博士論文（要約）

Purification Method of Tramp Elements in Structural Materials Scrap by using Semisolid Processing

（半溶融処理を利用した構造材料スクラップからの不純物元素の純化法）

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Metal alloy scraps such as aluminium alloy scrap and steel alloy scrap are widely used in manufacturing around the world in almost every industry including automotive, aircraft, aerospace, construction, transportation and food packaging. It has been known that the aluminium alloy scrap and steel alloy scrap can be recycled again and again very easily to produce the new metal alloy product from the old metal alloy scrap. Recycling of the metal alloy scrap provides the economic and environmental benefits comparing with the production of the primary metal from metal ore. For example, the extraction of primary aluminium from bauxite ore is very expensive because the large amount of electricity is necessary to melt the alumina (Al_2O_3), which has the melting point of over 2000˚C. Thus, the producers in industrial field are greatly interested in production of secondary metal from the metal scraps. Although there are so many benefits in the recycling of the metal alloy scraps, the accumulation of the tramp elements is an increasing problem in the repeated recycling process. Thus, the effective separation technology of tramp elements is very important in the recycling process. There are two parts in this study, one is purification of aluminium alloy scrap and another part is purification of steel alloy scrap.

Aluminium and its alloy are widely used in the world for the practical applications such as aerospace industry, electrical application and food packaging due to the properties of light weight, good electrical and thermal conductivities and corrosion resistance. But, the production of primary aluminium is very energy-intensive process. Recycling is the method of the production of the secondary aluminium alloy from the aluminium scrap and it is very important method in the recycling industry. According to the literature cites, aluminium alloy scrap can be recycled for many times without losing of its quality. The problem is increasing the tramp elements including iron, silicon, magnesium, copper and manganese in the repeated aluminium recycling process. These tramp elements can give negative effect on the recycled aluminium product which is produced from the aluminium alloy scrap.

Thus, it is necessary to eliminate or control the concentration of the tramp elements before producing the secondary aluminium alloy products. In the conventional recycling process, the primary aluminium is used to reduce the concentration of tramp elements in aluminium alloy scrap. But, underground resources of bauxite ore, which is necessary to produce primary aluminium are expected to be depleted in the future. According to the several literatures cites, there are mainly two types of separation technology. One is pre-melting technology, which is physical separation of the solid scraps to separate the metals and elements. Another one is melt-technology (Refining technology), which is chemical or metallurgical separation of the tramp elements from the metal alloy scrap during melting.

In this study, the metal alloy scraps were purified by using the backward extrusion process under the semisolid condition, based on the metallurgical separation method. The purifying principle is that the liquid metal starts to solidify from the wall of the container and progressing gradually towards to the central part of the container. After achieving the semisolid state, the liquid phase containing the tramp elements accumulated in the central part. Finally, this liquid phase was extracted by using the backward extrusion method.

The Objectives of the whole study are as follows:

(1) To clarify the backward extrusion method under semisolid condition, whether it is suitable for purification of both aluminium alloy scrap and steel alloy scrap or not
(2) To understand the exact mechanism of the purification process for the metal alloy scrap
(3) To investigate the process parameters of purification process on the purification of the metal alloy scrap
(4) To know how the process parameters effect on the purity of the metal
(5) To test this backward extrusion method under semisolid condition for purification of aluminium alloy scrap as an industrial scale
(6) To know how the repeated backward extrusion method effects on both purification in the unextruded part and densification in the extruded part of the extruded sample

The experiments were carried out by using the wrought aluminium alloys A7N01 and A7075, cast aluminium alloy AC4C, ADC12 based hypereutectic aluminium alloy, aluminium beverage can scrap. The range of semisolid temperatures was estimated by measuring the cooling curve with a DL 708E 8Ch, Digital Scope for each of these alloy scraps. The billet diameter and height is 32mm and 40mm, respectively in prototype scale experiments and 60mm and 90mm in industrial scale experiments. Before backward extrusion, the temperature distribution of the aluminium alloy scraps was measured during the semisolid condition. It was found that the temperature of the center point of the central part had the highest temperature. It means that the liquid phase accumulates in the central part. After backward extrusion was conducted at the suitable semisolid condition, the formed specimen was cut along the axial direction, which was followed by polishing and etching to investigate the microstructure. Microscopic observations were carried out in the extruded part and the unextruded part. The hardness of the sample was measured with a Rockwell hardness tester. Finally, the extruded part and the unextruded part of the extruded samples were analyzed by using an Electron probe micro-analyzer (EPMA), Scanning electronic microscope (SEM) and Energy-dispersive Spectroscopy (EDS) to evaluate the distribution of chemical elements in the unextruded part and the extruded part after backward extrusion.

