ELIMINATION OF PRIMARY SILICON PHASE IN HYPER-EUTECTIC AL-Si ALLOY BY MOLTEN SALT PROCESS

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ABSTRACT

The detrimental effects arising from the presence of nonmetallic inclusions in aluminum are well known. On the other hand, aluminum is one of the materials with high recyclability among many metals, and over 60 percent of aluminum alloys are recycled and reused in Japan. Unfortunately, the application of recycled aluminum is limited to use for some purposes since the recycled aluminum contains several different phases, e.g., inclusions, precipitates etc. Therefore, the elimination of nonmetallic inclusions, particularly silicon phases in hyper-eutectic Al-25Si alloy, using molten equimolar KCl-NaCl salts system was investigated experimentally. The amount of silicon in hyper-eutectic Al-Si alloy was gradually reduced to about 15% with the cycle number of treatment in molten equimolar KCl-NaCl salts. X-ray diffraction and fluorescent X-ray analysis indicate that the silicon in aluminum alloy is transferred to the molten salts.
INTRODUCTION

Aluminum and its alloys have high recyclability. Since we are face-to-face with an energy and resource crisis at the turn of the century, their recycling is now being investigated and developed(1,2). However, it is very difficult for the current techniques to eliminate impurities melting in matrices, since aluminum is one of the very active metals. Therefore, scraps containing high level impurities are recycled by blending primary metals and/or scraps of low level impurities together. And in addition, various other techniques e.g the method using the difference in affinities for oxygen and for nitrogen, and the process using the difference of the specific weight between aluminum and impurities are also being developed. However, all of these are not enough to overwhelm the other recycling techniques and more effective new process are required now(3). In the present study, we investigated the elimination of the primary silicon phase from Al-Si alloys using equimolar KCl-NaCl molten salts and discuss the effectiveness and possibility of the process as the practical recycling technique.

EXPERIMENTAL

The specimens used were hyper-eutectic Al-25Si alloy whose composition is Si=24.6, Cu<0.1, Mg<0.2, Fe=0.2, and the residual part is aluminum. The salts used consist of NaCl and KCl basically. Several percentages of sodium fluorides were added to remove the surface oxide films on specimens. Prior to treating, the mixed salts were heated to 1033K and maintained at this temperature for about an hour in order to reduce the moisture in the salts.

Each specimen(15g) was immersed into molten salts at the adequate temperatures(1033K and 923K for 0.9ks-9ks). The experimental procedure is shown in Fig.1. The molten salts in mullite crucibles were agitated intermittently during the treatment in the electric furnace. After immersion treatment, the salts containing a specimen were slowly cooled to room temperature in the furnace, and then the specimen and salts were mechanically separated. During the operation, the atmosphere in the furnace was not regulated,
since the molten salts acted as protection against the ambient atmosphere. The primary silicon phase in the specimens was confirmed by optical microscope, and the silicon contents were measured by fluorescent X-ray analysis (FLX). In order to confirm the separated silicon phase, the salts were examined by X-ray diffraction analysis (XRD) and the extent of elimination of Si phases was measured.

RESULTS AND DISCUSSION

Fig. 2 shows the correlation between the amount of residual silicon in specimens and the dehydration time prior to treatment of salts. The specimens were heated to the temperature which coexistence region of solid silicon phase and liquid aluminum phase in equilibrium phase diagram. Although the non-treated hyper eutectic Al-Si alloy contained about 25% Si, the amount of the residual silicon in the specimen after the 1st. cycle treatment was less than 20%. Fig. 2 also indicates that the silicon in specimens was eliminated gradually in the following 2nd. and 3rd. cycle treatments, respectively.

Fig. 3 shows the correlation between the amount of the residual silicon in specimens and treatment time, when molten salts were dehydrated for 7.2ks; other conditions were the same as described above. For the specimen in the 1st. cycle for 0.9ks, there was little difference between the amount of silicon for the non-treated specimen and that for the treated one.

