(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 862 962 A1

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
22.04.2015 Bulletin 2015/17

(21) Application number: **13804761.8**

(22) Date of filing: **30.05.2013**

(51) Int Cl.:
C25C 3/18 *(2006.01)*

(86) International application number:
PCT/CN2013/076442

(87) International publication number:
WO 2013/185540 (19.12.2013 Gazette 2013/51)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **11.06.2012 CN 201210188422**
23.01.2013 CN 201310024018

(71) Applicant: **Inner Mongolia United Industrial Co. Ltd.**
Inner Mongolia 010020 (CN)

(72) Inventors:
- **SUN, Songtao**
Hohhot
Inner Mongolia 010020 (CN)
- **FANG, Yulin**
Hohhot
Inner Mongolia 010020 (CN)

(74) Representative: **Groth & Co. KB**
P.O. Box 6107
102 32 Stockholm (SE)

(54) **ELECTROLYTE USED FOR ALUMINUM ELECTROLYSIS AND ELECTROLYSIS PROCESS USING THE ELECTROLYTE**

(57) The present invention relates to an electrolyte for aluminum electrolysis and an electrolysis process using the electrolyte. The electrolyte in the present invention employs a pure fluoride salt system and is composed of the following components by mass percent: 20-29.9% of NaF, 60.1-66% of AlF_3, 3-10% of LiF, 4-13.9% of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 0.6-0.995; or the electrolyte is composed of the following components by mass percent: 30-38% of NaF, 49-60% of AlF_3, 1-5% of LiF, 1-6% of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 1.0-1.52. The electrolyte provided in the present invention has low liquidus temperature, good alumina solubility and high electric conductivity, and plays good roles in reducing energy consumption, enhancing current efficiency and improving working environment in the electrolysis process.

EP 2 862 962 A1

Description

Field of the Invention

[0001] The present invention relates to an electrolyte for aluminum electrolysis and an electrolysis process using the electrolyte, belonging to non-ferrous metal smelting industry.

Background of the Invention

[0002] Aluminum electrolysis refers to acquisition of aluminum by means of an electrolysis method. In the prior art, a traditional Hall-Heroult molten salt aluminum electrolysis process is typically adopted for aluminum electrolysis. This process is featured by use of a cryolite-alumina molten salt electrolysis method in which cryolite Na_3AlF_6 fluoride salt melt is taken as flux, Al_2O_3 is dissolved in fluoride salt, carbon body is taken as an anode, aluminum liquid is taken as a cathode, and electrolytic aluminum is obtained by performing electrochemical reaction at the anode and cathode of the electrolytic cell at a high temperature ranging from 940 to 960°C after a strong direct current is introduced. Due to high electrolysis temperature, the traditional aluminum electrolysis process has such characteristics as large volatilization amount of electrolyte, large oxidization loss of a carbon anode, large energy consumption, large thermal loss and poor electrolysis working environment.

