RESEARCH ON MANUFACTURING ALUMINUM - RARE EARTH ALLOY WITH A HIGH CONTENT OF RARE EARTH (> 20% RE) FROM TOTAL RARE EARTH OXIDES BY THERMIT REDUCTION

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ABSTRACT: In this report, several theoretical principles of thermit reduction method used for metal oxides to obtain metals, ferroalloys and ligatua with technical purity are presented. Manufacture of aluminum-rare earth alloys by thermit reduction is also described in the report.

Data that are generalized based on thermo-kinetic calculation of the thermit reduction and selection of technological flow-sheet based on thermal effect will partly clarify research results in investigating typical features of the process and identify measures to reduce metal loss in discharged slags.

INTRODUCTION

In the mechanical manufacture industry, besides cast iron and steel, non-ferrous alloys with special characteristics such as chemical, mechanical, thermal persistances as well as light weight, easy to cast and easy to mechanical processing etc. always play an important role. These alloys are normally produced from base metals such as Al, Ti that are then added with rare metals and rare earth etc. The Al-RE alloy is one of ligatures to be used for that purpose.[4]

To meet the increasing demand on the use of rare earth elements in manufacturing new materials of metals, ferrous and non-ferrous alloys, the research on manufacturing alloys of rare earth elements and several non-ferrous metals in which there are Al-RE, Al-Si-RE with a possible maximum content of rare earth, is considered necessary and right work to do.

RESULTS OF EXPERIMENT

1. Objective, requirement and task

- Researching technological conditions (temperature, time, composition of raw materials, furnace materials etc.) to manufacture Al-RE alloys from total rare earth oxides by thermit reduction in the induction furnace of midium or high frequencies or in the resistance furnace with temperature up to 1700^{0}C.

- Setting up a procedure with appropriate technological conditions to manufacture Al-RE alloys.

- Analyzing and testing the quality of research products: rare earth content exceeding 20%.

2. Research method

2.1. Research content

The process of thermit reduction takes place according to the following equation:

$$2/m\text{Me}_n\text{O}_m + 4/3\text{Al} = 2n/m\text{Me} + 2/3\text{Al}_2\text{O}_3 \qquad (1)$$

Al-RE alloy is formed from total rare earth oxides RE_2O_3 by thermit reduction of Al according to the following equation:

$$RE_2O_3 + 2Al = 2RE + Al_2O_3 \qquad (2)$$

The reaction (2) takes place at temperatures higher than 1200^0C. The higher the temperature is, the stronger the reaction is. Due to chemical characteristics of rare earth metals, at high temperatures, they quickly react with oxygen in the air to produce RE_2O_3. Therefore, in order to obtain Al-RE alloys with required composition, on the one hand, it is necessary to have a protective medium in the form of flux additives to separate rare earth metals from oxygen in the air. On the other hand, there should be an exceed amount of Al metal in the mixture of raw materials to dissolve generated rare earth metals.

According to the simple state diagram of Al-RE system (figures 1, 2, 3 and 4), the higher the temperature is, the larger the content of rare earth metals is, but the more flammable it is. Hence, it is very important to choose appropriate temperature to produce alloys and flux additives. [6], [13]

2.2. Technological procedure

2.2.1. The first procedure:

Stage 1: Put the chosen and weighed flux additive salts (based on the ratio of each batch) into a baking cup.

Stage 2: Put the cup into burning chamber of the furnace and raising the temperature

Stage 3: When the additive salts are moltening, little by little put aluminum metal in the forms of wire or clot until the required amount of aluminum (according to the calculation for each batch) is completely moltened.

Stage 4: When the aluminum is completely moltened and dissolved into flux additives, continue to increase heat to reach the chosen temperature for each experimental batch.

Stage 5: When the temperature reachs the chosen level, gradually put the amount of total rare earth oxides that are weighed according to the appropriate ratio for each batch) into moltening system and stir evenly; slightly stir several times in the required period of time.

Note: *The process of checking raw materials and mixing has been conducted when the temperature of input material exceeds 700^0C (when aluminum metal in the load of raw materials is at $T_{melt.}$).*

Stage 6: When the time is enough, taking the baking cup off the furnace, pouring the mental and slag into the mould;

Stage 7: Cool down, take off slag layers on the metal surface (slag and metal are separated in the refining process).

Finish the procedure of an experimental batch.

2.2.2. The second process:

Stage : Thoroughly mix main materials *(after weighing based on the chosen ratio):*

- Al metal in the shape of small clot with the size of d=5÷10 *mm*;
- Total rare earth oxides REO in the flour form.

Stage 2: Put the raw materials into a baking cup;

Stage 3: Cover the surface of the load of raw materials with flux additive salts (after weighing and mixing according to the calculated ratio for each batch

Stage 4: Put the cup into the burning chamber of the furnace and raise the temperature;

Stage 5: When temperature reaches the chosen level, slightly stir several times in the required period of time.

