"Investigation of Temperature Effect on Impurities' Distribution Coefficient in Molten Aluminum through Theoretical Calculation and Experimental Fractional Crystallization"

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Abstract

Aluminum, in highly pure form, has increasingly been used in highly corrosion resistant applications or as an alternative to copper in conductive parts, especially for high voltage cables and transformers due to its inherent electrical conductivity characteristics. These properties also enables the use of high purity Aluminum in the production of electronic capacitor hard-disks, sputtering targets as well as in LCDs displays. The most common methodology to produce ultrapure Aluminum is through a combination of a three-layer electrolytic refining process together with fractional crystallization, mostly commonly Zone Melting. In order to achieve a purity of up to 6N with the aid of zone melting, many passes has to be performed, taking several hours to be accomplished.

This paper introduces for the first time an alternative approach for the purification of Aluminum, offering a high potential to meet the same purification degree and quality aspects while reducing the overall process time. Firstly, distribution coefficients of main impurities in Aluminum – a deciding factor to forecast and assess the removal behavior of impurities - were studied theoretically as a function of temperature using thermochemical calculation in FactSage™. Secondly, this innovative method using a rotating and gas cooled crystallizer ("cooled finger") was developed to validate the principle and an experimental distribution coefficient values were obtained and compared with theoretical values.

1 Introduction

Fractional crystallization principle: fractional crystallization is the crucial process for ultra-purity refining of metals and metalloids. Crystallization from the melt has the great advantage of high selectivity in comparison to other pyro-metallurgical melting processes. Thereby, distribution of impurities during the phase transition liquid/solid is used for refining of the initial metal as well as for doping of accompanying elements (e.g. to produce extrinsic semiconductors). An important parameter for impurity distribution in the target metal is the distribution coefficient (see fig 1), which describes the ability to separate the different components in the melt [1][2]. To remove unwanted elements from the target metal, the solubility of the impurities in the melt and in the crystal must be different. The distribution coefficient k is generally defined (Eq. 1) as the ratio of the concentration of an element in the solid phase (C_S) divided by the concentration in the liquid phase (C_L).

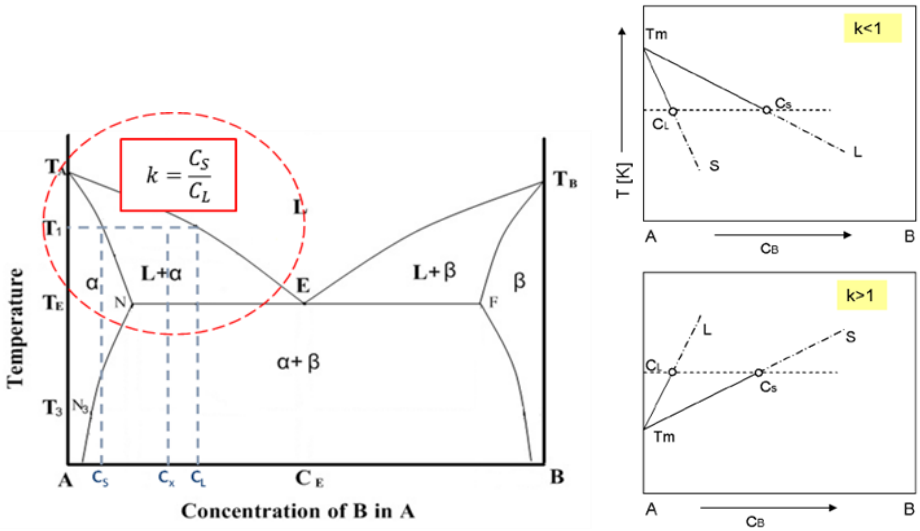


Figure 1: (Left) an exemplary binary phase diagram illustrating the calculation of distribution coefficient and (right) the influence of distribution coefficient on the melting temperature [3]

$$k = \frac{C_S}{C_L} \tag{1}$$

k– Distribution coefficient; C_S – concentration in solid; C_L– concentration in liquid

Here, the distribution coefficient of any chemical composition is depending on thermodynamical properties of components, kinetics on the interface liquid/solid, diffusion and convection on the phase boundary[4][5]. The distribution coefficient can take values smaller or bigger than one. Elements with k-values of <1 decrease the melting point and have a limited solubility in the target metal (fig. 1 upper right). If the distribution value k << 1 (for example, 0.01), the solubility of the target metal is extremely low, thereby a separation by fractional crystallization principle can be realized very well. If the k-value is greater than one, however, not only the melting temperature of the target metal is increased but also the impurities will concentrate itself on the crystallized solid [6][7].

