J. Shanghai Jiaotong Univ. (Sci.), 2012, 17(3): 263-267
DOI: 10.1007/s12204-012-1265-1

Recycling of Aluminum from Fibre Metal Laminates

ZHU Guo-liang[1,2*] (祝国梁), *XIAO Yan-ping*[1,3] (肖艳萍), *YANG Yong-xiang*[1,3,4*] (杨永祥)
WANG Jun[2] (王　俊), *SUN Bao-de*[2] (孙宝德), *BOOM Rob*[1]
(1. Department of Materials Science and Engineering, Delft University of Technology, 2628 CD Delft, The Netherlands;
2. State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200240, China;
3. Department of Metallurgical Engineering, Anhui University of Technology, Ma'anshan 243002, Anhui, China;
4. Institute of Ferrous Metallurgy, Northeastern University, Shenyang 110819, China)

Abstract: Recycling of aluminum alloy scrap obtained from delaminated fibre metal laminates (FMLs) was studied through high temperature refining in the presence of a salt flux. The aluminum alloy scrap contains approximately mass fraction $w(\mathrm{Cu}) = 4.4\%$, $w(\mathrm{Mg}) = 1.1\%$ and $w(\mathrm{Mn}) = 0.6\%$ (2024 aluminum alloy). The main objective of this research is to obtain a high metal yield, while maintaining its original alloy compositions. The work focuses on the metal yield and quality of recycled Al alloy under different refining conditions. The NaCl-KCl salt system was selected as the major components of flux in the Al alloy recycling. Two different flux compositions were employed at NaCl to KCl mass ratios of 44:56 and 70:30 respectively, based on either the eutectic composition, or the European preference. Different additives were introduced into the NaCl-KCl system to study the effect of flux component on recycling result. Although burning and oxidation loss of the alloying elements during re-melting and refining take place as the drawbacks of conventional refining process, the problems can be solved to a large extent by using an appropriate salt flux. Experimental results indicate that Mg in the alloy gets lost when adding cryolite in the NaCl-KCl salt system, though the metal yield can reach as high as 98%. However, by adding $w(\mathrm{MgF_2}) = 5\%$ into the NaCl-KCl salt system (instead of using cryolite) all alloying elements were well controlled to its original composition with a metal yield of almost 98%.
Key words: Al-Cu-Mg alloy, 2024 Al, recycling, cryolite, salt flux
CLC number: TG 29, TF 82　　**Document code:** A

0 Introduction

GLARE (glass fibre/epoxy reinforced aluminum laminate) has been used in the upper fuselage skin of superjumbo Airbus A380 because of its excellent properties[1-3]. GLARE recycling as a significant step in the GLARE life cycle should be seriously considered. Our previous work[4-5] indicates that thermal recycling is an effective solution for the GLARE recycling. S2-glass fibres and 2024 Al sheets can be well separated after the GLARE thermal dealmination. Recycled 2024 Al alloy quality is one of the vital criterions for the value of GLARE recycling, so 2024 Al alloy recycling (including re-melting and refining) is an important step to the whole GLARE recycling procedure. A higher recovery and yield of Al alloy with a similar composition to the initial alloy is preferred.

In this work, refining method[6-7] is employed because of the concise operation and the high quality recycled aluminum alloys. Although burning and oxidation loss during re-melting and refining are always the drawbacks of conventional method, the disadvantages can be solved to a large extent by using an appropriate salt flux. Moreover, if the flux can be repeatedly used due to the cleanliness of Al alloy scrap after simple treatment, the harmful impact of salt slag on environment can also be reduced because of the decreased amount of salt flux.

The salt fluxes for aluminum re-melting and refining are usually based on NaCl and KCl mixture because of the low cost and low melting point of these materials. The selected mass ratios of NaCl to KCl are 44:56 and 70:30 respectively, based on either the eutectic composition, or the European preference. Because fluoride addition to NaCl-KCl salt flux can dissolve $\mathrm{Al_2O_3}$ on Al scrap surface[8], accelerate metal coalescence[9] and obtain higher metal yield[6], the NaCl-KCl-$\mathrm{Na_3AlF_6}$ and NaCl-KCl-$\mathrm{MgF_2}$ system is employed as the salt flux in this work to study the effect of salt flux on alloy composition and metal yield during Al recycling.

