High Efficient Recovery of Pure Aluminum from Al-Sn and Al-Ni Alloys by Rheorefining Process

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An investigation was made on the rheorefining process of Al-Sn and Al-Ni alloys in order to reproduce efficiently high-purity metallic materials. The load applied to the Al-Ni and Al-Sn alloy ingots during rheorefining increased rapidly and subsequently changed with repeating of its alternate increase and decrease like a sawtooth. The height of the ingot during the rheorefining reduced with increasing load and reduced slightly with decreasing load. The chemical composition of an initial composition Al-50%Sn alloy ingot rheorefined by pressurizing the ingot for 72 ks at a plunger speed of 2.8×10^{-4} mm/s was 98% Al and less than 0.01% Sn. Thus, a large amount of tin could be almost completely removed from the alloy ingot, although a small amount of eutectic was formed by chemical reaction with the steel filter. In the rheorefining by pressurizing Al-Ni alloy ingots for 72 ks at a plunger speed of 2.8×10^{-4} mm/s, the nickel in the alloy ingots with initial compositions of Al-2%Ni, Al-1%Ni, Al-0.5%Ni and Al-0.2%Ni was also removed effectively. It was known in the rheorefined Al-Ni alloy ingot with the initial content of 0.5%Ni that the amount of exuded filtrate increased and the nickel content decreased with an increase in isothermal rheorefining temperature. It was observed in the microstructure of the rheorefined Al-Ni alloys having initial contents of 0.2 to 2 mass%Ni that the fraction of eutectic decreased with a decrease in initial nickel content of the alloy ingots. It was found that the slow rheorefining for 72 ks at a plunger speed of 2.8×10^{-4} mm/s was superior to the fast rheorefining for 7.2 ks at a plunger speed of 2.8×10^{-3} mm/s in order to remove impurities from the Al-Sn alloy ingot.

(Received November 29, 1996)

Keywords: purification, refining by fractional solidification, refining by fractional melting, aluminum-tin alloy, aluminum-nickel alloy, interdendritic flow, rheorefining

I. Introduction

Year by year, there is growing recognition, politically as well as socially, that the global problem of ecological system destruction must be solved. Therefore, expectations for the solution of the problem are high not only for an enhanced awareness of this problem by consumers who utilize industrial products and the regulations governing the uses of industrial products but also for the regeneration and recycling of waste industrial products.

The development of regeneration technology for high-purity metallic materials will be described briefly below. High-purity metal refining processes are roughly classified into the following four types: (1) electrochemical refining (electrolytic refining), (2) physical refining (vaporization refining), (3) chemical refining (refining by means of a chemical reaction), and (4) metallurgical refining (refining based on a phase diagram).

However, highly-efficient refining which permits the short-time processing of a large quantity of used metallic products is limited only to the metallurgical process. In the metallurgical process, refined metal is obtained by removing impurities from crude metal on the basis of a phase diagram. The metallurgical refining process is further classified as follows: (1) zone refining process, (2) refining process by removing impurities in the semi-solid

state, and (3) refining process by removing impurities as intermetallic compounds.

The authors have taken notice of the fact that the deterioration of metallic materials is caused mainly by the impurities which invade and then accumulate in grain boundaries or interdendritic space from the surrounding environment during the use of such metallic materials. The process is named "Rheorefining Process", which is a better term to express the refining with fluid flow in the semi-solid state, although it has been called refining by fractional solidification⁽¹⁾⁽²⁾. The definition of the term will be discussed in detail in Section IV.1.

In the rheorefining process, used metallic products are not fully melted but are heated to the solid/liquid coexisting temperature range, i.e. a semi-solid state, to melt the grain boundaries or interdendritic space, and then impurities that invaded and accumulated in the grain boundaries or interdendritic space according to respective application environments are liquefied and removed. The separation of liquid from the semi-solid alloy is done by squeezing out the liquid contaminated with a lot of impurities through a filter. In this manner, the process can efficiently remove a large quantity of impurities from used metallic products.

