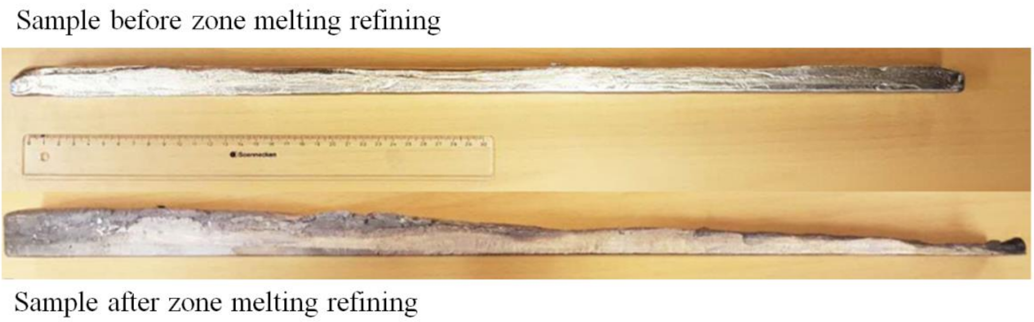

Figure 3: Obvious changes in the form of the Al-ingot after conducting the zone refining process

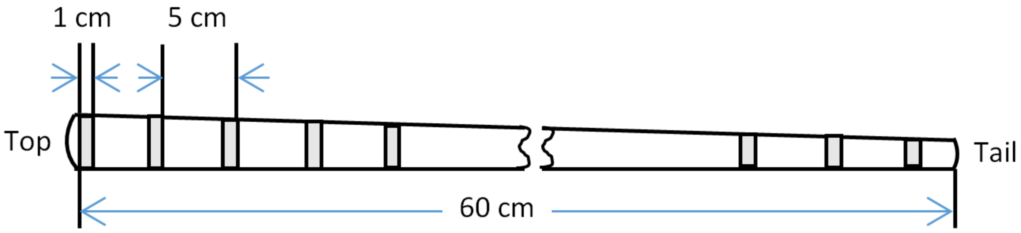

Figure 4: Positions used for chemical composition Analysis

4 Results and discussion

This paper only focuses on the purification of the first series of impurities - Fe and Si - in aluminium. Figure 5 shows the concentration distribution of impurities Fe and Si along the Al ingot with various velocities after zone melting refining with three passes. It can be observed that both impurities have been refined as an average by about 50% in the first half of the ingot, while they are enriched in the second half. It is however important to notice that according to Fig. 3 the mass changes along the first half of the ingot is very significant, i.e. the average total mass of the impurities in the first half part is apparently too high. This value could be probably lower if the mass of the material in this part after refining was the same as in the starting situation. It can be hence interpreted that the “real” removal efficiency (calculated as $\frac{m_{impurity,before} - m_{impurity,after}}{m_{impurity,before}} \times 100$) is even higher than 50%. Figure 5 confirms well the Pfann theory [3],[4], according to which C_s of those elements with distribution coefficient of $k \ll 1$ is exponentially increased from the beginning to the end of an ingot while zone refining. The theoretical distribution coefficient of Fe is 0.03 and that of Si is 0.14 [7]. Nevertheless, while using the same heating power, lower movement velocity of the zone results higher refining performance in the first half of the ingot. The relationship between k_{eff} and movement velocity of the zone in the case of Fe impurity has been illustrated in Fig. 6, calculated according to the Eq. (1), where D of Fe in the liquid Al is known to be 2.6×10^{-9} mm^2/s [8], and δ is assumed as 0.18 mm [7] for strong convection by electromagnetic field. When the movement velocity is settled to nearby 1 mm/min, the k_{eff} improves dramatically with the growing velocity. Accordingly, the k_{eff} of iron with coil movement velocity of 0.8 mm/min is the lowest, causing the highest refining efficiency.

Figure 7 shows the concentration distribution of the two investigated impurities, Fe and Si. The refining efficiency of Si is higher than Fe, though the k_{Si} is bigger than k_{Fe}. That is contributed to higher diffusion coefficient of Si (D_{Si}, 3.07×10^{-8} mm^2/s [9]) in molten aluminium than D_{Fe} (2.6×10^{-9} mm^2/s) - as k_{eff} decreases when D is increasing based on Eq. (1) - and leads to a higher removal efficiency (i.e. lower k_{eff} or lower C_S/C_L) for silicon compared to iron.

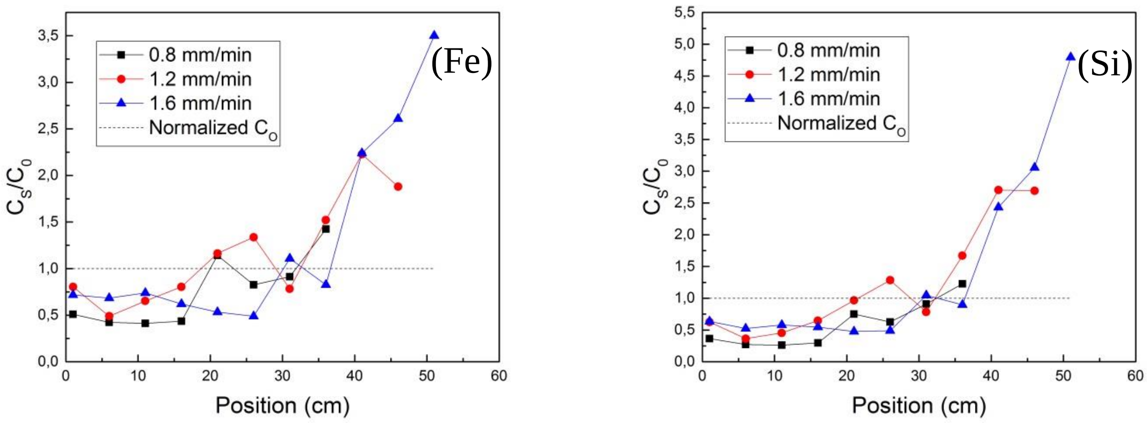

Figure 5: Concentration distribution profile heated with 10 kW after three passes against various velocities