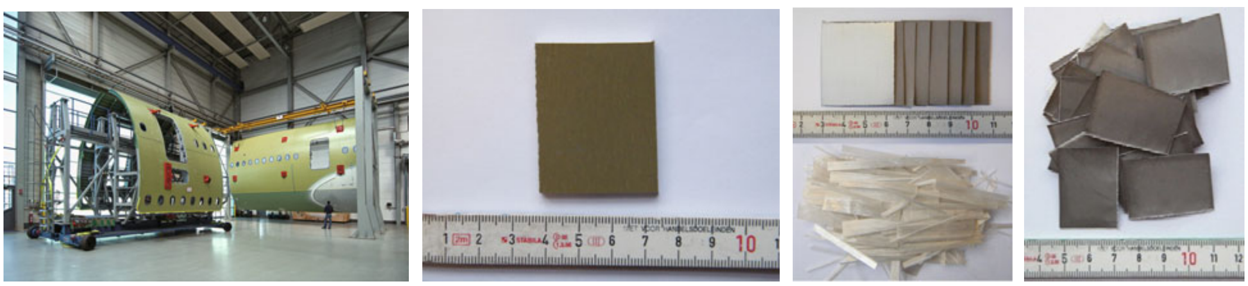
In this paper, the influence of two different types of

Received date: 2012-03-22
Foundation item: the Royal Netherlands Academy of Science and Arts (KNAW) (No. 10CDP026), the National Outstanding Young Scientist Foundation of China (No. 50825401), and the National Natural Science Foundation of China (No. 50821003)
*__E-mail:__ glzhu1983@hotmail.com, y.yang@tudelft.nl

fluxes based on the NaCl-KCl system on metal yield and quality of recycled 2024 Al alloy from delaminated GLARE scrap was studied. The fluxes are NaCl-KCl-Na_3AlF_6 and NaCl-KCl-MgF_2 respectively. In addition, the effect of additional fluoride amount in the NaCl-KCl system on recycling result was also investigated in this paper.

1 Experimental Details

The GLARE used in Airbus A380 (www.premium-aerotec.com), Al sheets and glass fibres after thermal delamination, and the delaminated 2024 Al sheets for re-melting are presented in Fig. 1. The re-melting and refining experiments were carried out in a high temperature chamber furnace (resistance heating, carbolite, maximum 1 600 °C). The size of 2024 Al scraps is 35 mm × 25 mm with a thickness of 0.4 mm, as shown in Fig. 1(d). An amount of 25 g 2024 Al alloy was put into an alumina crucible and the aluminum scrap was covered with salt fluxes to minimize the oxidation, enhance the coalescence of metal droplets and collect the various contaminants from the scrap. The furnace was heated up to 800 °C at a heating rate of 15 °C/min, and the holding time at 800 °C was 2 h. The nitrogen gas flow rate was controlled at 2 L/min to prevent Al from oxidation during re-melting and refining. The details about the used fluxes in experiments are described in Table 1, where w is mass fraction. The mass ratio of flux to Al scrap is 2:1 for all tests. High purity ($w > 99.7\%$) NaCl, KCl, Na_3AlF_6 and MgF_2 were used.



(a) GLARE used (b) New GLARE scrap (c) Afte delamination (d) For re-melting

Fig. 1 The GLARE used in Airbus A380 and scrap of GLARE before and after thermal delamination

Table 1 Experimental condition (the percentage of NaCl and KCl is mass fraction)

Experiment	Flux composition
1—5	44%NaCl-56%KCl with additional w = 0, 5%, 10%, 15%, 20% Na_3AlF_6 respectively
6—10	70%NaCl-30%KCl with additional w = 0, 5%, 10%, 15%, 20% Na_3AlF_6 respectively
11—14	44%NaCl-56%KCl with additional w = 5%, 10%, 15%, 20% MgF_2 respectively

After re-melting and refining, the crucibles with the samples were washed with hot water. Then the metal beads and the precipitates were filtered, dried and sieved. The filtered precipitates (dross) were prepared for X-ray diffraction (XRD) analysis (Bruker D8 advance X-ray diffractometer) to identify the phases included. After mass balancing, the metal yield was calculated and the size distribution of recovered metal beads was measured. The recycled Al alloys were prepared for the X-ray fluorescence (XRF) analysis (Philips PW2400 WD-XRF spectrometer) to compare the composition with the initial 2024 Al alloy.