In the present work, an investigation was made on the rheorefining process of Al-Sn and Al-Ni alloys in order to reproduce efficiently high-purity metallic materials.

II. Experimental Procedure

Al-50 mass%Sn alloy weighing 500 g in mass and Al-0.2, 0.5, 1 and 2 mass% Ni alloys, 300 g in mass, were selected. The solute elements of tin and nickel have no solubility in the aluminum matrix.

The main part of the experimental apparatus for recovering high-purity aluminum ingot is shown in Fig. 1. This figure shows the fundamental construction, which was set within a tungsten-mesh heater in a vacuum chamber (not shown). In this apparatus, aluminum products such as scraps were heated and kept in a solid/liquid coexisting state. In this state, only the grain boundary or interdendritic space where impurities were enriched was melted, thereby allowing the impurities contained in the melt to be efficiently removed.

The experimental procedure is as follows. First of all, the alloy specimen was melted twice to produce a homogeneous ingot. A specimen was inserted in the upper one of the three-stage graphite molds 60 mm in inner diameter and 15 mm in thickness shown in Fig. 1. The vacuum chamber was evacuated to attain a vacuum of 1×10^{-3} MPa. Then, the specimen was heated and kept isothermally for 7.2 to 10.8 ks within the solid/liquid coexisting temperature range. After the isothermal holding, pressure was applied to the surface of the specimen by advancing a plunger at a speed of 2.8×10^{-3} or 2.8×10^{-4} mm/s for 7.2 or 72 ks, respectively. Then the liquid, in which the impurities had concentrated, was exuded through two kinds of filters shown in Fig. 2 into the lower graphite mold, and the impurities were removed from the specimen. The squeezed-out liquid was solidified in the lower mold and was subjected to chemi-

cal analysis and mass measurement. The rheorefined ingot was solidified on the filter as it was. Next, the ingot on the filter was heated without pressurizing it and held at a given temperature within the semi-solid state temperature range. The experiments were carried out repeatedly with increasing rheorefining temperature until sufficient squeezing-out of the impurity-rich liquid was performed in order to determine the optimum rheorefining temperature. The experimental condition is summarized in Table 1.

The microstructure observation and the chemical analysis were made in the center of the exuded filtrates and the rheorefined ingot remained on the filter. The pore arrangement of the filter 75 mm in diameter and 10 mm in thickness used in the present work is shown in Fig. 2. Figure 2(a) shows a S35C carbon steel filter having uniform distribution of 121 pores 1.5 mm in diameter, which was used for the Al-Sn alloy. Figure 2(b) shows a 99%-purity alumina filter with uniform distribution of 121 pores 1.7 mm in diameter, which was used for the Al-Ni alloys.

In order to realize an extremely low plunger speed, a method to press the plunger on the upper surface of the ingot specimen with spiral rotation of a motor-driven rod was selected. The mechanism comprised an electric motor and a motor-driven rod with a clutch so that the plunger ceased to advance by loosening the clutch when the load applied to the ingot specimen exceeded the upper limit of 2 to 3 kN. The plunger speed and the load applied to the ingot specimen were simultaneously recorded on a recorder connected with a laser displacement meter and a load meter.

III. Experimental Results

1. Changes in rheorefined ingot height and applied pressure

An examination was made on the relation between the load applied to the upper surface of an ingot specimen and the displacement of its surface during rheorefining of the specimen inserted in the upper mold shown in Fig. 1. Two examples of the results are shown in Fig. 3. Figure 3(a) shows the first rheorefining cycle of an initial composition Al-1%Ni alloy ingot No. 4 shown in Table 1 with a small mass of exuded filtrate, where a small displacement means a small amount of exuded filtrate and vice versa. Figure 3(b) shows the third rheorefining cycle of an initial composition Al-2%Ni alloy ingot No. 3 shown in Table 1 with a large mass of exuded filtrate.

