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Preparation of Novel Al-Er Master Alloys in Chloride-Fluoride Melt

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Abstract. A novel Al-Er master alloy has been prepared through situ metallothermic reactions of $NaErF_4$ and aluminium melts. The compound $NaErF_4$ is formed as a result of the interaction of NaF and ErF_3 in the melt medium KCl. The metallothermic reactions produce erbium, which through low solubility in molten aluminium and forms intermetallic compound Al_3Er. The microstructures of the Al-Er master alloy with different contents of the alloying metal has been investigated. The results showed that the Al-Er master alloy mainly consisted of phases of α-Al and Al_3Er, that confirmed by the results of X-ray diffraction. Backscattered electron imaging of the Al-Er master alloy under a scanning electron microscope (SEM) revealed the presence of phase Al_3Er, which crystallized in the eutectic composition [Al+Al_3Er]. The observed microstructure is explained according to the eutectic reaction in an Al-Er phase diagram. The preparation of Al-Er master alloy by the metallothermic reduction method will allow to reduce energy consumption for master alloy production and to reduce the cost of aluminium alloys alloyed with Er through the novel master alloy.

Introduction

To improve mechanical properties and workability of aluminum alloys, it is now an effective method to add of trace amount of rare earth metals (REM) to aluminum melt. In the recent years of research studies the effect of low additions of erbium on the properties and microstructure of aluminum and its alloys has been intense [1-10]. The typical content of erbium in wrought and aluminium cast alloys are varies from 0.01 to 1.0 mass %, but preferably 0.1-0.3 mass % [11].

Erbium form thermodynamically stable $L1_2$-ordered Al_3Er precipitates during ageing heat treatment [12]. These precipitates can improve the creep resistance in coarse-grained Al-based alloys [13]. Erbium is potentially an efficient grain refiner for wrought and aluminum cast alloys [1, 3, 6, 8]. However, melting point and atomic weight of erbium are 1802 K (1529 °C), and 167.259 amu, respectively, much higher and larger than those of aluminum. Furthermore, the solubility of erbium in aluminum is extremely low. Therefore, it is necessary to prepare Al-Er master alloys for use in aluminum alloy production.

A master alloys is an intermediate alloy containing a sufficient content of the metal added to the melt for obtaining the required chemical composition, structural and technological properties of castings and ingots. Currently, Al-Er master alloys are prepared by direct alloying aluminium with erbium, respectively [6, 8, 9, 12]. In its pure form, Er has a high melting point, which leads to losses of the alloying element and the base during melting and significant contaminate of master alloys by non-metallic impurities. As indicated earlier, the use of pure Er is inefficient due to the long and incomplete assimilation of aluminium melts.

Research into the preparation of Al-Er master alloys is still very limited. Al-Er master alloys can be prepared by addition of mixture of salts, which reacts in-situ to produce erbium metal. It is known investigations into the preparation of aluminium master alloys with scandium [14-16], zirconium [17], yttrium [18] and multicomponent [18, 19] by metallothermic reduction of molten salts.

The aim of the present work was to study the preparation Al-Er master alloys by metallothermic reduction of chloride-fluoride melt, investigation of the microstructure and phase composition of master alloys with different content of erbium and find out optimum content of erbium in novel master alloys for foundry industry.

Experimental Procedure

In this study, erbium fluoride (ErF_3), sodium fluoride (NaF) and potassium chloride (KCl) were used as the raw materials to acquisition of chloride-fluoride melt (flux). Master alloys were prepared from pellets (round ingots) of Al (A99.9) diameter 5-10 mm and chloride-fluoride melt by an metallothermic reduction process. Reduction melting was carried out in graphite crucibles placed in a resistance furnace. In the laboratory scale melts were made by heating approximately 200 g of sample at 800 °C in the furnace. The Al pellets and flux were added to the graphite crucibles then placed in the furnace.

The powder X-ray diffraction (XRD-6000, «Shimadzu») measurement using Cu K_a radiation was carried out to identify the crystalline phase of the chloride-fluoride melt.

The microstructure characteristics of Al-Er master alloys were investigated by X-ray diffraction (XRD) and scanning electron microscope (Vega 3 LM, «Tescan»).