<u>*Note*</u>: *The process of checking and mixing raw materials are is conducted when temperature in the load of raw material exceeds 700^{0}C (when the aluminum metal in the load of raw materials is at $T_{melt..}$).*

Stage 6: When time is long enough, take the baking cup out of the furnace, pour the metal and slag into a mould;

Stage 7: Cool it down, take off slag layers on the surface of metal (slag and metal were separated into layers in the refining process).

Finish the procedure of an experimental batch.

Results of the experiments on the RE content in the Al-RE alloy and metal recovery yield in the fire refining batches are symbolized as follows: NĐ I(II)-n/1(2), TG I(II)-n/1(2), TL I(II)-n/1(2) in which:

NĐ - Study on the effect of temperature;

TG - Study on the effect of time;

TL - Study on the effect of the ratio of blending raw materials;

I - Study on the effect of factors in the salt group of CaF_2-$CaCl_2$-NaCl;

II - Study on the effect of factors in the salt group of Na_3AlF_6-Al_2O_3;

n - The order of the batches of fire refining experiments;

1 - Refining according to the 1st procedure;

2 - Refining according to the 2nd procedure.

3. Results of implementing study contents

3.1. Study on the effect of temperature

The study is aimed at pointing out the most suitable temperature to get the highest yield of rare earth metals in the fire refining processes. Investigation was carried out based on the two chosen flux additives and two remaining constant factors such as reaction duration and ratio of blending raw materials REO/Al.

Experiments on the effect of temperature were conducted based on state diagrams of Al and rare earth elements. The results are shown in the following tables.

3.1.1. The system of additive salt CaF_2-$CaCl_2$-NaCl.

Table 1: Effects of temperature in the process of fire- refining Al-RE alloy in the system of additive salt CaF_2-$CaCl_2$-NaCl

Sign of sample	Main blending ratio		Reaction duration *(hour/batch)*	Reaction temperature (°C)	RE content in alloy, %	RE recovery yield (%)
	REO/Al (kg/kg)	Surplus Al *(times)*				
NĐ I-1/1	1/3.75	1.25	0.5	1250	≈ 16.72	≈ 67
NĐ I-2/2					≈ 18.01	≈ 72
NĐ I-3/1				1300	≈ 17.27	≈ 68
NĐ I-4/2					≈ 18.52	≈ 74
NĐ I-5/1				1350	≈ 19.17	≈ 76
NĐ I-6/2					≈ 19.56	≈ 78

3.1.2. The system of additive salt $Na_3Al\,F_6$-Al_2O_3.

Table 2: Effect of temperature in the process of fire-refining Al-RE alloy in the system of $Na_3Al\,F_6$-Al_2O_3.

Sign of sample	Main blending ratio		Reaction duration *(hour/batch)*	Reaction temperature (°C)	RE content in alloy, %	RE recovery yield (%)
	REO/Al (kg/kg)	Surplus Al *(times)*				
NĐ II-7/2	1/3.75	1.25	0.5	1250	≈ 18.03	≈ 72
NĐ II-8/2				1300	≈ 18.53	≈ 74
NĐ II-9/2				1350	≈ 19.57	≈ 78

Conclusion: In the two systems of flux additives for forming slag, with the same main blending ratio REO/Al at 1/3.75 (the surplus aluminum 1.25 times higher than that of theoretical calculation) and the same reaction duration of 1/2 hour, at 1350°C, *thermit reduction reaction allows to get the best recovery yield of metals and maximum recovery yield at 78%. The application of the 2nd technological procedure shows more promising results.*

3.2. Study on effect of time

Based on the appropriate temperature in fire-refining process, the reaction will take place in the different intervals: 1/2 hour; one hour; 1.5 hours and 2 hours, with other factors remained constant such as temperature and blending ratio. The results are explained in the following tables.

Investigation in the interval of 1/2 hour has already conducted in the previous experiments (when studying on the effect of temperature in thermit reduction).

3.2.1. The system of flux additive salt CaF_2-$CaCl_2$-NaCl.

Table 3: The effect of time in the process of refining Al-RE alloy in the system of additive salt CaF_2-$CaCl_2$-NaCl

Sign of sample	Main blending ratio		Reaction duration (*hour/batch*)	Reaction temperature (^{0}C)	RE content in alloy, %	RE recovery yield (%)
	REO/Al (kg/kg)	The surplus Al (*times*)				
NĐ II-10/2	1/3.75	1.25	1350	1.0	≈ 19.75	≈ 79
NĐ II-11/2				1.5	≈ 19.32	≈ 77
NĐ II-12/1				2.0	≈ 18.67	≈ 75

3.2.2. The system of flux additive salt $Na_3Al\,F_6$-Al_2O_3.

Table 4: The effect of time in the process of refining Al-RE alloy in the system of $Na_3Al\,F_6$-Al_2O_3

Sign of sample	Main blending ratio		Reaction duration (*hour/batch*)	Reaction temperature (^{0}C)	RE content in alloy, %	RE recovery yield (%)
	REO/Al (kg/kg)	The surplus Al (*times*)				
NĐ II-13/2	1/3.75	1.25	1350	1.0	≈ 21.32	≈ 85
NĐ II-14/2				1.5	≈ 20.52	≈ 82
NĐ II-15/2				2.0	≈ 20.25	≈ 81

Conclusion: In the two systems of flux additive salts for forming slag, with the same ratio of main REO/Al at 1/3.75 (the amount of surplus aluminum higher 1.25 times than that of theoretical calculation) and at the same 1350^{0}C, with the reaction duration of one hour, the thermit reduction has got the highest recovery yield in the range of 79(I) - 85(II) %.