It was indicated that the load applied to the ingot increased rapidly and subsequently fluctuated with a repetition of increase and decrease alternately like a sawtooth. In this sawtooth-like variation, the gradient of increase in load was larger than that of decrease in load and was rather steeper than that of the initial steep increase in load. On the other hand, the displacement of the ingot height increased with increasing load and increased slightly with decreasing load. It was considered that the varia-

Fig. 1 An outline of the experimental apparatus used in the present work. 1: Middle mold, 2: Thermocouple for temperature control, 3: Upper mold, 4: Plunger, 5: Motor-driven rod, 6: Thermocouple for temperature measurement, 7: Specimen, 8: Filter, 9: Lower mold, 10: Support.

Table 1 Rheorefining parameters on Al-Sn and Al-Ni alloys.

Starting alloy No./mass%	Initial mass (g)	Path cycle	Isothermal holding	Rheorefining temp./time/speed	Exuded filtrate (g)	Rheorefining ingot (g)	Composition (mass%) Sn or Ni Al	
1 Al-50%Sn	497.62	1st	840 K $\times$ 18 ks	none	3.21		97.8	0.42
		2nd	850 K $\times$ 18 ks	none	0.97		98.4	0.41
		3rd	850 K $\times$ 10.8 ks	850 K $\times$ 7.2 ks, 2.8 mm/ks	77.46		83.2	15.9
		4th	850 K $\times$ 7.2 ks	850 K $\times$ 28.8 ks, 2.8 mm/ks	93.34		80.3	18.6
		5th	860 K $\times$ 7.2 ks	860 K $\times$ 7.2 ks, 2.8 mm/ks	39.08		75.4	23.6
		6th	870 K $\times$ 7.2 ks	870 K $\times$ 7.2 ks, 2.8 mm/ks	31.05		61.9	36.8
						252.51	14.0	82.9
2 Al-50%Sn	497.93	1st	870 K $\times$ 7.2 ks	870 K $\times$ 72 ks, 0.28 mm/ks	222.05		77.4	21.4
		2nd	870 K $\times$ 7.2 ks	870 K $\times$ 72 ks, 0.28 mm/ks	106.49		72.4	26.6
						169.39	<0.01	98.4
3 Al-2%Ni	266.46	1st	914 K $\times$ 7.2 ks	914 K $\times$ 72 ks, 0.28 mm/ks	8.19		5.69	94.31
		2nd	916 K $\times$ 7.2 ks	916 K $\times$ 72 ks, 0.28 mm/ks	0.86		6.26	93.74
		3rd	918 K $\times$ 7.2 ks	918 K $\times$ 72 ks, 0.28 mm/ks	115.82		5.24	94.76
						140.17	0.47	99.53
4 Al-1%Ni	298.04	1st	917 K $\times$ 7.2 ks	917 K $\times$ 72 ks, 0.28 mm/ks	31.99		5.13	94.87
		2nd	918 K $\times$ 7.2 ks	918 K $\times$ 72 ks, 0.28 mm/ks	5.85		5.38	94.62
		3rd	919 K $\times$ 7.2 ks	919 K $\times$ 72 ks, 0.28 mm/ks	8.07		3.86	96.14
		4th	920 K $\times$ 7.2 ks	920 K $\times$ 72 ks, 0.28 mm/ks	20.41		5.04	94.96
		5th	921 K $\times$ 7.2 ks	921 K $\times$ 72 ks, 0.28 mm/ks	4.36		3.77	96.23
						225.54	0.53	99.47
5 Al-0.5%Ni	299.76	1st	919 K $\times$ 7.2 ks	919 K $\times$ 72 ks, 0.28 mm/ks	2.23		5.31	94.69
		2nd	921 K $\times$ 7.2 ks	921 K $\times$ 72 ks, 0.28 mm/ks	4.99		4.11	95.89
		3rd	923 K $\times$ 7.2 ks	923 K $\times$ 72 ks, 0.28 mm/ks	6.34		3.01	96.99
		4th	925 K $\times$ 7.2 ks	925 K $\times$ 72 ks, 0.28 mm/ks	4.18		3.34	96.66
		5th	927 K $\times$ 7.2 ks	927 K $\times$ 72 ks, 0.28 mm/ks	6.55		2.04	97.96
		6th	929 K $\times$ 7.2 ks	929 K $\times$ 72 ks, 0.28 mm/ks	30.33		0.90	99.10
						246.39	0.14	99.96
6 Al-0.5%Ni	300.53	1st	926 K $\times$ 7.2 ks	926 K $\times$ 72 ks, 0.28 mm/ks	31.99		3.25	96.75
		2nd	928 K $\times$ 7.2 ks	928 K $\times$ 72 ks, 0.28 mm/ks	5.85		1.93	98.07
		3rd	930 K $\times$ 7.2 ks	930 K $\times$ 72 ks, 0.28 mm/ks	39.34		1.13	98.87
						241.06	0.25	99.75
7 Al-0.5%Ni	300.35	1st	929 K $\times$ 7.2 ks	929 K $\times$ 72 ks, 0.28 mm/ks	250.90		0.59	99.41
						49.26	0.18	99.82
8 Al-0.2%Ni	300.19	1st	927 K $\times$ 7.2 ks	927 K $\times$ 72 ks, 0.28 mm/ks	1.30		1.17	98.83
		2nd	932 K $\times$ 7.2 ks	932 K $\times$ 72 ks, 0.28 mm/ks	181.60		0.20	99.80
						117.29	0.15	99.85
9 Al-0.2%Ni	300.05	1st	928 K $\times$ 7.2 ks	928 K $\times$ 72 ks, 0.28 mm/ks	10.30		1.32	98.68
		2nd	930 K $\times$ 7.2 ks	930 K $\times$ 72 ks, 0.28 mm/ks	10.03		1.06	98.94
		3rd	932 K $\times$ 7.2 ks	932 K $\times$ 72 ks, 0.28 mm/ks	148.42		0.13	99.87
						133.32	0.070	99.930
10 Al-0.2%Ni	310.99	1st	929 K $\times$ 7.2 ks	929 K $\times$ 72 ks, 0.28 mm/ks	15.05		0.92	99.08
						296.05	0.12	99.88
11 Al-0.2%Ni	300.99	1st	932 K $\times$ 7.2 ks	932 K $\times$ 72 ks, 0.28 mm/ks	186.76		0.27	99.73
						113.75	0.088	99.912