2 Applied methodology "rotational cooled finger"

The process to be studied in this paper is based on an internally cooled crystallization unit (so-called "cooled finger), which is rotationally immersed into the molten Aluminum. Although this idea was patented 1982 in Japan (see fig. 2), until today neither scientific detail has been published nor the process been fundamentally investigated [8]. This is more remarkable, because all purification methods currently available are distinguished by complex technical systems and low efficiency. For example, while zone refining requires several passes with each taking a full day in order to improve the metal just to one purity-grade (reduction of foreign metals of a factor of 10) higher. According to Figure 2 the rotation is in correlation with a low temperature gradient between the melt and the „cooled finger" and the released crystallization heat causes a controlled metal layer deposition. The goal is a smooth-walled solidification without dendrite formation, in whose interspace melt could be entrapped. Via this concept, it should be possible to increase the purity from an initial 99.99% to at least 99.9995% in only one step [3].

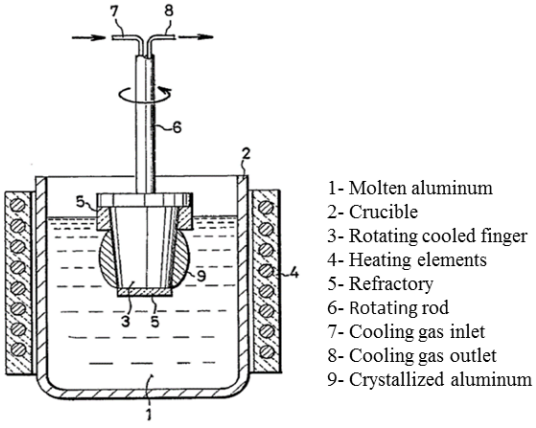


Figure 2: Principle of cooled finger crystallization concept [8]

3 Comparison of calculated distribution coefficient with experimentally obtained values

Calculation of distribution coefficient: The distribution coefficient as a function of temperature was calculated in FactSage, using the individual binary phase diagram of each system (Al-X) as well as using the Eq. (1). The X_S and X_L in the binary phase diagrams developed in FactSage were defined as a polynomial function of temperature as $X=aT^3+bT^2+cT+d$ with a $R^2 \sim 0.99999$. Using the individual constant factors for each equation at a specific temperature, X_S and X_L were calculated. Using Eq. (1) the distribution coefficient is calculated as $K = \frac{X_S}{X_L}$ and represented in figure 3. This coefficient is only valid if a complete mixing in the liquid is assumed (ideal system). Here the different tendencies of distribution coefficient in dependence of temperature for different impurities

have been illustrated. This figure shows that in contrast to iron, silicon, whose coefficients decrease due to the temperature rising, some impurities such as lead and nickel show an increasing pace with temperature. That means finding an appropriate crystallization temperature to remove all these impurities simultaneously would be a challenge. Though, according to fig. 3, these values still remain << 1, and even lower that of the iron, silicon and zinc at the same temperature.

Experimental-based distribution coefficient and comparison with FactSage-calculation: Generally for a non-ideal system with partial mixing in the liquid, the effective distribution coefficient based on BPS (*Burton–Prim–Slichter*) should be considered (see Eq. 2) [9][10] .

$$k_{eff} = \frac{C_S}{C_L} = \frac{k_0}{k_0 + (1-k_0)e^{\frac{G\delta}{D}}} \rightarrow \ln\left(\frac{1}{k_{eff}} - 1\right) = \ln\left(\frac{1}{k_0} - 1\right) - \frac{G\delta}{D} \quad (2)$$

In which C_S and C_L are the experimental values for the impurity concentration in solid as well as in liquid (e.g. here chemically analyzed through spark spectrometric method), k_0 is the equilibrium distribution coefficient, G the growth/solidification rate of the crystallization front, D the diffusion coefficient of each impurity in Al and δ is the diffusion layer thickness.

