

Effect of Impurity Elements in Recycled Ingots on Seizure Properties of Die-cast Cylinders made of Hypereutectic Al-Si Alloy

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要旨

近年、世界中でカーボンニュートラルに向けた取り組みが加速している。アルミニウム原材料においては、新地金から再生地金に置き換えることで原材料製造時に消費される電力の大幅削減が可能であり、再生地金の使用拡大がカーボンニュートラルに貢献できる手段の1つである。

本稿では、DiASil シリンダに再生地金を適用することを目的とし、再生地金に含まれる不純物元素が部品機能にどのような影響を及ぼすかを調査した。新地金と再生地金でシリンダを製造し、その焼付き特性を比較した結果、再生地金で製造したシリンダの方が劣る傾向が見られた。金属組織観察、台上試験、熱力学計算ソフトウェア等を用いて原因究明し、不純物元素の1つであるNiを含む化合物が焼付き特性に影響を及ぼす可能性を見いだした。

Abstract

In recent years, efforts to reduce CO₂ emissions (carbon neutrality) have accelerated worldwide. In the aluminum manufacturing industry, CO₂ emissions can be reduced by switching the raw materials of choice; from virgin ingots to recycled ingots. However, the possible characteristic change accompanying the usage of impurity-ridden recycled ingots severely limits its applications, which also limits its potential contribution to carbon neutrality. Determining how impurity elements present in recycled ingots can affect the function of manufactured components is a necessary first step towards expanding the usage of recycled ingots.

In this study, we aimed to apply recycled ingots to the monolithic cylinder made of hypereutectic Al-Si alloy and investigated how impurity elements in recycled ingots affect properties (especially seizure characteristic).

Die-cast cylinders using virgin and recycled ingots were manufactured and their properties were investigated. The elements that increased in the recycled ingots were Zn, Mn, and Ni. The effects of these elements on the seizure resistance were confirmed by reciprocating sliding test. In addition, we confirmed the differences in the compounds formed from metallographic observations and discussed the relationship between these compounds and seizure resistance using thermodynamic calculation software (Thermo-calc), among other methods.

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INTRODUCTION

Aluminum is widely used in transportation equipment and other applications and contributes to improved energy efficiency and reduced CO₂ emissions at the usage stage. However, the excessive amount of energy required to manufacture virgin aluminum ingots from natural resources means a high amount of carbon footprint

during the manufacturing stage. The CO₂ emissions of recycled aluminum ingots produced from scrap are about 3% of those of virgin aluminum ingots, so expanding the use of recycled ingots can contribute to carbon neutrality^[1].

DiASil Cylinder (die-casting monolithic cylinder) is made of hypereutectic Al-Si alloy. Primary Si particles with high

hardness on the cylinder bore surface can improve resistance against seizure and wear even without cast iron sleeve, and the sleeveless design can realize excellent heat dissipation and high strength-to-weight ratio^{[2][3]}. These characteristics make it an attractive choice to use in automobile parts, like cylinder blocks for example. To realize these special characteristics, virgin ingots with few impurities are used instead of recycled ingots. However, the actual effects of impurities are currently not well understood, so clarification of these effects will lead to the expansion of use of recycled ingots.

This study aims to evaluate the difference in material property of DiASil Cylinder manufactured using virgin ingots and recycled ingots (hereafter VC and RC, respectively). We particularly focused on seizure resistance property since it is one of the most important specifications of cylinder blocks. The chemical composition of each cylinder blocks is shown in Table 1. These cylinder blocks were T5 heat treated after die-casting.

Table 1 Chemical composition of cylinder

Sample	Chemical Composition (mass%)							
	Si	Cu	Mg	Fe	Zn	Mn	Ni	Sn
VC	17	4.2	0.3	0.6	0.0	0.0	0.0	0.0
RC	17	4.3	0.4	0.8	1.0	0.5	0.5	0.1

2 EXPERIMENTAL

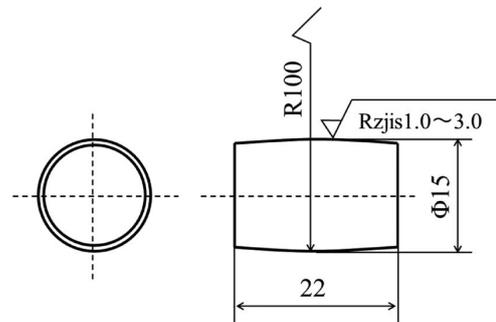
2-1. Metallography

A cross section near the cylinder bore surface was prepared and metallography was observed. To confirm the differences in intermetallic compounds in detail, analysis was also performed using FE-EPMA.