tions in load and displacement were caused by the restraint of the slip of clutch occurred by friction between the plunger and the motor-driven rod to press the plunger. This sawtooth-like change in load will be discussed in Section IV.3.

2. Chemical analysis of rheorefined alloys

(1) Rheorefining of the Al-Sn Alloy

Quantitative and qualitative analyses were made on the exuded filtrate containing impurities and the rheorefined ingots on the steel filter shown in Fig. 2(a). The results

are summarized in Table 1.

As seen from the table, a large amount of tin present in the initial composition Al-50%Sn alloy ingot was removed almost completely from the ingot and was enriched in the filtrate by the rheorefining.

(2) Rheorefining of the Al-Ni alloys

The rheorefining experiment was carried out on Al-Ni alloys containing 0.2 to 2 mass%Ni, replacing the carbon steel filter with a high-purity alumina filter shown in Fig. 2(b) to prevent contamination from the steel filter. The

Fig. 2 Shapes of (a) S35C carbon steel filter and (b) 99%-purity alumina filter used in the present work.

Fig. 3 Relation between the change in load applied to (a) Al-1%Ni alloy No. 4 and (b) Al-2%Ni alloy No. 3 shown in Table 1 and displacement of the ingot height with the time elapsed from the start of compression.

results are summarized in Table 1. As seen from the table, a considerable amount of nickel present in the Al-Ni alloy ingots was removed from the ingot and was enriched in the filtrate by the rheorefining.