3.3. Study on the effect of main blending ratio

Study on the effect of ratio of blending raw materials to the process of refining Al-RE alloys was based on the following factors:

- The suitable temperature in the reactions is chosen from experiments in the tables 1&2: 1350 ^0C;

- The suitable reaction duration is chosen from experiments in the tables 3&4: 1.0 hour per batch of baking;

- At the same time, based on the calculation under the equation (2) of thermit reduction reaction of the total rare earth oxides RE_2O_3:

$$RE_2O_3 + 2Al = 2RE + Al_2O_3,$$

The amount of aluminum in blending raw materials reacts with RE_2O_3 to obtain Al-RE alloy with the content of RE over 20% RE (≈ 25%) and the ratio of REO/Al = 1/2.58 ≈1/3.

However, due to chemical characteristics of rare earth metals, at high temperatures, these metals quickly react with oxygen in the air to form RE_2O_3. Therefore, in order to obtain Al-RE alloys with required composition, on the one hand, it is necessary to have a protective medium in the form of flux additives to separate rare earth metals from oxygen in the air. On the other hand, there should be an extra amount of Al metal in the mixture of raw materials to dissolve generated rare earth metals.

In fact, in the performed experiments, the content of aluminum is added 1.2 to 2 times bigger than that in theoretical calculation, meaning that the ratio of RE_2O_3/Al is equal to 1/3.6 : 1/6. Results of the experiments on the two flux additive salts to study the effect of ratio of blending raw materials are shown in the Tables 5&6.

3.3.1. The system of flux additive salts CaF_2- $CaCl_2$- NaCl.

Table 5: The effect of ratio of blending raw materials in the process of refining Al-RE alloy in the system of flux additive salts CaF_2-$CaCl_2$-NaCl

Sign of sample	Temperature of reaction *(^0C)*	Reaction duration *(hour/batch)*	Ratio of main blending		RE content in the alloy, %	Recovery yield of RE, *(%)*
			REO/Al (kg/kg)	Surplus Al *(times)*		
TL I-16/2	1350	1.0	1/4.2	1.4	≈ 22.05	≈ 88
TL I-17/2			1/4.5	1.5	≈ 22.75	≈ 91
TL I-18/2			1/6	2.0	≈ 22.85	≈ 91.5

3.3.2. The system of flux additive salts Na_3AlF_6- Al_2O_3

Table 6: The effect of ratio of blending raw materials in the process of refining Al-RE alloy in the system of flux additive salts Na_3AlF_6-Al_2O_3.

Sign of sample	Temperature of reaction (°C)	Reaction duration (hour/batch)	Ratio of main blending		RE content in the alloy, %	Recovery yield of RE, (%)
			REO/Al (kg/kg)	Surplus Al (times)		
TL II-19/2	1350	1.0	1/4.2	1.4	≈ 22.35	≈ 89
TL II-20/2			1/4.5	1.5	≈ 22.84	≈ 91.5
TL II-21/2			1/6	2.0	≈ 22.86	≈ 91.5

Conclusion: In the two systems of flux additive salts for forming slag at the same 1350°C and with the same reaction duration of 1.0 hour, the ratio of main REO/Al at from 1/4.5 to 1/6 (the amount of surplus aluminum from 1.5 to 2.0 times higher than that of theoretical calculation), the thermit reduction has got the higher recovery yields with the maximum yield of 91.5%.

CONCLUSION

1. Through results of study on thermit reduction of total rare earth oxides to obtain Al-RE alloys, we can point out the suitable temperature, duration and ratio of blending raw materials to get alloys with relative high recovery yields as follows:

- The temperature of reaction: 1350°C;
- The duration of reaction: 1.0 hour ;
- The blending ratio of REO/Al: 1/4.5 (*kg/kg*) (*surplus aluminum at 1.5 times*).

2. Based on testing and analyzing the quality of alloys obtained from experiments of thermit reduction of total rare earth oxides, the content of rare earth elements in the Al-RE alloys is determined in the range of 16.72 - 22.86%.

3. The process of thermit reduction in the system of flux additive salts Na_3AlF_6-Al_2O_3 gets the better results in comparison to that of CaF_2-$CaCl_2$-NaCl at the same condition with the same main parameters (temperature, time and ratio of blending raw materials). However, the price of criolite Na3AlF6 in the market is very high.

4. Since rare earth recovery yields are equal when the amount of aluminum used in the reaction is higher 1.5 to 2.0 times than that of theoretical calculation, it is possible to use this parameter with the surplus aluminum at 1.5 times (at the rate REO/AL = 1/4.5) to save the amount of input aluminum.

5. Due to the scope of study and budget of the project, the study on the effect of slag system to the process of thermit reduction is not further conducted.

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