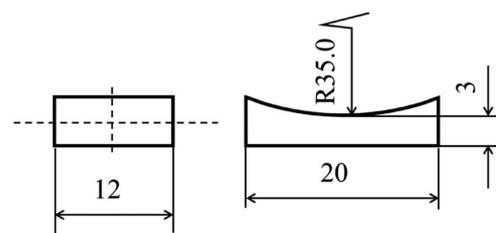
2-2. Seizure properties of VC and RC

Seizure properties were evaluated by using SRV tester from Optimol Instruments Prüftechnik GmbH. Figure 1 shows the shape of test specimens. Barrel-shaped test specimens were prepared from a continuous cast bar used for a forged piston production. This is made of Al-12mass%Si-4Cu alloy and given T7 heat treatment. On

the surface, Fe-Sn plating was treated. Cylinder test specimens were cut out of the actual cylinder as shown in Figure 2 to remain the curved shape and cross-hatched pattern.



(a) Barrel-shaped test specimen



(b) Cylinder test specimen

Fig. 1 Geometry of test specimen for SRV test

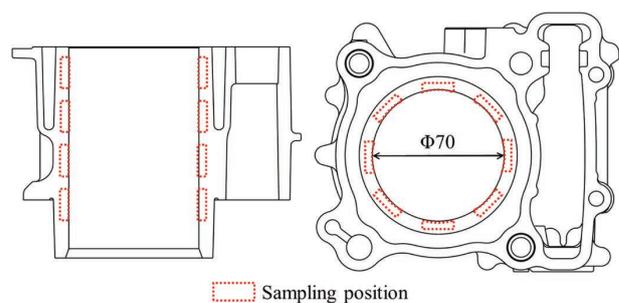


Fig. 2 Sampling position of cylinder test specimen

A schematic illustration of SRV tester and an image of each test specimen contact are shown in Figure 3 and 4. The barrel-shaped test specimen and the cylinder test specimen were installed on the upper and lower specimen holders respectively. The lower specimen holder was filled with oil enough to entirely immerse the contact area between each test specimen. The setting temperature was adjusted so that the oil temperature could be held at 150 degrees Celsius. After initially running for 60 seconds with a vertical load of 50N as a

running-in period, the load was increased to 600N to cause seizure. During the test, the vertical load, horizontal stroke, and friction coefficient were monitored by the equipped sensors. An example of the behavior of stroke and friction coefficient when seizure occurs is shown in Figure 5. Distinct peaks were observed shortly after the 60 second mark, and also around the 150 second mark. The irregular peak at 60 seconds was thought to be caused by the load being raised to 600N. The irregular peaks observed at 150 seconds was thought to be the result of mild adhesion which would eventually develop into seizure. The seizure occurrence point was considered to be the point wherein the sudden drop in stroke value to almost zero and the abrupt increase in friction coefficient was observed simultaneously. In this example, the seizure time is 163s. Detailed test conditions are summarized in Table 2. Each test was conducted 3 times. (Quality of the cylinder test specimens was assumed to be no different depending on the sampling position, and three were used at random from the test specimens in Figure 2.)