The effect of rheorefining temperature on the weight of exuded filtrate and the nickel content of the filtrate is shown in Fig. 4 for a rheorefined alloy ingot No. 5 shown in Table 1 with an initial composition of Al-0.5%Ni. It was shown that the weight of exuded filtrate increased and the nickel content of the filtrate decreased with an increase in rheorefining temperature.

The optimum rheorefining temperature will be discussed in Section IV.4 on the basis of the fractions of liquid measured from the chemical composition of the

Fig. 4 Relation among the rheorefining temperature, the exuded filtrate in mass and the nickel content of the filtrate after the rheorefining of an initial composition Al-0.5%Ni alloy ingot No. 5 shown in Table 1.

exuded filtrates and calculated from the equilibrium phase diagram.

3. Microstructure of rheorefined alloys

The microstructure of two cakes rheorefined from an alloy ingot with the initial composition of Al-50%Sn was examined using optical microscopy, as shown in Fig. 5. Figure 5(a) shows the microstructure after the sixth cycle of the rheorefining in the alloy ingot No. 1 shown in Table 1. White aluminum primary crystals and two kinds of impurities, i.e. gray tin particles and dark eutectics occurred by partial melting on the steel filter were observed. The tin particles must be formed on the process of squeezing out a large amount of Sn-rich liquid insoluble to aluminum between the aluminum primary solids⁽³⁾. Figure 5(b) shows the microstructure after the second cycle of the rheorefining in the alloy ingot No. 2, in which tin particles were almost completely removed. It could be confirmed that the bright area indicated primary crystals of pure aluminum and the relatively dark area indicated eutectics composed of impurities existing in the interdendritic space between the aluminum crystals, i.e. Al-Sn, Al-Sn-Fe and Al-Fe eutectics. Most of the impurities were likely to contaminate the alloy ingot due to their reaction with the carbon steel filter shown in Fig. 2(a) during the heating and isothermal holding of the alloy ingot in a semi-solid state.

The microstructures of rheorefined Al-Ni alloys containing initial contents of 0.2 to 2 mass%Ni are shown in Fig. 6. Figure 6(a) shows the microstructure after the 3rd cycle of the rheorefining in the Al-2%Ni alloy ingot No. 3. Figure 6(b) shows the microstructure after the 5th cy-

Fig. 5 Microstructures of two cakes rheofined at (a) the 6th cycle in the alloy No. 1 and (b) the 2nd cycle in the alloy No. 2 of an initial composition Al-50%Sn alloy ingots shown in Table 1.

cle of the rheorefining in the Al-1%Ni alloy ingot No. 4. Figure 6(c) shows the microstructure after the 3rd cycle of the rheorefining in the Al-0.5%Ni alloy ingot No. 5. Figure 6(d) shows the microstructure after the 3rd cycle of the rheorefining in the 0.2%Ni alloy ingot No. 9. It was seen that the fraction of eutectic decreased with a decrease in initial nickel content of the Al-Ni alloy ingots.

Next, the local compositions of the eutectics and the neighboring matrix were examined qualitatively using scanning electron micrography (SEM) and Energy Dispersive X-ray analysis (EDX). The SEM microstructure and the relative intensity of characteristic X-ray in a rheorefined Al-Ni alloy No. 10 in Table 1 with the initial content of 0.2%Ni are shown in Fig. 7. It was found that nickel was enriched at the site A and contained slightly at the site B in the eutectic region, but there was no nickel at the site C in the matrix region.

4. Effect of plunger speed on the chemical composition of rheorefined ingots

An examination was made on the effect of plunger speed on the chemical analysis value of rheorefined ingots with the initial composition of Al-50%Sn. The relation between the aluminum and tin contents of the filtrate, and the weights of the rheorefined ingots Nos. 1 and 2 in Table 1 are shown in Fig. 8.