Results and Discussion

The preparation of Al-Er master alloy was studied by aluminothermic reduction of chloride-fluoride melts and shown on the following chemical reaction which is supposed to follow via reaction (1):

$$3NaErF_4 + 12Al = 3Al_3Er + Na_3AlF_6 + 2AlF_3 \quad (1)$$

were Al acted as both a reductant as well as base of the master alloy. Mixture of the salts ErF_3 and NaF participate on the formation of the complex compound $NaErF_4$ in the presence of KCl melt. Erbium content in obtained master alloy depended on the amount of erbium fluoride in original melt.

Mixtures of ErF_3, NaF, KCl melt in a ternary eutectic relationship. $NaErF_4$ formation was confirmed by X-ray diffraction (XRD) analysis of the sample of flux (Fig. 1). The observed peaks were identified as $NaErF_4$ and KCl medium (substrate).

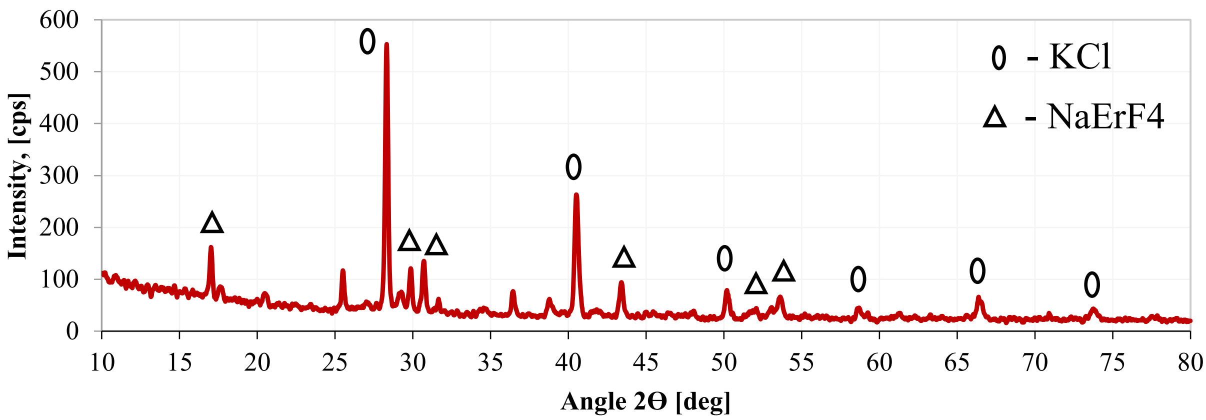
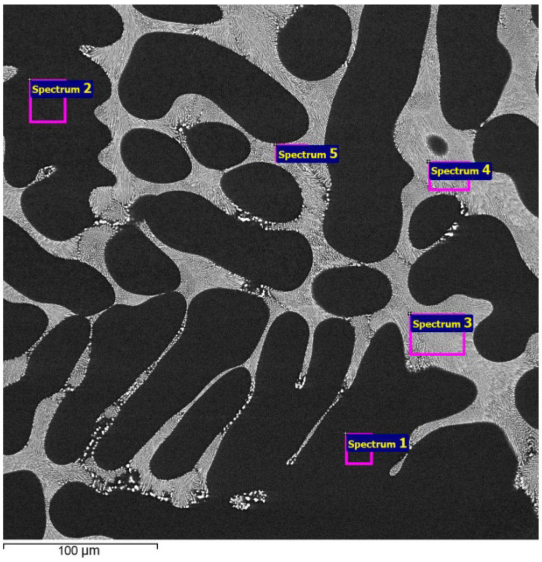


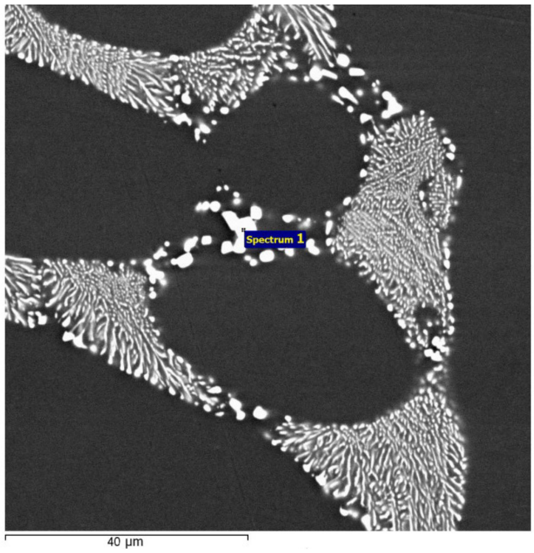
Fig. 1. XRD analysis of the chloride-fluoride melt for preparation Al-Er master alloys.