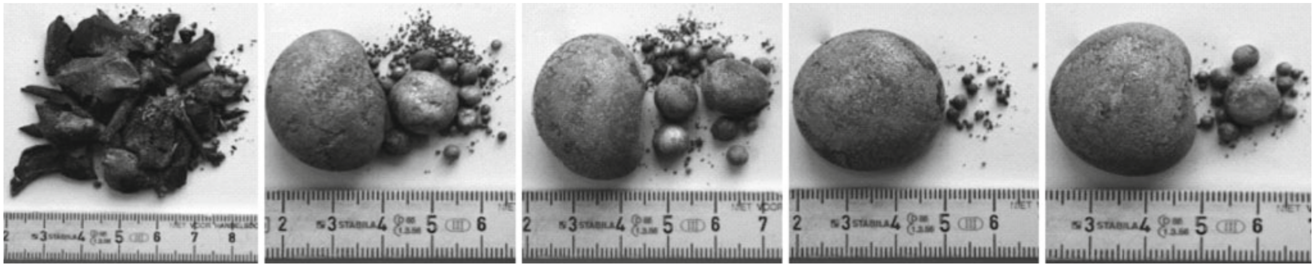
2 Results and Discussion

2.1 Refining Under 44%NaCl-56%KCl-Na_3AlF_6 Salt

The 2024 Al alloys after recycling with different cryolite additions in the 44%NaCl-56%KCl salt mixture (Experiments 1—5) are presented in Fig. 2. The recycling results by using flux without cryolite addition are unsatisfactory, but big metal beads are easily formed even if the additional cryolite is just $w = 5\%$. Aluminum is surrounded by the Al_2O_3 film during recycling, and the NaCl and KCl cannot destroy the oxide layer between molten flux and aluminum. This leads to very poor aluminum coalescence. But after the addition of cyolite in the salt flux, the Al_2O_3 films are dissolved into the cryolite[8] and the metal beads can be obtained due to the significantly improved coalescence.

One big metal bead together with a small quantity of small metal beads is observed even if the cryolite addition is only $w = 5\%$, and the small beads are entrapped in the salt during re-melting. But the increase of cryolite amount in the salt flux has little influence on the metal coalescence when the additional cryolite amount in salts is $w \geqslant 10\%$.

Effect of the cryolite addition on the metal yield and the size distribution of metal beads is shown in Fig. 3,



(a) $w(Na_3AlF_6)=0$ (b) $w(Na_3AlF_6)=5\%$ (c) $w(Na_3AlF_6)=10\%$ (d) $w(Na_3AlF_6)=15\%$ (e) $w(Na_3AlF_6)=20\%$

Fig. 2 Al alloy after recycling with a salt flux of 44%NaCl-56%KCl-Na_3AlF_6

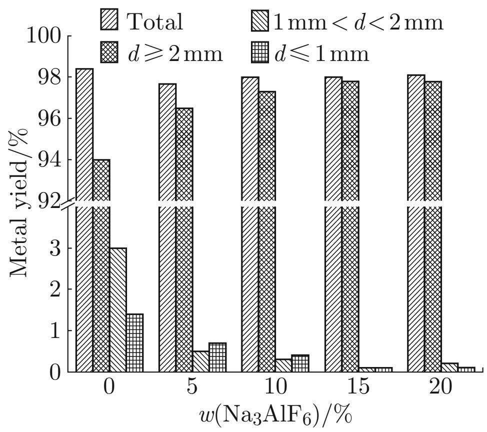


Fig. 3 Metal yield and size distribution of the recovered metal beads versus Na_3AlF_6 with a salt flux of 44%NaCl-56%KCl

where d is the metal bead diameter. The total metal yields (the mass fraction of obtained metal after recycling in total metal of scrap) are 98.40%, 97.68%, 97.97%, 97.98% and 98.08% when the additional cryolites in the NaCl-KCl salt mixture are w = 0, 5%, 10%, 15% and 20% respectively. Because the impurity oxides on the surfaces of aluminum scrap are not removed due to the negligible solubility of alumina in the NaCl-KCl system, the total (apparent) yield after recycling without cryolite addition in the salts is higher than others. The yields of big metal bead ($d \geqslant 2$ mm) are 93.98%, 96.52%, 97.34%, 97.81% and 97.76% when the additional cryolites are w = 0, 5%, 10%, 15% and 20% respectively. The high yield is attributed to the lower melting point of equimolar NaCl-KCl system which has a good fluidity together with the beneficial influence of cryolite on metal coalescence.