According to the results of optical microscopic images, it was found that coarse grains were formed in the unextruded part and the small grains were formed in the extruded part. And, the liquid phase accumulated on the grain boundaries of the extruded part. According to the results of Rockwell hardness testing, the hardness of the extruded part had higher hardness than that of the unextruded part. It seems that the unextruded part was enriched with highly purified aluminium due to having lower hardness than the extruded part. From the results of EPMA analysis, it was found that the weight percentage of aluminium was increased from 92.55% to 95.15% in the unextruded part of A7N01 alloy, from 92.7% to 97.6% in the unextruded part of AC4C alloy, from 88.02% to 94% in the unextruded part of A7075 alloy and from 96.4% to 99.12% in the unextruded part of aluminium beverage can scrap ingot. The amounts of the tramp elements of Mn, Si, Fe, Mg, Cu and Zn except Cr were reduced in the unextruded part of extruded samples of aluminium alloy scrap. The repeated backward extrusion provides more efficient purification of aluminium alloy scrap.

In ADC12 based hypereutectic aluminium alloy, which contains Silicon as the main alloying element, the weight percentage of Si was about 16% before purification. After backward extrusion process under the semisolid condition, it was found that the flakes of silicon were still remained even in the unextruded part. It was clarified that Si, the main tramp element in ADC12 based hypereutectic alluminium alloy, could not be removed from the samples, regardless of the extrusion ratio. It can be confirmed that the Si content at the eutectic point is 12.6% in Al-Si phase diagram. Since the Si content was over eutectic percentage before purification, it was difficult to separate out the Si under the semisolid condition. Thus, it was confirmed that this backward extrusion process under semisolid condition is suitable only for hypoeutectic aluminium alloy scrap.

The process parameters such as extrusion temperature, extrusion ratio are also affecting on the purification of aluminium alloy scrap according to the results of purification of A7075 alloy by using the manual press for backward extrusion process. Moreover, the backward extrusion was conducted under the semisolid condition by using the AC mechanical Servo Press (Komatsu- H1F110) as an industrial scale for purification of A7075 wrought aluminium alloy. And, the process parameters including the semisolid temperature, backward extrusion ratio, maximum initial extrusion speed and load were investigated. There were optimum values of process parameters in the condition of this proposed purification process.

As a second part of this study, the purification of steel alloy scrap was conducted by using the backward extrusion process under the semisolid condition. Steel is the most widely used in the practical applications such as construction, transportation and food packaging and it is also known as the world's most recycled metal. And, steel scrap is an essential raw material to produce new steel product and in hot work steel production. Steel alloy scrap can also be recycled repeatedly like aluminium alloy scrap. And, it is necessary to control the concentration of the tramp elements including copper, tin, zinc, nickel and lead which have negative influence effect on the mechanical properties of steel product and hot forming ability in the rolling process. The copper, zinc and tin are the most undesirable tramp elements in the recycling process of steel alloy scrap. Thus, in this study, the backward extrusion method was conducted to purify the steel alloy scrap and to clarify whether this method is suitable for purification of steel alloy scrap or not.

As the experimental trail, stainless steel SUS 304 containing the chromium and nickel as the main alloying elements and steel beverage can scrap were selected. The size of the billet was 30mm diameter and 35mm height. The range of semisolid temperature of stainless steel SUS304 and steel beverage can scrap were measured by using the cooling curve with a DL 708E, Digital Scope. After achieving the suitable semisolid temperature state, the backward extrusion was carried out to separate the liquid phase containing the tramp elements and the solid phase containing the purified metal. According to the results of optical microstructures, it was seen that coarse grains were formed in the unextruded part while the small grains were formed in the extruded part like purification of aluminium alloy scrap. From the results of EPMA analysis, enrichment of chromium was observed in the unextruded part and enrichment of nickel and iron were observed in the extruded part. This backward extrusion method under the semisolid condition has a tendency for phase separation of chromium and nickel in the stainless steel SUS304.

As the results of purification of the steel beverage can scrap, it was found that weight percentage of iron was increased from 98% to 99% in the unextruded part and the tramp elements such as copper, zinc and tin were separated in the unextruded part after purification process. Aluminium and silicon were also reduced except chromium and manganese. Thus, it was confirmed that this backward extrusion method at the semisolid state is applicable for not only purification of steel alloy scrap but also for separation of two different elements in metal alloy.

The backward extrusion method under semisolid condition is very simple and quick for purification of the metal alloy scraps. The extruded part containing the tramp elements can be cut easily. The results from the purification of aluminium alloy scrap used in this study would provide to produce new aluminium alloy products from the aluminium alloy scrap, especially in production of wrought aluminium alloy because the wrought aluminium alloy cannot be produced without reducing the tramp elements in repeated recycling process. Thus, this backward extrusion method is useful as a manufacturing process of purified aluminium, which is necessary to produce new aluminium alloy products in the aerospace industry.