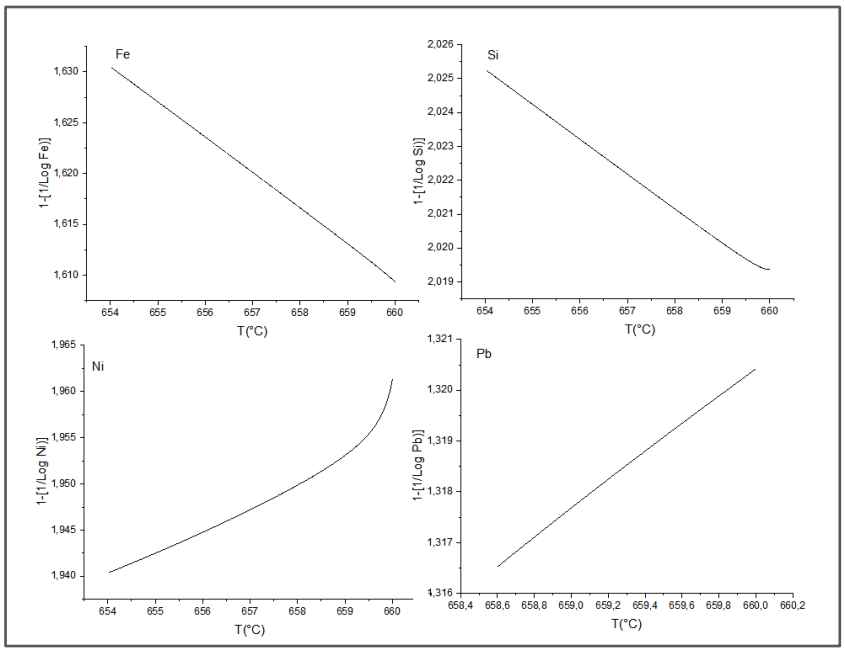


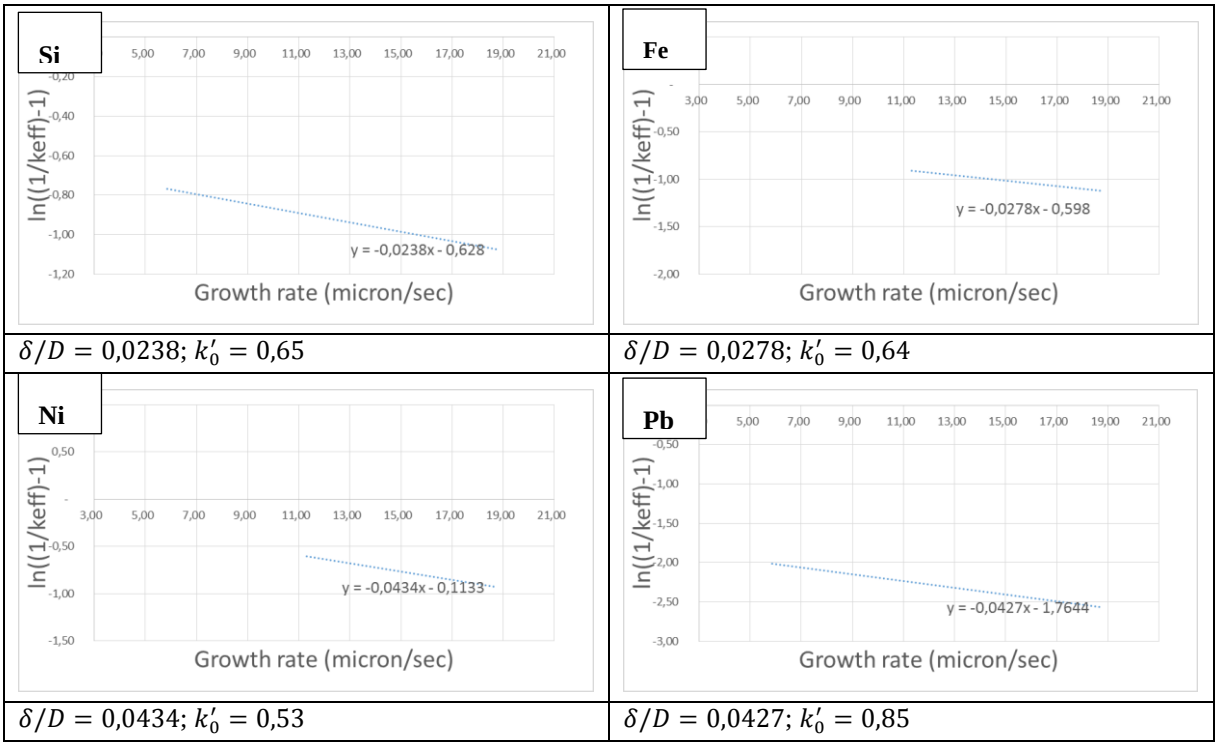
Figure 3: Distribution coefficient of the most common Aluminum impurities versus temperature in the case of a complete mixing, calculated through FactSage.