It is clear that the metal yield increases with the cryolite amount in salt when the addition amount is $w \leqslant 10\%$, but the increase of cryolite amount becomes meaningless for improving the metal yield when the cryolite amount is $w \geqslant 10\%$.

The XRF results of recycled Al alloys are listed in Table 2. It is found that all magnesium is lost in the recycled 2024 aluminum during re-melting with NaCl-KCl-Na_3AlF_6 flux due to the reaction between magnesium and cryolite:

$$3Mg + 2Na_3AlF_6 \rightarrow 3NaMgF_3 + 2Al + 3NaF.$$

But other alloying elements (Cu and Mn) are well kept and impurity elements (Fe, Si, Ti) concentrations are not increased, just Al concentration is slightly improved due to extra Al formation during the reaction between magnesium and cryolite. Some Na, K and Cl are also detected in the aluminum beads after recycling. These elements come from the entrapped NaCl and KCl according to the detected concentration ratios of Na, K and Cl. Considering that the entrapped chlorides can move to the molten flux layer easily during the industrial scale recycling, entrapped NaCl and KCl will not be a problem for reuse of the recycled Al alloy.

Table 2 Compositions of 2024 Al alloy after recycling with flux 44%NaCl-56%KCl-Na_3AlF_6 (mass fraction of other elements is not higher than 0.05%)

Experiment	w/%										Metal yield/% ($d \geqslant 2$ mm)
	Cu	Mg	Mn	Fe	Si	Ti	Na	K	Cl	Al	
1	4.37	1.13	0.642	0.126	0.165	0.030	–	–	–	93.45	–
2	4.14	–	0.619	0.137	0.157	0.047	0.012	0.033	0.047	94.89	96.52
3	4.15	–	0.644	0.140	0.151	0.030	0.044	0.170	0.236	94.17	97.34
4	4.12	–	0.620	0.126	0.163	0.031	0.096	0.045	0.187	94.66	97.81
5	4.17	–	0.640	0.129	0.144	0.034	0.118	0.106	0.281	94.21	97.76

2.2 Refining Under 70%NaCl-30%KCl-Na_3AlF_6 Salt

The salt composition of 70%NaCl-30%KCl was selected based on the preferred European melt salt composition. After recycling with 70%NaCl-30%KCl-Na_3AlF_6 (Experiments 6—10), the total metal yields of recycled 2024 Al with $w = 0$, 5%, 10%, 15% and 20% additional cryolites in fluxes are 97.48%, 96.93%, 97.40%, 96.95% and 97.49% respectively. The yields of big metal bead ($d \geqslant 2\,\mathrm{mm}$) are 93.38%, 95.22%, 96.76%, 96.50% and 97.15% when the additional cryolites are $w = 0$, 5%, 10%, 15% and 20% respectively. The difference among big metal bead yields is small when the cryolite amount in salt flux is $w \geqslant 10\%$, indicating that $w = 10\%$ cryolite addition in salt flux is enough, which is consistent with the recycling result with flux 44%NaCl-56%KCl-Na_3AlF_6. Furthermore, equimolar NaCl-KCl gives better metal coalescence than the salt flux composition based on 70%NaCl-30%KCl according to the yield of big metal beads, which is attributed to the lower melting point of equimolar NaCl-KCl.