In the fast rheorefining of the alloy ingot No. 1 at a plunger speed of 2.8×10^{-3} mm/s, the chemical composition of the exuded liquid was evaluated from the solid

Fig. 6 Microstructures of four cakes rheofined at (a) the 3rd cycle in an initial composition Al-2%Ni alloy No. 3, (b) the 5th cycle in an Al-1%Ni alloy No. 4, (c) the 3rd cycle in an Al-0.5%Ni alloy No. 5 and (d) the 3rd cycle in an Al-0.2%Ni alloy No. 9 shown in Table 1.

Fig. 7 Relation between the SEM microstructure and EDX analysis in the rheorefined cake of an initial composition Al-0.2%Ni alloy ingot No. 10 shown in Table 1.

Fig. 8 Relation between the aluminum and tin contents of the filtrate exuded through the filter and the weight of rheorefined ingots Nos. 1 and 2 shown in Table 1 with an initial composition of Al-50mass%Sn.

line to be 68%Sn and 32%Al at a rheorefined ingot of 250 g in mass, where the solid line was calculated by least squares method. On the other hand, in the slow rheorefining of the alloy ingot No. 2 at a plunger speed of

2.8×10^{-4} mm/s, the chemical composition of the exuded liquid was calculated by interpolation of two measured values to be 76%Sn and 24%Al at a rheorefined ingot weighing 250 g in mass. Thus, tin could be removed completely in the slow rheorefining of the alloy ingot No. 2.

It was confirmed that the slow rheorefining was superior to the fast rheorefining in order to remove impurities from the Al-Sn alloy ingot.

IV. Discussion

1. Background of rheorefining process

A major technical problem in refining by removing liquid enriched with impurities in semi-solid state is difficulty arising from dendritic morphology formed in usual solidification processes. It is difficult to separate the liquid in interdendritic spaces from the semi-solid state metal, because the liquid is entrapped completely by the solid. Then, Mehrabian *et al.* proposed two refining processes of separation of entrapped liquid from the solid during partial solidification which was accompanied by vigorous agitation⁽⁴⁾. In one process, the particulate solid was separated from the liquid by atomization. In the other process, the separation between the particulate

solid and the liquid was achieved by preferential draining of the liquid from the semi-solid slurry. However, a significant disadvantage occurs in both processes. It is an increase in impurity concentration of the particulate solid, which is promoted by vigorous turbulent mixing during the solidification with mechanical agitation⁽⁵⁾.

Lux and Flemings proposed a refining method to squeeze liquid out of semi-solid material employing compression not but mechanical agitation⁽¹⁾⁽²⁾⁽⁶⁾. When the metal was held isothermally, it was called refining by fractional solidification⁽¹⁾⁽²⁾. The degree of purification of Sn-Pb alloys was obtained by X-ray fluorescence analysis as "refining ratio", i.e. the ratio of the solute concentration in the refined material to the initial solute concentration in the starting material⁽¹⁾⁽⁶⁾. It was concluded that the amount of liquid removed depended on fraction of solid and applied pressure, and not on plunger speed in the range of 10^{-2} to 1 mm/s ⁽¹⁾. However, it is confirmed in the present work that the slow rheorefining in the alloy ingot No. 2 shown in Table 1 at a plunger speed of $2.8 \times 10^{-4} \text{ mm/s}$ is superior to the fast rheorefining in the alloy ingot No. 1 in Table 1 at a plunger speed of $2.8 \times 10^{-3} \text{ mm/s}$.

When the metal was heated during squeezing, it was called refining by fractional melting⁽²⁾⁽⁶⁾. This process achieved experimentally a refining ratio of as low as 10^{-4} on Sn-Pb alloys, which was comparable to that obtained by multi-pass zone refining. In the present work, the refining ratio was measured as the ratio of the solute content in the rheorefined material by emission spectrochemical analysis to the initial solute content in the starting material. The rheorefining process has also accomplished experimentally a refining ratio of less than 2×10^{-4} on an alloy ingot with the initial composition of Al-50%Sn, as shown in Table 2.

