EQUILIBRIUM BETWEEN SILICON AND CALCIUM IN MOLTEN ALUMINUM

Motohiro Nagao and Seiji Nishi

Process Technology Research Laboratory
KOBE STEEL, LTD.
5-5, Takatsukadai 1-chome, Nishi-ku, Kobe, 651-2271 Japan

ABSTRACT When recycling aluminum it is essential to control the impurity elements which enter the molten metal from scrap. This paper describes the formation method of intermetallic compounds when silicon is removed as an impurity element. From thermodynamic calculation, calcium is chosen as an additional element and the relationship between silicon and calcium content in molten aluminum in the static holding state was investigated. Furthermore, the removal of intermetallic compounds by centrifugation was carried out and equilibrium between silicon and calcium was discussed.

Keywords: *aluminum recycling, intermetallic compounds, silicon removal, equilibrium, electro-magnetic processing, centrifugation*

1. INTRODUCTION

Recycling is very important from the standpoint of environment and energy preservation. Among many kinds of metals, reduction smelting of aluminum from bauxite requires a lot of electric energy, although remelting of aluminum requires only 3% of the energy of smelting. Therefore, the recycling of aluminum could be a highly cost effective process. Although the remelting of aluminum scrap is a standard technique, the scrap-diluting method using virgin aluminum ingots and the cascade method to convert production scrap to a lower grade product are common. As the generation of aluminum scrap is predicted to increase, "product to product" technology , by which items can be made from the same type of scrap, is required.

Removal of impurity elements at the liquid state is most significant because the solid state screening process has the possibility of mixing dissimilar materials. As a method of refining for molten aluminum, electrolytic refining, zone refining and segregation methods are well-known for high purity aluminum, however they have not been put to practical use for the recycling of scrap. On the other hand, the formation method of intermetallic compounds is proposed as a refining process. In this method, a special element is added to the molten metal to form intermetallic compounds with a removed element. This process is thought to be suitable for the treatment of larger-scale molten metal without the need for new facilities, although this process has a problem with the residue of additional elements.

Silicon is selected as the object of removed elements, because wrought aluminum scrap is likely to get contamination from aluminum castings scrap, and scrap from brazing sheets for automobiles is predicted to increase. At first, an additional element was chosen by thermodynamic calculation, and the relationship between silicon and chosen calcium content in molten aluminum in the static holding state was investigated. Furthermore, the removal of intermetallic compounds by centrifugation and the equilibrium between silicon and calcium were discussed.

2. THERMODYNAMIC CALCULATION

One of the most important factors is the selection of additional elements in the formation method of intermetallic compounds. Although manganese was given as an additional element for impurity iron[1], the reports have not mentioned an additional element for impurity silicon. So we try to choose an additional element for formation of the intermetallic compounds with silicon on the basis of thermodynamic calculations. The standard free energies ΔG° of formation for silicides were calculated by using a thermo-chemical database ChemSage[2]. Fig.1 shows the standard free energies of formation for silicides as a function of temperature. This figure suggests that calcium silicide has the lowest standard free energy. Then, calcium was chosen as an additional element for removal of silicon.

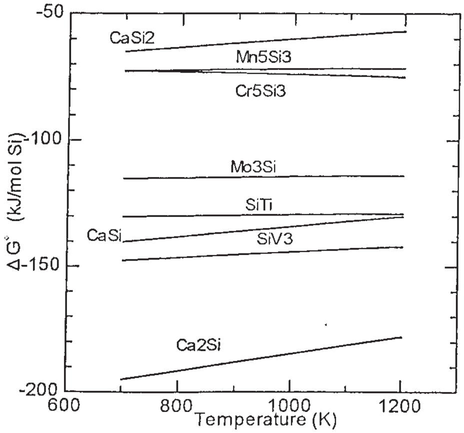

Fig.1 Standard free energies of formation for silicides

3. EXPERIMENTAL PROCEDURE

3.1 Static holding experiment

About 3kg of the Al-Si alloy was melted in an electric furnace and heated to a temperature of 1053K. Aluminum of 99.7 mass% grade and pure silicon were used as raw materials. Metallic calcium was added and the molten metal was kept at 1053K for 30 minutes in order to homogenize and dissolve the alloying elements. Table 1 shows the arranged contents of silicon and calcium in the experiments. Then, the melts were cooled to a fixed temperature of 923K and 963K, respectively, and maintained for 60 minutes. It was proved that 60 minutes is enough for the melt to achieve steady state[3]. After static holding, samples were taken from the melt and analyzed by inductively coupled plasma atomic emission spectrometry(ICP-AES).