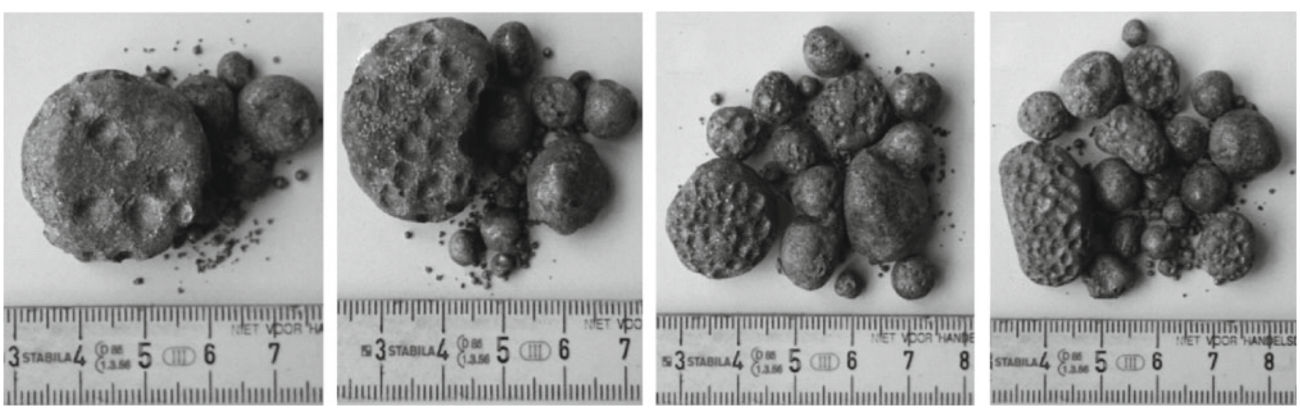
The compositions of recycled Al alloy are similar to those of recycled Al alloy by using 44%NaCl-56%KCl-Na_3AlF_6. All Mg in the recycled Al alloy is lost due to the reaction between cryolite and Mg. But other alloying elements (Cu and Mn) are well kept and impurity elements (Fe, Si, Ti) concentrations are not increased. Moreover, small amounts of NaCl and KCl are also entrapped in Al alloy during re-melting.

2.3 Refining Under 44%NaCl-56%KCl-MgF_2 Salt

The recycled Al alloys after recycling with 44%NaCl-56%KCl-MgF_2 (Experiments 11—14) are illustrated in Fig. 4. Different from the influence of cryolite on metal agglomeration behavior, the increase of MgF_2 leads to smaller sized beads, indicating that the metal coalescence capacity is reduced with increasing the amount of MgF_2 in salts flux. The possible reason is that the viscosity of molten slat flux increases with the MgF_2 addition amount, while the high viscosity is unfavorable for the movement of aluminum droplets through the molten salt. Comparing with the recycling by using the cryolite addition in salt flux, the disadvantage of MgF_2 addition on coalescence capacity is visible, and many pits caused by neighboring beads are found on the surface of recycled metal beads, indicating that the neighboring droplets cannot accumulate to one big bead.

The total metal yields are very close, though the MgF_2 addition amounts increase from $w = 5\%$ to $w = 20\%$. All total metal yields are about 98.50%, as shown in Fig. 5. The obtained results are different with the research results of van Linden and Stewart[10] who found that the metal yield was increased with the increase of MgF_2 concentrations up to $w = 10\%$. The yields of big beads are 97.74%, 97.65%, 97,21% and 96.84% when the MgF_2 addition amounts in salt flux are $w = 5\%$, 10%, 15% and 20% respectively. Big metal bead yield decreases with the MgF_2 addition amount, especially when the amount is $w \geqslant 5\%$, which is also attributed to the increased viscosity with increasing the amount of MgF_2 in flux. The total yields of MgF_2 addition are obviously higher than those of cryolite addition. The big bead yields of MgF_2 addition are also higher than those of cryolite addition when the MgF_2 and cryolite addition amounts are $w \leqslant 10\%$, but the situation is reversed when the MgF_2 and cryolite addition amounts are $w \geqslant 10\%$.

The compositions of recycled Al alloys after using MgF_2 as the additional fluoride in the salt flux are listed in Table 3. Mg and other alloying elements are well controlled during recycling. Moreover, the amount of entrapped chloride salts is slightly lower than that of cryolite addition, indicating that the salt flux with MgF_2 addition has better metal/salt separation performance than salt flux with cryolite addition. But the higher viscosity of flux with the MgF_2 addition inhibits the coalescence of droplets, and leads to a lower coalescence ability compared to flux with the cryolite addition.