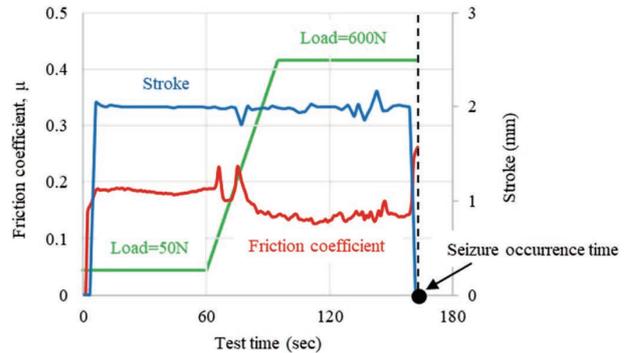


Fig. 5 An example of SRV test result

Table 2 Detailed condition of reciprocating slide test

Frequency	10Hz
Stroke	2mm
Oil	SAE 10W-40
Lubrication condition	Immersion
Oil temperature	150±5 degree Celsius
Running-in	50N, 60s
Vertical load	600N
Test duration	Until seizure (Max 1800s)

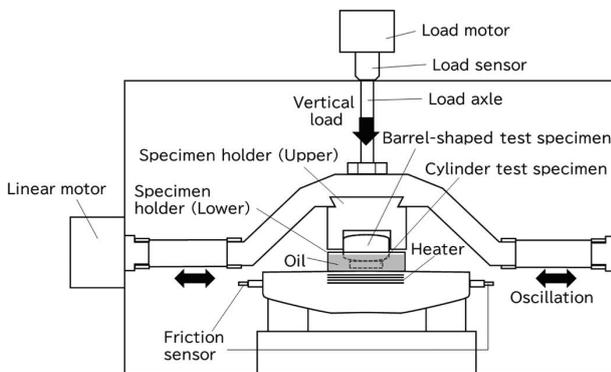


Fig. 3 Schematic illustration of SRV test

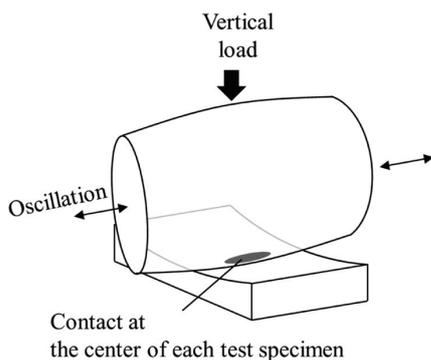


Fig. 4 Contact area between test specimens

3 RESULTS AND DISCUSSION

3-1. Metallography

Figure 6 shows cross section optical microscopy images of the metallography of the VC and RC. There is no marked difference in primary Si.

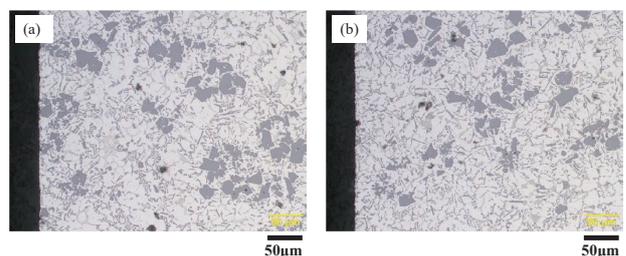


Fig. 6 Metallography of (a) VC (b) RC cross sections

Figure 7 shows the results of intermetallic compounds analysis by FE-EPMA. Two differences were observed: first is Cu-based compounds, and second is the shape of Fe-based compounds. As for the Cu compounds, it is assumed that not only Al-Cu compounds (considered CuAl₂) but also Al-Cu-Ni compounds were precipitated due to the increase of Ni in the RC. As for the shape of

the Fe-based compounds, needle-like morphology was observed in the VC, while a more massive shape was observed in the RC. A study conducted by Komiyama et al. reported that the needle-like compounds are thought to have changed to massive compounds due to the increase of Mn^[4], and the results of this study are similar to his findings. Although segregation of Zn contained in RC was observed, it was detected in both compound and matrix phases (no blue area), so it is safe to consider that Zn is mainly solid soluble.