Using the experimental results and the chemical analysis of the products, k_{eff} can be calculated as $k_{eff} = \frac{C_{on\ cold\ finger}}{C_{crucible\ residue}}$. That means, C_S is in this case the concentration of the impurity in already crystallized material and C_L is the concentration of the same impurity remained in the molten phase (crucible residue). On the other hand, the solidification velocity (G) for different trials can be calculated through measuring the thickness of the crystallized material over the known period of dwelling time (as micron/sec). With the help of these two known variables (K_{eff} and G), the trend line of

y=Ax+B can be drown, where y is the K_{eff}, x is the G, A (slope) is $-\delta/D$ and B (intercept) is ln $(1/k_0' - 1)$. From this trend line, the k_0' - the empirical values of distribution coefficient - can be evaluated for each impurity and compared to the theoretical value from FactSage.

Application of the Burton–Prim–Slichter model (BPS): Figure 4 represents the implementation of the experimental values of C_S and C_L (via chemical analysis) as well as the empirical k_{eff} into the BPS model to calculate the experimental k_0'. The preliminary results obtained showed a correlation of the δ/D coefficient in relation to impurities that has similar distribution coefficients. While the k_0 for iron and Silicon are 0,03 and 0,13 respectively, the obtained coefficients and k_0' were also close to each other. Same effect can be observed for the Ni and Pb system. This confirms the validity of the empirical results at least for the binary systems investigated in this paper in correlation with the theoretical calculated values.

The difference between the thermodynamic distribution coefficients obtained from the binary phase diagram (k_0) and the k_0' obtained by BPS method is related to the efficiency of the system, which must be improved for example by reducing the growth rate. That in turn will led to an increase in the overall purification efficiency, since more time is given to allow the segregation of impurities on the growth front. Rotation speed will also play an important role on promoting the mixing of the segregated impurities from the growth boundary layer to the bulk melt and hence on increasing the purification effectiveness. In the case of Ni and Pb, the obtained k_0' was expected to be similar, as seen for Fe and Si. This difference could indicate a correlation between the impurities present in the system with the Pb and/or Ni.



$\delta/D = 0{,}0238$; $k_0' = 0{,}65$	$\delta/D = 0{,}0278$; $k_0' = 0{,}64$
$\delta/D = 0{,}0434$; $k_0' = 0{,}53$	$\delta/D = 0{,}0427$; $k_0' = 0{,}85$

Figure 4: Implementation of the experimental values of C_S and C_L into the BPS model for Silicon, Iron, Nickel and Lead

4 Conclusion

The use of cooled finger has shown a good potential as an alternative method to purify aluminum and demonstrated much lower process time in comparison with Zone melting. The removal efficiencies of the impurities from aluminum via experimental investigation do not show always accordance to the calculated values of distribution coefficient in FactSage. That is due to the lack of taking the interaction of the accompanying elements into account. FactSage theoretical calculation applied in this study was based only on binary (e.g. Al-X), although the empirical investigations took place considering multi-component systems.

The graphs of BPS model were confirmed to be valid for binary systems Al-Si, Al-Ni, Al-Pb and Al-Fe. An improved precision and better correlation between the BPS model and the theoretical values could be achieved through an increase in data points across a wide growth rate range, and by decreasing the influence of experimental and analytical uncertainties. Additionally, implementation of this model exclusively into a binary system would be beneficial to avoid the influence of accompanying elements in the overall purification results.

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