Experiments of eliminating the destructive effects of excessive Fe inclusions for Al secondary products

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Abstract: Excessive Fe content in Al alloys caused the serious decline of mechanical properties, such as the ductility and impact toughness. Carried out the experiments of eliminating the destructive effects of excessive Fe content by flux-adding technology, which including removing a part of Fe content from Al scrap melt and modifying the morphology of Fe rich precipitates. The experimental results showed that, the ratio of removing Fe element was above 20%, and the morphology of Fe rich precipitates changed from Lamellar to bulk or lath precipitations under the process parameters: the fluxing-agents composed of borax, and MnCl₂ (mixed by mass ratio of 1:1), and the adding amount of fluxing-agents was about 1.5%; thrown the fluxing-agents into the Al scrap melt by powder injection process and kept for 30 min.

1. Introduction
Promoting the technological progress and improving production efficiency of Al scrap recycling industry were complied with the developing requirements of green, ecological and circular economy. And manufacturing the high performance Al alloy productions by Al scrap recycling process was the chasing target of the scrap recycling industries all over the world. According to industry experts predicted, by 2030, the amount of recycled Al production globally will reach 22 to 24 million tons, and 15% ~ 20% of these products would be applied in the field of high technology [1].

But the critical problem of Al scrap recycling process was that, too much inclusion elements were brought into from the Al scrap raw materials. Because the wide various types of alloy scrap materials were mixed together in the course of purchasing and acquisition process, inevitably some metals and non-metallic inclusions were involved, and resulted that the contents of impurity elements in Al secondary products mostly exceeded the composition allowable range of national standard, especially Fe and Si. At present, developed large amount of research works about the technologies of removing Fe element from Al scrap melt or improving Fe-rich precipitates morphology, mainly including: (1) dilution methods[2], which adding a certain amount of pure aluminum ingots in the Al scrap melt to reduce the content of Fe elements; (2) element neutralization technology[3], which modified the precipitation morphology of primary Fe phase by adding Mn, Cr and other elements; (3) electromagnetic separation process[4], which removing the Fe rich precipitates from the Al melting by utilizing the difference of their magnetic properties; (4) Fe removing technology by chemical reaction between borides and Fe element in Al melting[5]; (5) purification and modification mechanisms of RE elements[6]. Although some technologies were widely applied for Al recycling process, large
amount of inclusion elements were still brought into Al scrap melt. Therefore, in order to eliminate
destructive effects of Fe inclusions and ensure the Al secondary products with excellent quality, some
technologies about Fe removal from Al scrap melt and improving the morphology and distribution of
Fe-rich precipitates, should be paid enough attentions [6].

2. Materials and experimental procedures
Excessive Fe content had always been considered as one of the main harmful impurities within Al
alloys (especially in wrought Al alloys) [7]. When the Fe content in Al alloys exceeded a certain value,
the brittle Fe-rich precipitates, such as α-Fe2SiAl8 or β-FeSiAl3 and others, which possessed very high
hardness and emerged in the shape of elongated and flaky appearance, would be produced in Al alloy
organizations. The existence of brittle precipitation phases resulted in the fragmentation effects on Al
matrix, and reduced the strength, plasticity, toughness, machining performances, and so on.[8]. In this
paper, carried out feasible experiments of removing Fe element and modifying the precipitates
morphology by the technology of adding fluxing-agents into the Al melt.

Materials used in experiments included: (1) Al scrap materials derived from Ye-Chiu Metal
Recycling (China) Ltd. (2) The flux components, including borax, manganese chloride(MnCl2), were
AR chemical reagents. Its physical characteristics displayed as shown in Tab.1. Instruments for
performance measurements and microstructure analysis included: used the 5kg induction furnace to
carry out the smelting process, SEA1000A X-ray fluorescence analyzer to measure the chemical
composition, D/max-2200/PC X-ray powder diffraction to perform the slag phase analysis, optical
microscopy or scanning electron microscopy (SEM) to analysis the microstructure, and TWV-1S type
micro-accelerometers to measure the surface hardness and interfacial hardness distribution, WDW-200
material tensile testing machine to measure the strength and elongation percentage.