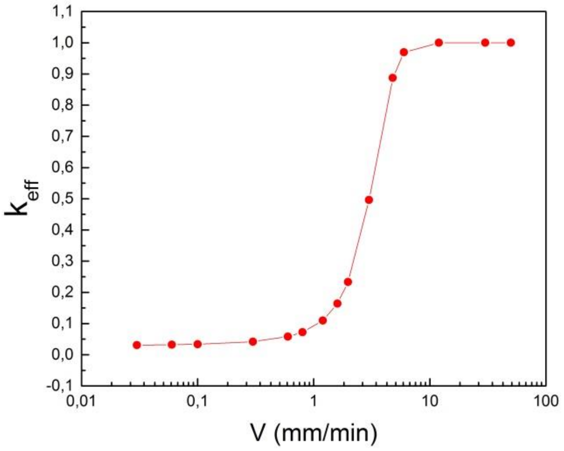

Figure 6: Relationship between effective distribution coefficient k_{eff} and zone movement velocity for Fe impurity

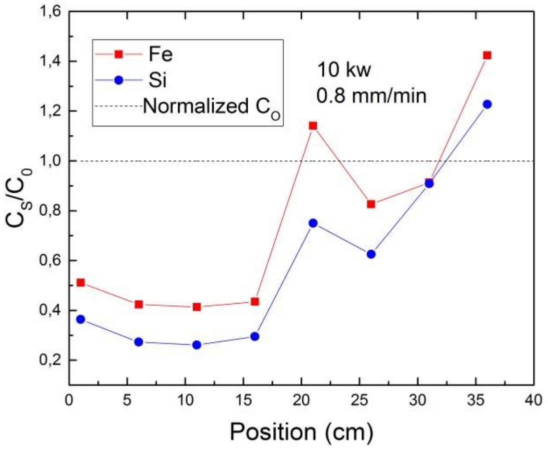

Figure 7: Comparison of concentration distribution of Fe and Si at same operational conditions

In the experimental condition of zone movement velocity of 1.2 mm/min the sample refined with 10 kW, showed the lowest refining efficiency in the first half of the ingot, while no distinct difference has been seen between the samples with the power of 9.5 kW and 9 kW (see Fig. 8). Thus, large values of power will not result necessarily in better purification, at least not for up to three passes.

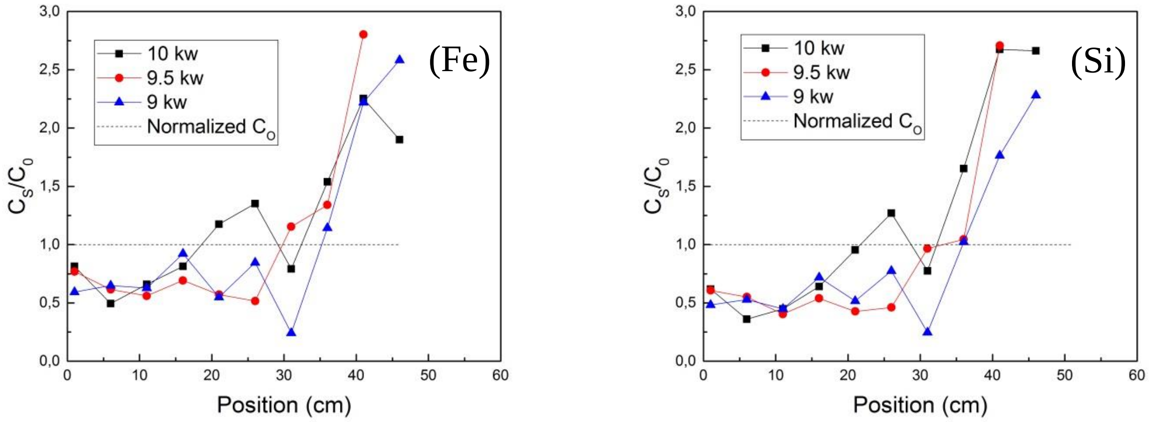

Figure 8: Concentration distribution profile with travelling velocity 1.2 mm/min after three passes against various powers

5 Conclusion

The effects of zone movement velocity and induction heating power on zone refining of impurities Fe and Si in Al have been investigated in this paper. The results show that the refining efficiency of Al is dependent on both mentioned process parameters. Low movement velocity (0.8 mm/min) can result in good purification level, but high heating power (10 kW) will lead to unsatisfactory efficiency, in the case of applying three passes. In addition, the refining efficiency of Si is higher than

Fe in Al under same experimental conditions due to the lower effective distribution coefficient k_{eff} of Si, though its equilibrium distribution coefficient k is higher.

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Editor’s Note:

Figure 2 presented in this article is credited to Martin Braun.

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