The general information of the phase diagram Al-Er system the reported in [20]. By the data of the analysis of equilibrium phase diagrams [21] of binary systems, the microstructure of the Al-Er master alloys should contain primary crystals of an aluminum solid solution (Al) and an [(Al) + Al_3Er] eutectic. Analysis of the microstructures of the master alloys under a scanning electron microscope (SEM) (Fig. 2) confirms the data of the phase diagrams. It can be seen from Fig. 2 that the microstructure of Al-3.4% Er master alloy contains primary crystals of (Al) and a dispersed eutectic mixture. Erbium actively react with aluminium and forming intermetallic compounds in the eutectic and in highly disperse form.

The SEM images of samples of Al-Er master alloys with mass % of Er 4.2 and 6.1 prepared by metallothermic reduction of chloride-fluoride melt are shown in Fig. 3 and Fig. 4 respectively.



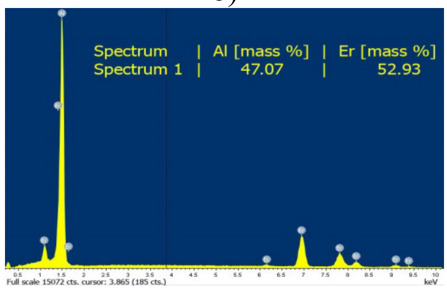
a)



b)

Spectrum	Al [mass %]	Er [mass %]
Spectrum 1	99.69	0.31
Spectrum 2	99.58	0.42
Spectrum 3	87.23	12.77
Spectrum 4	87.51	12.49
Spectrum 5	87.83	12.17

c)



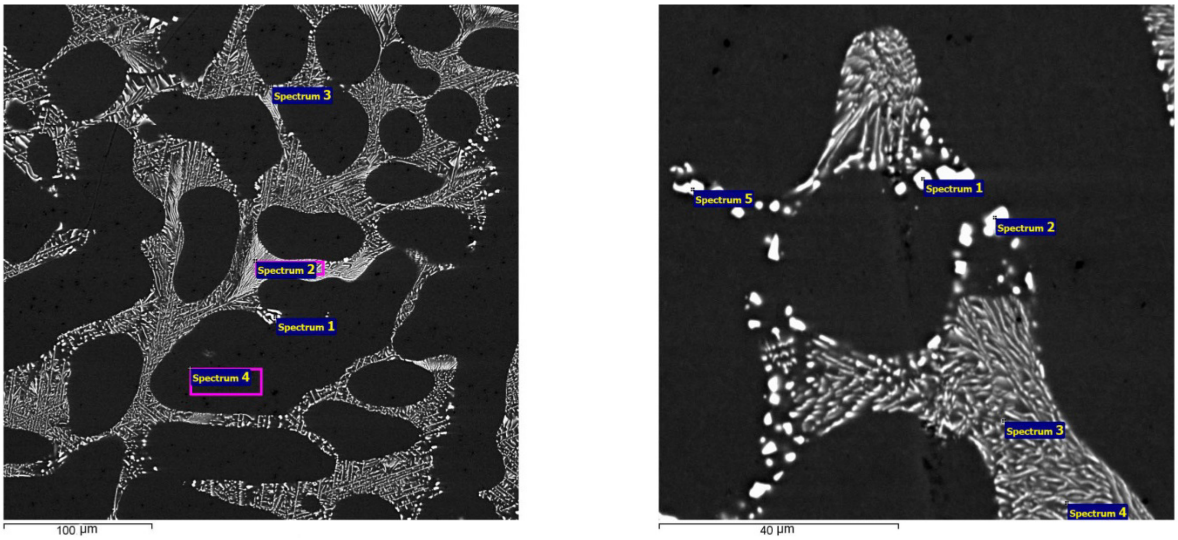
d)

Fig. 2. Microstructure and results of energy dispersive spectrum (EDS) analysis of Al-Er master alloys with 3.4 mass % Er: a) SEM image; b) SEM image; c) results of EDS analysis of (a); d) spectrum of EDS analysis of (b).