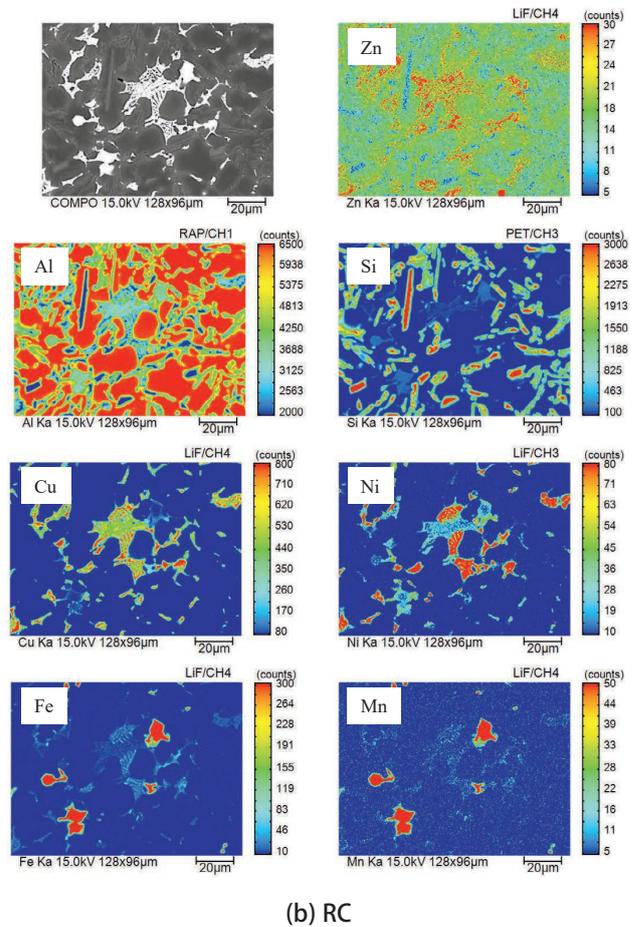
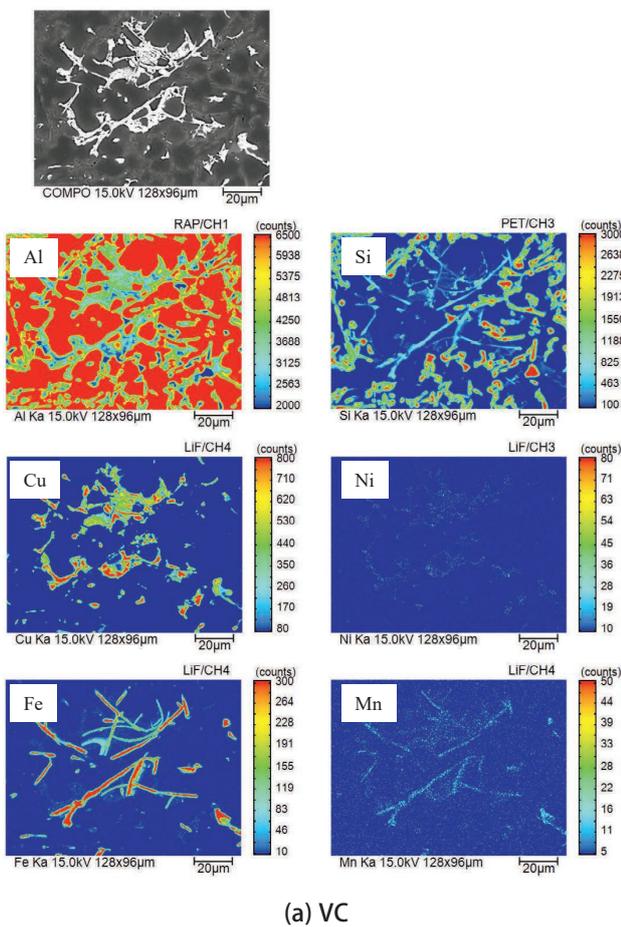


Fig. 7 FE-EPMA analysis results of intermetallic compounds

3-2. Seizure properties

The results of the comparison of seizure occurrence time in the SRV test are shown in Figure 8. Dots indicate the results of the three tests, bars indicate the average of the three tests. Seizure occurrence time includes running-in time of 60 sec. As can be seen in Figure 8, the RC tended to take a shorter time to seizure than the VC, suggesting that the RC may have inferior seizure resistance.