Finally, it is concluded that the refining by partial solidification by Mehrabian *et al.*, and the refining by fractional solidification and fractional melting by Lux *et al.* have the same concept as the application of rheology in the semi-solid state to purification of metals, so that these refining methods can be widely defined as the rheorefining process in the present work.

2. Advantages of rheorefining process

The rheorefining process has the following advantages⁽⁷⁾:

(1) Conventionally, aluminum alloys have been refined by injecting a large quantity of chlorine gas which exerts a deleterious effect on the environment. However, the rheorefining process eliminates the necessity of using environmentally toxic chlorine.

(2) With the conventional technology for recycling materials in which those materials are fully melted using massive amount of fuel, a large quantity of CO_2 has been generated and has had a negative effect on the ecological system. However, the rheorefining process makes it possible to keep the generation of CO_2 to a minimum.

(3) For aluminum alloys, even when remelted for regeneration, their applications have conventionally been limited due to the difference in chemical composition between cast and wrought aluminum alloys. Unlike wrought alloys, cast alloys are regulated to maintain the magnesium content of 0.1% or less and the manganese content that is as low as possible. However, the rheorefining process can remove any magnesium and manganese that may be enriched in the grain boundaries or interdendritic space. Therefore, the rheorefining process can be applied to the regeneration of aluminum alloys regardless of whether they were cast or wrought, thus greatly simplifying the aluminum alloy regeneration process.

3. Sawtooth-like change in load during rheorefining

The sawtooth-like change in load on the rheorefining process, as shown in Fig. 3, is considered as follows. When the driving rod presses the plunger with no slip of clutch, the ingot height decreases by the pressing. The load increases linearly by the elastic force of the driving rod to press the plunger. When the elastic force applied to the driving rod exceeds the friction force of clutch to endure the operation of the rod, the clutch begins to slip and the driving rod ceases to press the plunger. The liquid enriched with impurities in the semi-solid alloy ingot is squeezed out through the filter during the slip of clutch, so that the height of the ingot decreases gradually

Table 2 The recovered Al in mass, Al purity and Al percentage and the refining ratio for rheorefined Al-Sn and Al-Ni alloy ingots.

No.	Starting alloy composition (mass%)	mass (g)	Recovered Al in mass (g)	Recovered Al purity (mass%)	Recovered Al percentage (%)	Refining ratio
1	Al-50%Sn	497.62	252.51	82.9	84.1	0.28
2	Al-50%Sn	497.93	169.39	98.4	66.7	<0.0002
3	Al-2%Ni	266.46	140.17	99.53	53.4	0.235
4	Al-1%Ni	298.04	225.54	99.47	76.0	0.53
5	Al-0.5%Ni	299.76	246.39	99.86	82.5	0.28
6	Al-0.5%Ni	300.53	241.06	99.75	80.4	0.50
7	Al-0.5%Ni	300.35	49.26	99.82	16.5	0.36
8	Al-0.2%Ni	300.19	117.29	99.85	39.1	0.75
9	Al-0.2%Ni	300.05	133.32	99.93	44.5	0.35
10	Al-0.2%Ni	310.99	295.05	99.88	95.3	0.60
11	Al-0.2%Ni	300.99	113.75	99.91	37.8	0.45

Fig. 9 Relation between the measured and calculated fractions of liquid and the rheorefining temperature in Al-Ni alloy ingots Nos. 3 to 11 shown in Table 1 with the initial contents of 0.2 to 2 mass%Ni.

with a decrease in load. The gradient of decrease in load decreases with the elapsed time and also with decreasing fraction of liquid remaining in the rheorefining ingot. When the force applied to the driving rod becomes low as compared with the frictional force of the clutch, the clutch ceases to slip and the driving rod begins to press the plunger.