Fig 2-4 indicate that increasing erbium level results in coarsening intermetallic compounds Al_3Er in eutectic composition. The summarized data about size of the dendrite cells of (Al) and erbium content in the eutectic of master alloys are shown in Table 1.

Table 1. The size of the dendrite cells and erbium content in the eutectic.

Master alloys, [mass %]	Size of the dendrite cells of (Al) [μm]	Erbium content in the eutectic [mass %]
Al-3.4 Er	40 ± 8	12.5
Al-4.2 Er	42 ± 4	16.0
Al-6.1 Er	53 ± 9	8.6



a) b)

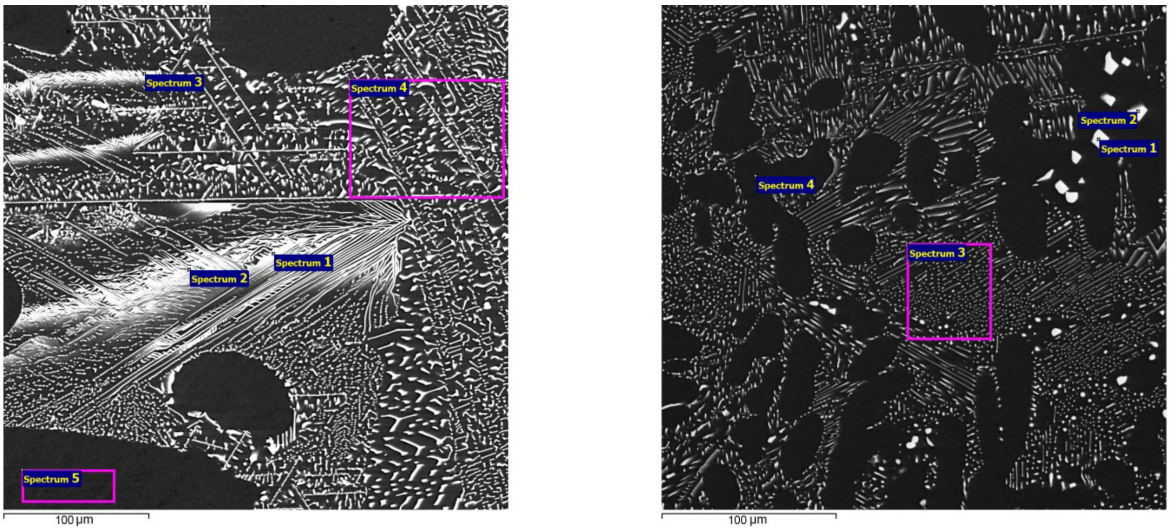
Spectrum	Al [mass %]	Er [mass %]
Spectrum 1	58.05	41.95
Spectrum 2	85.12	14.88
Spectrum 3	65.88	34.12
Spectrum 4	99.73	0.27

c)

Spectrum	Al [mass %]	Er [mass %]
Spectrum 1	56.63	43.37
Spectrum 2	45.47	54.53
Spectrum 3	82.18	17.82
Spectrum 4	83.50	16.50
Spectrum 5	51.16	48.84

d)

Fig. 3. Microstructure and results of energy dispersive spectrum (EDS) analysis of Al-Er master alloys with 4.2 mass % Er: a) SEM image; b) SEM image; c) results of EDS analysis of (a); d) results of EDS analysis of (b).



a) b)

Spectrum	Al [mass %]	Er [mass %]
Spectrum 1	81.72	18.28
Spectrum 2	82.72	17.28
Spectrum 3	92.00	8.00
Spectrum 4	91.04	8.96
Spectrum 5	99.83	0.17

c)

Spectrum	Al [mass %]	Er [mass %]
Spectrum 1	35.47	64.53
Spectrum 2	40.78	59.22
Spectrum 3	90.99	9.01
Spectrum 4	99.62	0.38

d)

Fig. 4. Microstructure and results of energy dispersive spectrum (EDS) analysis of Al-Er master alloys with 6.1 mass % Er: a) SEM image; b) SEM image; c) results of EDS analysis of (a); d) results of EDS analysis of (b).