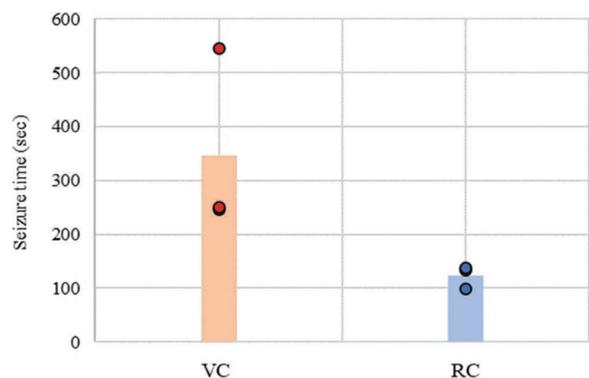


Fig. 8 Seizure occurrence time in SRV test

3-3. Investigation of the difference in seizure resistance

To investigate the cause of the difference in seizure resistance between the VC and RC, the SRV test was stopped before seizure occurred, and the surface conditions were compared. The test load was set at 400N, slightly lower than the value in Table 2, and the test was stopped 10 seconds after reaching 400N. The timing of the test stops and the behavior of the friction coefficient for each material at that time are shown in Figure 9.

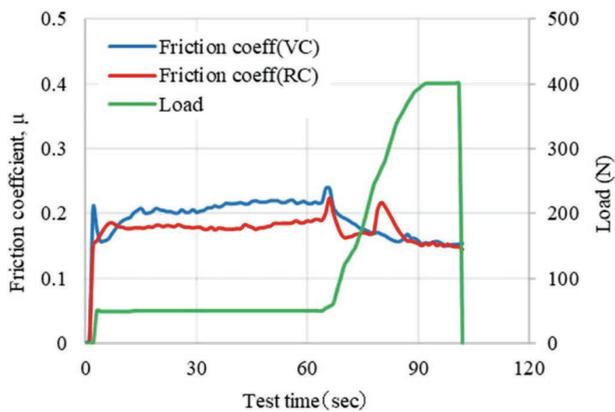


Fig. 9 Test stop timing and friction coefficient

SEM images and EDS mapping images of the surface observations of barrel-shaped specimens after the test are shown in Figure 10. Only in the RC, aluminum-based adhesions that possibly originated from the cylinder specimen was observed in the center of the sliding area. Since it can be considered that the presence of this substance affected the difference in seizure resistance, a more detailed analysis was conducted. Firstly, quantitative analysis of adhesion was performed using FE-EPMA. The results are shown in Table 3. The adhesion contains not only Al and Si from the cylinder specimen, but also a large amount of Fe and Sn (about 10 and 6 mass% respectively). In order to separate whether the large amounts of Fe and Sn detected were from in the adhesion itself or whether they originated from the plating of the barrel-shape specimen below the adhesion, depth profiling was performed using AES. Fig. 11 shows the result (elements below 5% are omitted from the graph). Focusing on the area that seems to indicate the

composition of adhesion (below in Fig. 11), the amount of Fe is quite large compared to the amount contained in the cylinder, and it is inferred that the adhesion is an alloy formed by the mixture of Al and Fe derived from the wear debris of the cylinder and barrel-shaped specimen. This suggests that the temperature of the sliding surfaces reached or was close to the melting point of the aluminum alloy.

Secondly, the results of that analysis were compared with the original composition to consider which components were affected. The results of the adhesion analysis include the components of oil residues and barrel-shaped specimens, so they cannot be simply compared as is. Therefore, the relative ratio of the amount of each elements against the amount of Al (how much is the ratio when the Al content is set to 1) were calculated before doing the comparison. Table 4 shows the results. Components that were thought to be derived from oil residues or barrel-shaped specimen were excluded from the comparison. It is indicated that the adhesion has a particularly high ratio of Cu and Ni compared to the original composition.

From the above results, the following may be considered.

- Adhesion, which are thought to affect seizure resistance, develops from melting due to heat generated by friction.
- Al-Cu-Ni compound contained only in the RC promote the formation of adhesion.

In other words, the results suggest that adhesion is generated when the material reaches near the melting point of the aluminum alloy, and the presence of Al-Cu-Ni compound may have affected the thermodynamic properties of the material.