(a) $w(MgF_2) = 5\%$ (b) $w(MgF_2) = 10\%$ (c) $w(MgF_2) = 15\%$ (d) $w(MgF_2) = 20\%$

Fig. 4 Al alloy after recycling with flux 44%NaCl-56%KCl-MgF_2

Table 3 Compositions of 2024 Al alloy after recycling with flux 44%NaCl-56%KCl-MgF_2 (mass fraction of other elements is not higher than 0.05%)

Experiment	w/%										Metal yield/% ($d \geqslant 2$ mm)
	Cu	Mg	Mn	Fe	Si	Ti	Na	K	Cl	Al	
11	3.94	1.02	0.592	0.114	0.143	0.030	0.006	0.013	0.043	94.16	97.74
12	4.05	0.99	0.618	0.128	0.148	0.027	0.012	0.022	0.110	93.92	97.65
13	3.97	1.00	0.590	0.113	0.135	0.038	–	0.032	0.066	94.03	97.21
14	4.07	1.04	0.602	0.121	0.154	0.032	0.010	0.018	0.036	93.97	96.84

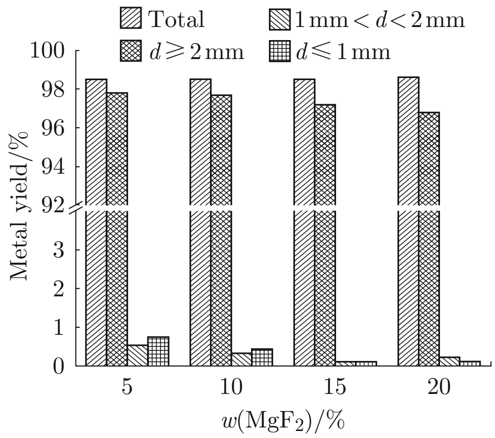


Fig. 5 Metal yield and size distribution of metal beads versus MgF_2 with flux 44%NaCl-56%KCl

3 Conclusion

After GLARE thermal delamination, the obtained 2024 Al sheets are recycled by the conventional refining method using the molten salt. For the NaCl-KCl-Na_3AlF_6 flux system, $w = 10\%$ additional cryolite is preferred, and the large metal bead yields are 97.34% and 96.76% when the employed mass ratios of NaCl and KCl in flux are 44:56 and 70:30 respectively. For the NaCl-KCl-MgF_2 flux system, $w = 5\%$ additional MgF_2 with the big metal bead yield of 97.74% is preferred and the metal yield decreases with the MgF_2 addition when additional MgF_2 is $w \geqslant 5\%$. The concentrations of alloying elements and impurity elements in recycled Al alloys are consistent with the nominal composition of 2024 Al alloy after re-melting with flux NaCl-KCl-MgF_2, but all Mg is lost when flux NaCl-KCl-Na_3AlF_6 is employed due to the reaction between Mg and cryolite.

References

[1] VLOT A, GUNNINK J W. Fibre metal laminates: An introduction [M]. Dordrecht: Kluwer Academic Publishers, 2001.

[2] HINZ S, OMOORI T, HOJO M, et al. Damage characterisation of fibre metal laminates under interlaminar shear load [J]. *Composites: Part A*, 2009, **40**(6-7): 925-931.

[3] ALDERLIESTEN R C, HOMAN J J. Fatigue and damage tolerance issues of Glare in aircraft structures [J]. *International Journal of Fatigue*, 2006, **28**(10): 1116-1123.

[4] YANG Y X, BOOM R, IRION B, et al. Recycling of composite materials [J]. *Chemical Engineering and Processing: Process Intensification*, 2012, **51**: 53-68.

[5] YANG Y X, ZHU G L, XIAO Y P. Recycling of fibre-metal laminates [J]. *Advanced Materials Research*, 2011, **295-297**: 2329-2332.

[6] XIAO Y, REUTER M A. Recycling of distributed aluminum turning scrap [J]. *Minerals Engineering*, 2002, **15**: 963-970.

[7] XIAO Y P, REUTER M A, BOIN U. Aluminum recycling and environmental issues of salt slag treatment [J]. *Journal of Environment Science and Health*, 2005, **40**: 1861-1875.

[8] HRYN J N, DANIELS E J, GURGANUS T B, et al. Products from salt cake residue-oxide [C]// *Proceedings of the 3th International Symposium on Recycling of Metals and Engineered Materials*. Alabama: TMS, 1995: 905-936.

[9] PETERSON R D. Effect of salt flux additives on aluminum droplet coalescence [C]// *Proceedings of the 2th International Symposium on Recycling of Metals and Engineered Materials*. Alabama: TMS, 1990: 69-84.

[10] VAN LINDEN J H L, STEWART Jr D L. Molten salt flux composition effects in aluminum scrap remelting [C]//*Proceedings of the Technical Sessions by the TMS Light Metals Committee at the 117th TMS Annual Meeting*. Phoenix, Arizona: TMS, 1988: 391-398.