Table 1 Arranged content of molten aluminum (mass%)

Si	1.0	1.0	2.0	3.0	5.0	5.0	8.0	8.0	10.0	10.0
Ca	3.0	2.0	3.0	2.0	2.0	3.0	2.0	3.0	2.0	3.0

3.2 Removal of intermetallic compounds

Using the same raw materials, about 20kg of Al-5mass%Si-3mass%Ca alloy was melted in an electric furnace and heated to a temperature of 1053K. The melt was maintained at this temperature for 30 minutes in order to homogenize and dissolve the alloying elements. Then, the melt was cooled to a fixed temperature of 963K and maintained for 30 minutes. After static holding, about 10kg of the melt was poured into the centrifugation apparatus with an electro-magnetic stirring coil shown in Fig.2. The temperature of the melt goes down and the melt solidifies during stirring because the apparatus has no heating system. Two patterns of experiments for rotation speed, 100 and 200rpm, were carried out to make certain of the influence of stirring force on removal of intermetallic compounds. After the experiments, the solidified ingot was cut in the center and the distributions of the intermetallic compound in the cross-section were investigated. The intermetallic compounds were also analyzed by electron probe micro analysis(EPMA).

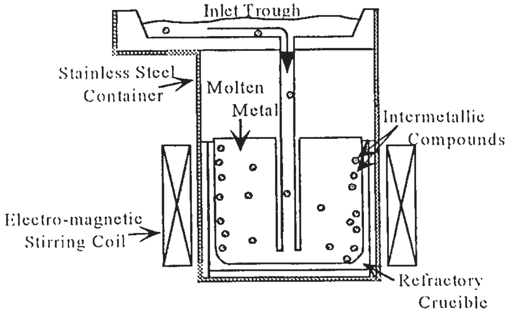

Fig.2 Schematic diagram of centrifugation apparatus by electro-magnetic stirrer

4. RESULTS and DISCUSSION

4.1 Static holding experiment

Fig.3 shows the changes in silicon and calcium contents in the static holding experiments. Silicon and calcium contents in the molten aluminum decrease together by the formation and sedimentation of the intermetallic compounds during static holding at 963K. The ratios of decrease

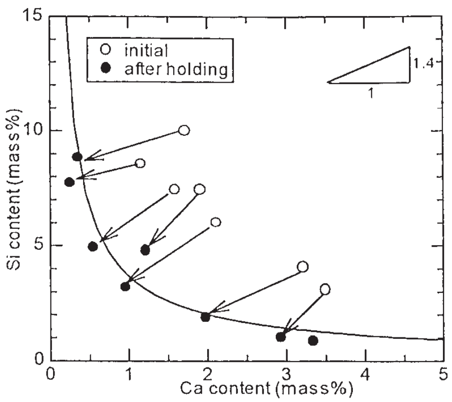

Fig.3 The change in silicon and calcium contents by static holding at 963K

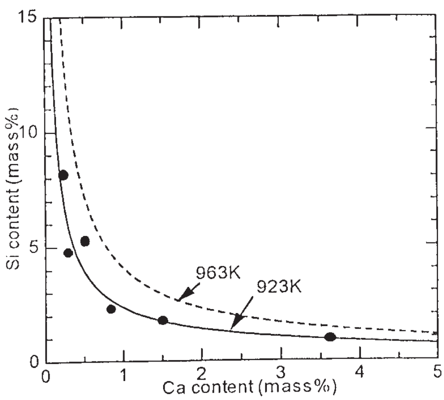

Fig.4 Relationship between silicon and calcium contents after static holding

in silicon content to that in calcium content are almost 1.4 to 1.0 which is equivalent to 2 atoms of silicon to 1 atom of calcium.

Fig.4 shows the relationship between silicon and calcium contents after the static holding experiments at 923K. The content of silicon is inversely proportional to the content of calcium, and its concentration product at 923K is smaller than that at 963K. The formation of the intermetallic compounds tends to proceed at lower temperature.

4.2 Removal of intermetallic compounds

Photo 1 shows the cross-section of the ingot after the centrifugation experiment. The "clean area" and "condensation area" of the intermetallic compounds in the outside of ingot, and the "mixed area" in the inside are observed. These results mean that the intermetallic compounds concentrate on the outside from the effect of centrifugation, however, those on the inside suspend in the melt by turbulence of metal flow. The "clean area" in the case of the experiment at 100 rpm is wider than that at 200 rpm, because the turbulence on the inside at 100 rpm is smaller than that at 200 rpm. Optimization of rotation speed is necessary for effective removal of the intermetallic compounds.