[0003] In the prior art, in order to lower electrolysis temperature, a low temperature molten salt system for aluminum electrolysis is described in Chinese patent document CN101671835A, the molten salt composition of the system includes AlF_3, Al_2O_3 and one or more salts selected from the group consisting of KF, NaF, MgF_2, CaF_2, NaCl, LiF, and BaF_2, wherein according to mole percentage, the content of AlF_3 is 22-50%, the content of Al_2O_3 is 1-25% and the content of the rest components is 25-77%. The electrolysis temperature of the electrolyte can be lowered to be within a wide area from 680°C to 900°C for the purpose of operations. In the aforementioned electrolyte, however, BaF_2 is liable to sedimentation in the electrolysis process due to large density, so it is hardly applied to industrial production in an extensive fashion; use of MgF_2 and CaF_2, which are high-melting-point substances, will increase the liquidus temperature of the entire system and will also degrade the electric conductivity and the alumina solubility of the electrolyte; because NaCl has a relatively low melting point, addition of NaCl is a way of lowering the liquidus temperature of the electrolyte, however, NaCl imposes a corrosion effect on such metals as Cu, Fe, Al and Ni at the aforementioned electrolysis temperature and will further lead to corrosion of metal parts like electrolytic cell accessories, this corrosion effect dramatically shortens the service life of electrolysis devices, furthermore, NaCl is extremely liable to volatilization in the electrolysis process so as to form HCl gas that is harmful to human body, so until now, NaCl has not been widely applied to industrial production; in addition to addition of NaCl, decrease of the molar ratio of NaF to AlF_3 can also lower the liquidus temperature of the electrolyte in light of common knowledge in this art, but in the existing industry, the molar ratio of NaF to AlF_3 is generally larger than 2.2, this is because an unsolvable problem will arise if the liquidus temperature of the electrolyte is further lowered and the electrolysis temperature is lowered correspondingly, namely, NaF and AlF_3 will lead to a 'crusting' phenomenon of the cathode in the process of low-temperature electrolysis, the reason for this 'crusting' phenomenon is that sodium ions and aluminum ions in the electrolyte will gather at the cathode in the electrolysis process to generate sodium cryolite, which is seldom molten at a low temperature due to its high melting point, as a result, the surface of the cathode is covered by a layer of refractory cryolite crust to affect normal electrolysis in the electrolysis process tremendously.

[0004] Whether an electrolyte can be successfully applied to industrial production is based on comprehensive consideration for many factors like its liquidus temperature, volatility, electric conductivity, alumina solubility, preparation environment and whether stable electrolysis process can be guaranteed, however, due to the above problems in the prior art, industrial application of the electrolyte is significantly limited, and it is an unsolved problem in the prior art to find a way of avoiding corrosion to electrolysis devices and damage to human body and ensuring proper electric conductivity and alumina solubility as well as no 'crusting' phenomenon of the prepared electrolyte while the liquidus temperature of the electrolyte is further lowered.

Summary of the Invention

[0005] The technical problem to be solved by the present invention is that, the prior art is incapable of avoiding corrosion to electrolysis devices and damage to human body and ensuring proper electric conductivity and alumina solubility as well as no 'crusting' phenomenon of the prepared electrolyte while the liquidus temperature of the electrolyte is further lowered. Thus the present invention provides an electrolyte for aluminum electrolysis, which is low in liquidus temperature, free from corrosion to an electrolytic cell, not liable to volatilization, proper in electric conductivity and alumina solubility and free from 'crusting' phenomenon, and an electrolysis process using the electrolyte. The technical solution for the electrolyte for aluminum electrolysis and the electrolysis process using the electrolyte in the present invention is as follows: An electrolyte for aluminum electrolysis is composed of the following components by mass percent: 20-29.9% of NaF, 60.1-66% of AlF_3, 3-10% of LiF, 4-13.9% of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 0.6-0.995;
or composed of the following components by mass percent: 30-38% of NaF, 49-60% of AlF_3, 1-5% of LiF, 1-6%

of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 1.0-1.52.

[0006] The molar ratio of NaF to AlF_3 is 0.6-0.7 or 1.12-1.52.

[0007] The liquidus temperature of the electrolyte ranges from 620 to 670°C.

[0008] The liquidus temperature of the electrolyte ranges from 640 to 670°C.

[0009] The electrolysis temperature of the electrolyte ranges from 720 to 760°C.

[0010] An electrolysis process using the electrolyte for aluminum electrolysis comprises the steps of:

(1) mixing specified amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; or mixing specified amounts of NaF, AlF_3, LiF and KF, heating the resultant mixture until the mixture is molten, and then adding Al_2O_3 to obtain a melt; and

(2) heating up the melt prepared in step (1) to 720-760°C and then carrying out electrolysis.

[0011] The melt prepared in step (1) is electrolyzed at 730-750°C.

[0012] Al_2O_3 is quantitatively supplied in the electrolysis process.