4. Optimum rheorefining temperature

The best way of rheorefining is to remove liquid enriched with impurities as much as possible from the semi-solid alloy ingot in the only one cycle of heating, isothermal holding and rheorefining process. It is thus necessary to know the optimum rheorefining temperature of an alloy ingot. Then, the optimum rheorefining temperature was determined as follow. The relation between the fraction of liquid and the rheorefining temperature in Al-Ni alloys Nos. 3–11 shown in Table 1 are summarized in Fig. 9. The measured fraction of liquid is assumed to be the ratio of the total volume of filtrates, which had been exuded through the filter, to the volume of the starting ingot. The solid line showing the fraction of liquid is also calculated on the assumption of the equilibrium solidification, because the isothermal holding before the rheorefining has a time enough to achieve equilibrium in the coexisting phases. According to Fig. 9, it is considered that the optimum rheorefining temperature must be 918, 931 and 932 K in the alloys with initial compositions of Al-2%Ni, Al-0.5%Ni and Al-0.2%Ni, respectively, because the measured fractions of liquid are almost equal to the calculated ones. On the other hand, the optimum rheorefining temperature in Al-1%Ni alloy is expected to be 922 K by extrapolation of the measured fractions of liquid.

V. Conclusions

An investigation was made on the rheorefining process of Al-Sn and Al-Ni alloys in order to reproduce efficiently high-purity metallic materials. The results are summarized as follows.

(1) The load applied to the Al-Sn and Al-Ni alloy ingots increased rapidly and subsequently changed with

repeating of its alternate increase and decrease like a saw-tooth during the rheorefining. The ingot height during the rheorefining decreased with increasing load and decreased slightly with decreasing load.

(2) In the rheorefining by pressurizing an initial composition Al-50%Sn alloy ingot for 7.2 and 72 ks at plunger speeds of 2.8×10^{-3} and 2.8×10^{-4} mm/s, respectively, the tin and aluminum contents of the refined ingots were 14.0% and less than 0.01% Sn, and 82.9% and 98% Al, respectively, after the rheorefining at 870 K. Thus, a large amount of tin was completely removed from the Al-50%Sn alloy ingot in the slow rheorefining for 72 ks at 870 K at a plunger speed of 2.8×10^{-4} mm/s. Similarly, the nickel and aluminum contents in the rheorefined alloys with the initial compositions of Al-2%Ni, Al-1%Ni, Al-0.5%Ni and Al-0.2%Ni were 0.47, 0.53, 0.14 to 0.25 and 0.07 to 0.15% Ni and 99.53, 99.47, 99.75 to 99.86 and 99.85 to 99.93% Al, respectively after the rheorefining for 72 to 432 ks at a plunger speed of 2.8×10^{-4} mm/s.

(3) The exuded filtrate increased and the nickel content in an initial composition Al-0.5%Ni alloy ingot decreased with an increase in rheorefining temperature.

(4) In the microstructure after the rheorefining for 7.2 and 72 ks at a plunger speed of 2.8×10^{-3} mm/s, white aluminum primary crystals and two kinds of impurities, i.e. gray tin particles and dark eutectics formed by partial melting on the steel filter, were observed. After the rheorefining for 72 ks at 870 K at a plunger speed of 2.8×10^{-4} mm/s, tin was completely removed, although eutectics were formed due to partial melting on the steel filter. It was observed in the microstructure of the rheorefined Al-Ni alloys containing initial contents of 0.2 to 2 mass%Ni that the fraction of the eutectics decreased with a decrease in initial nickel content of the ingots.

(5) It was found that the rheorefining for 72 ks at a plunger speed of 2.8×10^{-4} mm/s was superior to the rheorefining for 7.2 ks at a plunger speed of 2.8×10^{-3} mm/s in order to remove impurities from an alloy ingot with the initial composition of Al-50 mass%Sn.

Acknowledgment

This work was performed as a part of the leading research on Ecofactory of Industrial Science and Technology Frontier Program, MITI.

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