In the "clean area", silicon and calcium contents are 0.71 and 0.41mass%, respectively. Its concentration product is smaller than that obtained from the static holding experiments. This suggests that a lot of formed intermetallic compounds are suspended in molten aluminum at the

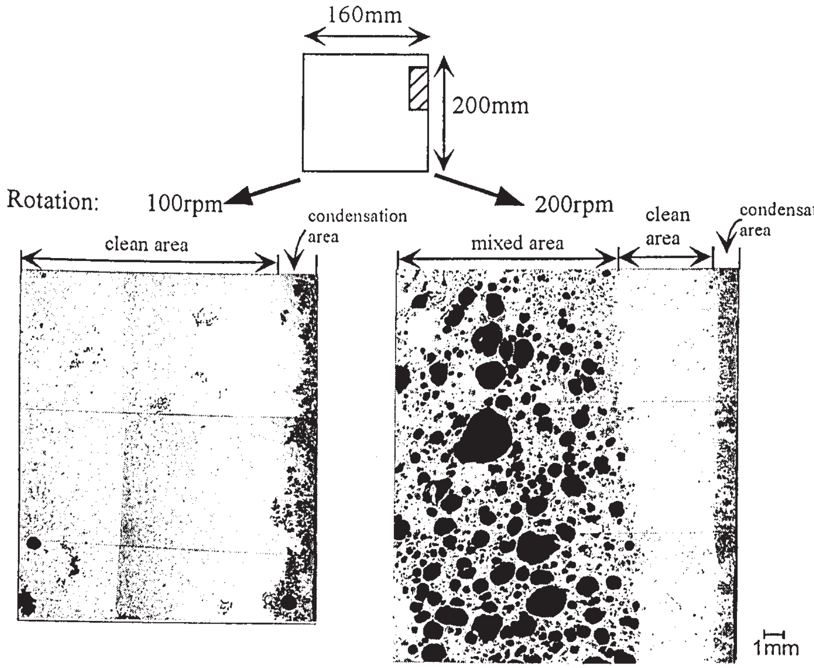

Photo1 Cross-section of the ingot after centrifugation experiment

static holding experiments. These contents obtained from the centrifugation experiment are thought to be the thermodynamic equilibrium contents of silicon and calcium.

Photo 2 shows the analysis results of intermetallic compounds by EPMA. Intermetallic compounds are composed of silicon, calcium and aluminum. Table 2 shows the content of the intermetallic compounds by the point analysis. It is clear that the main intermetallic compound is $CaSi_2Al_2$ from these analysis. This is in good agreement with the results from the static holding experiments.

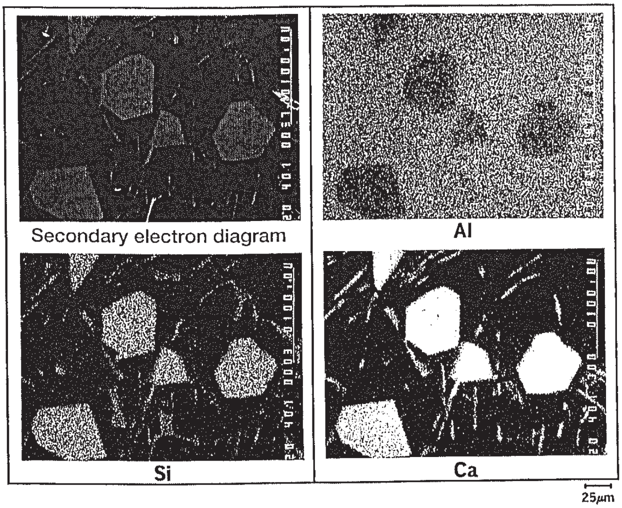

Photo 2 Element analysis of intermetallic compound by EPMA

Table 2 Chemical composition of the intermetallic compounds

Element	Mass%	Mol%
Si	36.136	38.794
Ca	27.544	20.721
Al	36.229	40.485

4.3 Equilibrium between silicon and calcium

As the formed intermetallic compound is $CaSi_2Al_2$, the reaction of formation and its equilibrium constant K are represented by equations(1) and (2), respectively.

$$Ca + 2Si + 2Al = CaSi_2Al_2 \qquad (1)$$

$$K = \frac{a_{Ca} \cdot a^2_{Si} \cdot a^2_{Al}}{a_{CaSi2Al2}} \qquad (2)$$

Assuming that $a_{Al} = a_{CaSi2Al2} = 1$, and the interaction between silicon and calcium are negligible, equation(3) is approximately obtained.

$$2 \log [mass\%Si] + \log [mass\%Ca] = C\ (const.) \qquad (3)$$

Silicon and calcium contents are 0.71 and 0.41mass%, respectively in the liquid state at 963K without intemetallic compounds. Using these values, equation(4) is obtained from equation(3).

$$2 \log [mass\%Si] + \log [mass\%Ca] = -0.68 \qquad (4)$$

This equation(4) is thought to be the thermodynamic equilibrium relation between silicon and calcium at 963K.

5. CONCLUSION

Removal of impurity silicon by the formation method of intermetallic compounds was investigated. It was found that;

(1) In molten aluminum, silicon and calcium form the intermetallic compound of $CaSi_2Al_2$.

(2) Sedimentation of a part of its formed intermetallic compounds occurs in the static holding of melt. Their removal could be carried out by centrifugation using electro-magnetic force.

(3) Equilibrium relationship between silicon and calcium contents in the molten aluminum is derived after removal of the intermetallic compounds.

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