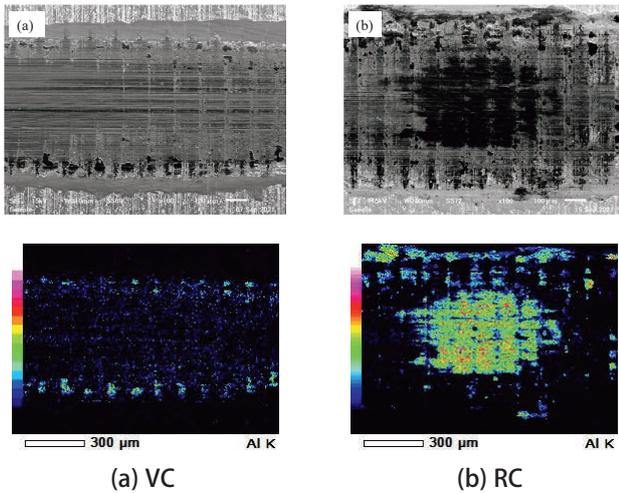


Fig. 10 Surface observation

Table 3 Chemical composition of adhesion

Al	Cu	Si	Mg	Fe	Zn	Mn
51.36	4.70	11.58	0.37	10.95	0.93	0.36
Ni	Sn	C	O	P	S	Ca
0.74	6.10	6.82	4.62	0.50	0.62	0.36

(mass%)

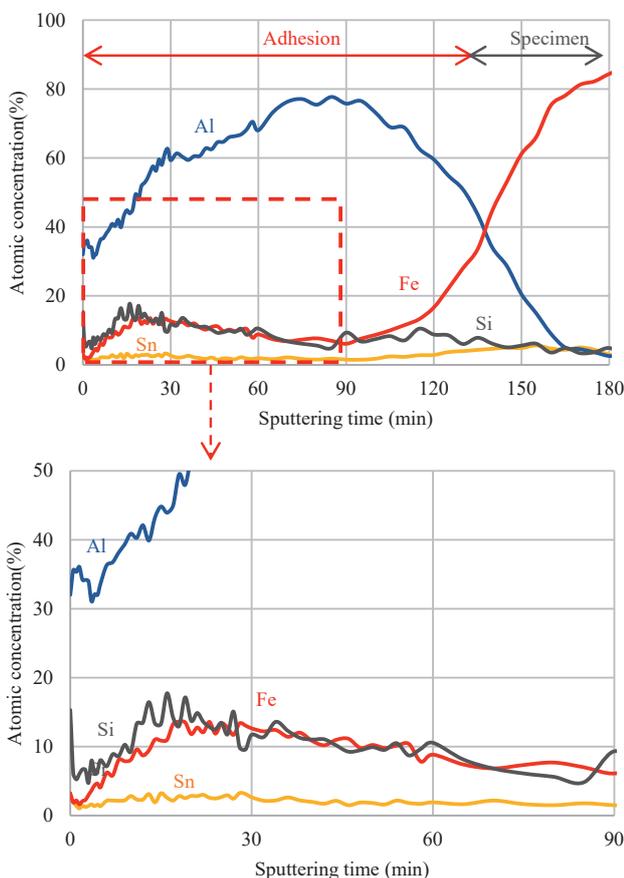


Fig. 11 Depth profile

Table 4 Comparison of adhesion and original composition

	The ratio when the Al content is set as 1 (a.u.)					
	Si	Cu	Mg	Zn	Mn	Ni
Adhesion	0.225	0.092	0.007	0.018	0.007	0.014
Original	0.223	0.057	0.004	0.013	0.007	0.007