Experimental procedures as follows: (1) filled Al scrap materials into the furnace, heated and
melted into Al liquids; took samples for measuring Fe content, microstructure analysis, and tensile
tests; (2) thrown the flux agents into Al melting and took measures such as stirred methods, to make
the reaction between the fluxing-agents and Al scrap melts completely; (3) carried out the
refining process, and promoted the reaction molten slag to float up to the surface; (4) removed the
slags, took samples for measuring Fe content, microstructure analysis, and tensile tests; (5) took the
slag samples and analyzed the slag composites.

Table 1 Composition and physical properties of the flux.

| Flux components | Chemical formula | Melting point, °C | Density, g/cm³ | specifications | remarks |
|-----------------|------------------|------------------|---------------|----------------|---------|
| borax           | Na₂B₄O₇         | 742              | 1.73          | AR             |         |
| manganese       | MnCl₂           | 650              | 2.977         | AR             |         |

3. Results and discussion
3.1 Effects of borax added amount
The chief functions of borax embodied in removing Fe elements from Al melts, and the basic principle
was [9]:

$$Na₂B₄O₇(s) + 4Al(l) + 8Fe(l) = 2Al₂O₃(s) + 4FeB(s) + Na₂O(s)$$  \hspace{1cm} (1)

Individually added borax into Al scrap molten, whether by immersion process or by powder
injecting method, the iron-removing efficiency was limited, the relative rate of Fe removal δ was about
12%, the absolute amount of Fe removal Δ was only about 0.08%, as shown in Fig.1 and Fig.2. As the
density of borax (2 g/cm³) was smaller than Al melt (2.7 g/cm³), borax powder was easily floated up
from Al melting, and had no adequate time to carry out the chemical reaction completely. Because the
Fe content in Al scrap products generally exceeded 0.6%, some even more than 1%, obviously, adding
borax individually would not meet the requirements of manufacturing high performance productions
by Al scrap recycling.
\[
\delta = \frac{c_0 - c_1}{c_0} \quad (2)
\]
\[
\Delta = c_0 - c_1 \quad (3)
\]

Where \(\delta\) was relative rate of Fe removal; \(\Delta\) was absolute amount of Fe removal; \(c_0\) was the original Fe content; \(c_1\) was the Fe content after flux treatments;

3.2 Effect of adding MnCl\(_2\) powder individually

The chief functions of MnCl\(_2\) added into the flux were that, the chemical reaction occurred between the manganese chloride and Al melts, as following [10]:

\[
3\text{MnCl}_2 + 2\text{Al} = 3\text{Mn} + 2\text{AlCl}_3 \uparrow \quad (4)
\]

The reaction products included AlCl\(_3\) and Mn. The boiling point of AlCl\(_3\) was 183°C, and in Al melt, AlCl\(_3\) was vaporized and formed small air bubbles which can bring out the precipitates containing Fe phase or other reaction products successfully.

In addition, Mn, as another reaction product, improved the acicular and lamellar Fe precipitates to be transformed into the regular containing Mn compounds in the form of squares, fishbone and petal shape, and reduced the harmful effects.

When MnCl\(_2\) powder was added into Al scrap molten individually, the effect on iron-removing was also limited, as shown in Fig.3. The principal reason was that, MnCl\(_2\) powder can’t occur chemical reaction with Fe element existed in Al slag molten, thus only played a certain role in Fe-removing by the floating up of AlCl\(_3\) bubbles and taking some inclusions containing Fe out of Al scrap molten. But the effects of improving the Fe-rich precipitates morphology were noticeable, as illustrated in Fig.4.