As mass % content Er increase from 3.4 to 4.2, the mass % Er in the eutectic increases from 12.5 to 16.0. With further increase of erbium content up to 6.1 mass % its content in the eutectic decreases to 8.6 mass %. Apparently, this is due to the coarsening of intermetallic particles of Al_3Er by diffusion resistance and reduces the dissolution of erbium in aluminum. It can be seen from Fig. 4 that the microstructure the of Al-6.1 % Er master alloy contains primary crystals of (Al), the eutectic [(Al) + Al_3Er], which is crystallized as a coarse needle-shaped and single precipitation of the phase Al_3Er considerably affecting the dissolutions rate of master alloy.

Overall, the microstructure of the master alloys is fine enough for effective and fast dissolution in the aluminum melt for producing aluminium alloys with low additions of erbium [14].

The XRD analysis of the prepared master alloys has shown the presence of two metallic phases: solid solutions of aluminium (Al) and intermetallic compound Al_3Er (Fig. 5), which could be in accordance with the phase diagrams.

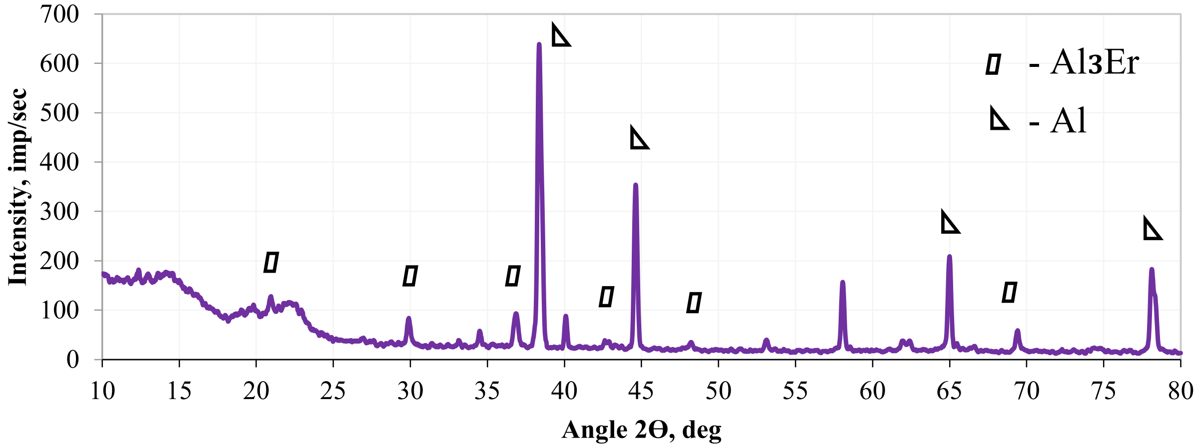


Fig. 5. XRD analysis of the Al-Er master alloys.

The economic results of the process are evident from a comparison of cost of raw materials required for preparation of Al-Er master alloys by aluminothermic reduction of chloride-fluoride melt as well as direct alloying process. The cost of erbium salts as other salt of rare earth is an order of magnitude lower than cost of corresponding metals [22].

Conclusions

The novel Al-Er master alloys were prepared by the method of metallothermic reduction of chloride-fluoride melt. The interaction between NaF and ErF_3 salts leads to the formation of the complex compound, which produce metal through metallothermic reactions with aluminium melt.

Master alloys prepared by aluminothermic reduction of chloride-fluoride melt used instead of master alloys prepared by direct alloying process to reduce cost of production of alloys and energy-efficiency while adding of erbium to aluminum alloys, which is due to the production technology of pure metals from compounds.

The microstructures of the Al-Er master alloy with different contents of the alloying metal have been investigated. The method of metallothermic reduction of chloride-fluoride melt allows to preparation of Al-Er master alloys with content of Er up to 6 mass % with a fine-grained structure. Erbium content in obtained master alloy depended on the amount of erbium fluoride in original melt.

The master alloys were composed of α-Al and Al_3Er phases. With the increase of Er element from 3.4 to 6.1 mass %, the amount of Al_3Er phase increased and morphology changed from dispersive to coarse needle-shaped.

According to the microstructures analysis of the master alloy it is good enough to be used in the foundry industry.

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