3-4. Discussion using thermodynamic calculation

Finally, thermodynamic calculation software (Thermo-calc) with the TCAL8 Al-alloy database was used to discuss the previous results. The compositions used in the calculations are shown in Table 1. The calculated equilibrium phase at T5 temperature for each material are shown in Table 5. The VC and RC show differences in $Al_{15}Si_2(FeMn)_4$ (=AL15SI2M4) and Al_7Cu_4Ni (=AL7CU4NI), which is consistent with the differences seen in the actual observations (Figure 7). Special attention was paid to Al_7Cu_4Ni , and the changes near the melting point of the aluminum alloy were calculated. The changes in the liquid and Al_7Cu_4Ni phases at 500-600°C are shown in Figure 12(a), (b). The Al_7Cu_4Ni phase of the RC disappeared around 530-540°C, and the percentage of liquid phase tended to increase rapidly at the same temperature indicated by orange arrow in Fig. 12(a). Such a rapid increase in the liquid phase is not seen in the VC. The rapid increase in the liquid phase may promote the growth of larger wear debris which leads to the considerable deterioration of seizure resistance. Taken together with the previous experimental results, it is inferred that this rapid increase in the liquid phase associated with the melting of Al_7Cu_4Ni affected the ease of adhesion generation, which may have led to the difference in the seizure resistance.

Table 5 Equilibrium phases at T5

Phase	VC	RC
FCC_Al	71.42%	69.21%
DIAMOND_A4	16.37%	16.25%
AL2CU_C16	7.83%	6.61%
AL9FE2SI2	2.98%	2.97%
Q_ALCUMGSI	1.24%	1.14%
AL15SI2M4	0.08%	1.67%
AL7CU4NI	—	1.95%

(mass%)

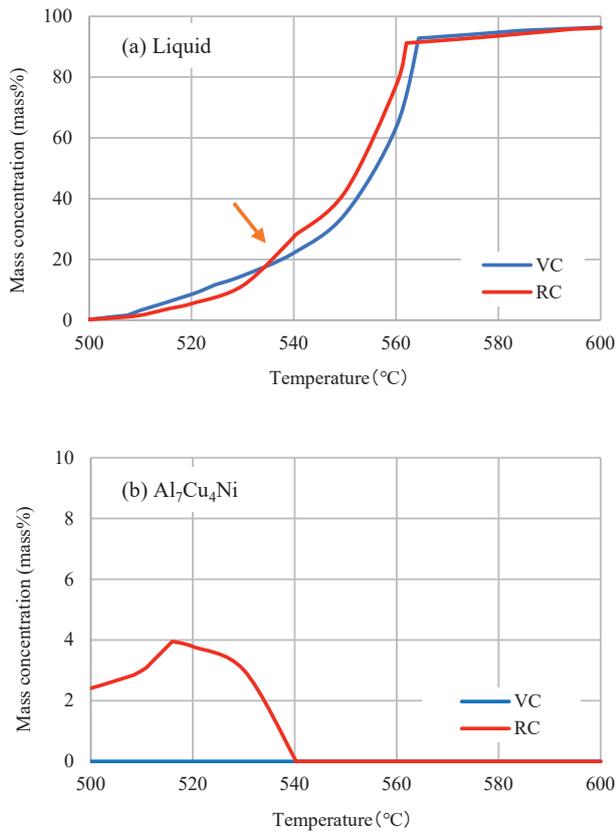


Fig. 12 The changes in (a) liquid and (b) Al₇Cu₄Ni phase

4 CONCLUSION

In this study, the effects of impurity elements in recycled ingots on seizure properties of hypereutectic Al-Si alloy were investigated. The conclusions are as follows.

1. Use of recycled ingots with high Mn and Ni content allows Al₁₅Si₂(FeMn)₄ and Al₇Cu₄Ni compounds to precipitate.
2. The RC may have inferior seizure resistance. Before seizure occurred, aluminum-based adhesion was observed only in the RC and this substance affected the difference in seizure resistance.
3. The adhesion is an alloy formed by the mixture of Al and Fe derived from the wear debris of the cylinder and barrel-shaped specimen and has a particularly high ratio of Cu and Ni compared to the original composition. Results of Thermo-calc calculations of the RC showed a rapid increase of percentage of liquid phase around 530-540°C due to melting of Al₇Cu₄Ni phase. Consequently, this led to the development of

adhesion, which may have affected the seizure resistance.

To apply recycled ingots to DiASil Cylinder, it is considered necessary to limit the amount of Ni to prevent the formation of Al₇Cu₄Ni.

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