3.3 Effect of flux composites
The density of composite fluxes composed of borax and MnCl₂ powder (mass ratio of 1:1) was significantly increased, reached to 2.35 g/cm³, closer to the melting point of Al scrap melt. Therefore, when added into the melt, the flux mixture would stay in the melt for a longer time, and promote the chemical reaction between the flux components and Fe inclusions in Al scrap melt to carry out more completely. Thus, adding the composite fluxes into Al scrap melt increased the Fe-removal ratio compared with individually adding borax. When the adding amount of composite fluxes was about 1.5% of Al melting mass, achieved good Fe removal efficiency; the absolute amount of Fe removal reached 0.15%, the relative rate of Fe removal was about 20%, as shown in Fig.5 and Fig.6. The other reason was that, the birth of AlCl₃ by the reaction between MnCl₂ and Al melt could easily bring the reaction products, such as FeB compounds, out of Al melt, therefore adding MnCl₂ into the flux was benefit for removing Fe inclusions. In addition, Mn element was produced by the reaction of composite flux and Al melt, could improve the precipitates morphology, as shown in Fig.7. Thus, adding the composite fluxes composed of borax and MnCl₂ into Al scrap melt could have dual functions of Fe removal and modifying the precipitates morphology.

But with the increase of the flux addition amount, the Fe removal ratio was not improved obviously, the main reasons reflected in two aspects, (1) with the development of the Fe-removal process, the contents of Fe in Al scrap melt decreased, the ability of Fe-removal reaction by composite fluxes would be dropped down; (2) An excessive dose of composite flux easily was concentrated together, and floated up out of Al melt.

Although the generation of Mn element could reduce the destructive effects of excessive Fe content by producing (Fe,Mn)Al₆ et al. The Mn contents was increased with the increase of adding composite flux, which could make the contents of Mn element beyond the scope of the national standards; and excessive Mn element played limited roles in improving the precipitation morphology, therefore, the adding amount of composite flux should not be too much.
By XRD analysis of the slag sampling, as schematic in Fig. 8, found the reaction product of FeB in the slag samples, and proved that the borax played main role in the Fe-removal reaction.

3.4 effect of standing time after adding composite flux

The standing time was the delayed duration after the composite Flux was thrown into the Al scrap melt. With the extension of the standing time within 30 min, the Fe-removal efficiency was constantly raised up; But over 30 minutes after, made little impact on the Fe-removal ratio, as shown in Fig.9. The composite fluxes was thrown into the Al scrap melt, although the addition of MnCl₂ increased the density, the flux was still light-weighted compared with the Al melt, the flux would gradually float up out of the melt; therefore, the residence time of the composite flux in Al scrap melt was limited, and the Fe-removal reaction stopped slowly.

![Fig.9 effect of standing time](image)

1- by powder injecting; 2- by immersion process

Effects of the standing time on improving the Fe-rich precipitates morphology were not significant. At first, the reaction between MnCl₂ and Al melt occurred violently, Mn element was produced rapidly; secondly, with the prolongation of time, the Fe-rich precipitates, which composed of Fe, Mn and other elements, would occur the aggregation and settlement.

3.5 The quality of Al secondary ingots

After dealing with composite flux to the Al scrap melts, the quality of Al secondary ingots had been significantly improved, as shown in Fig.10 and Fig.11. The tensile strength increased from 107 MPa to 145 MPa, and the elongation increased from almost 0 to 8% or so.

![Fig 10 stress-strain curve of original Al scrap ingot process](image)  ![Fig 11 stress-strain curve of ingot by fluxing process](image)

4 Conclusion

Carried out feasible experimental research on the technology of decreasing the destructive impact of excessive Fe contents on Al secondary productions by adding composite fluxes into Al scrap melt, and
drawn the following conclusions:

1. The best technological parameters was that: (1) the composite fluxes composed of borax and MnCl₂ mixed with the mass ratio of 1:1; (2) added the composite fluxes in the Al scrap melt at 730-750 °C, by powder injection method; (3) standing for 30 min can obtain excellent effects;

2. Achieved the Fe-removal ratio of 20%, basically eliminated the lamellar or coarse Fe-rich precipitates, and changed into bulky or other round morphology;

3. Increased mechanical properties of the Al secondary ingots, the tensile strength raised up to 145 Mpa, and the elongation reached 8%, can greatly improve the work performances.

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