However, the following 2nd. and 3rd. treatments decreased the silicon content in specimens down to 20% and 18%, respectively.

On the other hand, the silicon in the specimen treated in the 1st. cycle for 3.6ks was eliminated to an amount less than 20%. These results suggest that the elimination process needs an adequate time for contacting both solid and liquid phases during treatment.

Fig. 4 shows variations of the amount of residual silicon in treated specimens with the number of times for agitation. The amount of residual silicon in treated specimen has a
tendency to decrease to a certain extent by agitation in KCl-NaCl molten salt. This suggests that during agitation in molten salts solid silicon comes into contact with the liquid molten salt, resulting in the transfer of silicon from hyper-eutectic Al-Si alloy to the molten salt. There is little difference between the amount of residual silicon in the specimen after the 1st. cycle of treatment by agitating, no agitating, and that by agitating four times. These results suggest that the solid silicon phase was thoroughly miscible with the liquid molten salt by agitation.

Fig.5 shows the XRD spectrum for residual materials in the treated salt. These salts were washed with water and filtrated after treatment and submitted to XRD. The two silicon peaks at 28 and 47 deg./2θ were observed for the treated salt. These peaks indicate the presence of silicon that was transferred from the treated specimen. This result suggests that this process using molten salts makes it possible to eliminate the primary silicon phase from the hyper-eutectic Al-Si alloy.

Fig.6 shows the variation of the amount of residual silicon in the treated specimen with the difference of the treatment temperatures. The sample is on the liquidus line at 1033K, and it is in the coexisting region of both the solid and liquid phase at 923K. A part of primary silicon phase exists as a solid phase at 923K, though almost all phases of specimen are more liquid at 1033K. So, solid silicon particles can more easily contact the molten salt during the 923K treatment than at 1033K. Consequently, it has been considered that the amount of residual silicon in the 923K treated specimen is less than that of the 1033K treated one. Nevertheless, the silicon was eliminated by this molten salt process and the amounts of residual silicon in treated specimen decreased with increasing treatment numbers of cycle at either condition.

The precise mechanism for the elimination process has not been clarified yet. However, all these results confirm that the primary silicon phase can be eliminated from hyper-eutectic Al-Si alloy by using the molten salt. Although the mechanism has nor been clear yet, part of the explanation can
be deduced from earlier experiments.(4,5,6)

CONCLUSIONS

The elimination process of primary silicon phases in hyper-eutectic Al-Si alloys was investigated by using a KCl-NaCl molten salts system, and the following results were obtained.

(1) The primary silicon phase in hyper-eutectic Al-Si alloy transferred from the melting alloy to molten salts by treatment at adequate temperatures.

(2) Application of this process will make it possible to eliminate the impurities contained in the recycled aluminum alloy.

ACKNOWLEDGMENT

The authors would like to thank the Research Foundation for the Electrotechnology of Chubu for supporting this foreign voyage (Nagoya). The major part of this work was supported by the Okasan-Kato Foundation (Tsu).

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cutting samples

preparing molten salt (1033K)

immersing samples into molten salt

holding with agitation

cooling

separation metal and salt

aluminum

salt

XRD, XPS, EDX analysis

analytical conditions

XRD : Cu anode, 40kV, 20mA, 8deg./ min.
XPS : 7kV, 30mA
EDX : 20kV, 2x10^10A, W.D. 15mm

Fig.1 Flowchart of experimental procedures

Fig.2 Changes of the amount of residual Si in the treated specimens for 3.6ks at 1033K in KCl-NaCl molten salt
**Fig. 3** Changes of the amount of residual Si in the treated specimens at 1033K in KCl-NaCl molten salt.

**Fig. 4** Changes of amount of residual Si in the treated specimen by agitation times in KCl-NaCl molten salts.
Fig. 5 XRD spectra for residual materials in the treated salt for 3.6ks at 1033K: (sample/salt=1/10)

Fig. 6 Changes of the amount of residual Si in the treated specimens for 3.6ks in KCl-NaCl molten salt

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