[0013] The electrolyte for aluminum electrolysis and the electrolysis process using the electrolyte in the present invention have the advantages below:

(1) The electrolyte for aluminum electrolysis in the present invention employs a pure fluoride system and is composed of the following components by mass percent: 20-29.9% of NaF, 60.1-66% of AlF_3, 3-10% of LiF, 4-13.9% of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 0.6-0.995; or the electrolyte is composed of the following components by mass percent: 30-38% of NaF, 49-60% of AlF_3, 1-5% of LiF, 1-6% of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 1.0-1.52. The advantages resulted from this are as follows:

1. Low liquidus temperature and no 'crusting' phenomenon. In the invention, an electrolyte with a pure fluoride system is employed, substance composition in the electrolyte is defined, the contents of these substances are further defined and the molar ratio of NaF to AlF_3 is 0.6-0.995 or 1.0-1.52, so that the liquidus temperature of the electrolyte is lowered to 640-670°C, as a result, electrolysis can be carried out at 720-760°C according to the electrolysis process, which reduces volatilization loss of fluoride salt, avoids corrosion to electrolysis device and damage to human body, improves working environment, greatly reduces energy consumption in the electrolysis process and achieves the aims of energy saving and emission reduction; and meanwhile, in the present invention, proper amounts of LiF and KF are added and can be combined with sodium ions and aluminum ions in the electrolyte to form lithium cryolite and potassium cryolite with low melting points, thus ensuring no crusting phenomenon in the electrolysis process.

2. High alumina solubility. Compared with the existing industry, the electrolyte for aluminum electrolysis in the present invention has no CaF_2 and MgF_2 added therein, instead, KF in an appropriate proportion, which has the function of increasing alumina solubility and dissolution velocity, is added to a system in which the molar ratio of NaF to AlF_3 is 0.6-0.995 or 1.0-1.52, and therefore, the shortcoming of low alumina solubility in the low-molar-ratio electrolyte is improved.

3. High electric conductivity of the electrolyte. The electric conductivity of the electrolyte decreases as the temperature decreases, so typically, the electric conductivity at a low electrolysis temperature hardly meets the demand in a normal electrolysis process; the electrolysis temperature is lowered by lowering the liquidus temperature of the electrolyte in the present invention, however, the electric conductivity of the electrolyte at a low temperature can still meet the demand in the electrolysis process because LiF with a larger electric conductivity is added and component proportions in the electrolyte are optimized, thus enhancing the current efficiency in the electrolysis process. According to the invention, the content of LiF is defined as 3-10% or 1-5% in the electrolyte system, this is because too low content of LiF fails to improve electric conductivity and to prevent crusting, and too high content of LiF results in decrease of the alumina solubility, and the above two situations are effectively avoided by defining the content of LiF in the present invention.

4. Reduction of metal corrosion. There is no corrosion to an electrolytic cell device when the electrolyte with the above proportions is used, so that the service life of the electrolytic cell device is prolonged.

(2) In the electrolysis process of the present invention, specified amounts of NaF, AlF_3, LiF, KF and $Al_20_3$are mixed, the resultant mixture is heated to form a melt; or specified amounts of NaF, AlF_3, LiF and KF are mixed, the resultant mixture is heated until the mixture is molten, and then Al_2O_3 is added to obtain a melt; afterwards, the melt prepared is electrolyzed at 720°C-760°C. Electrolysis temperature is directly associated with volatilization of the electrolyte, energy consumption of the process, electric conductivity and alumina solubility, and the

inventor of the present invention, by long research, set the electrolysis temperature within a range from 720°C to 760°C in a matching way based on the components and content characteristics of the electrolyte in the present invention, thus volatilization of the electrolyte and energy consumption in the electrolysis process are remarkably reduced while both the electric conductivity and the alumina solubility are increased, and the economic efficiency of the process is improved.

[0014] Preferably, the electrolysis temperature is further set within a range from 730 to 750°C in the present invention.

[0015] For more easily understanding the technical solution of the present invention, further description will be made below to the technical solution of the present invention in conjunction with the embodiments.

Detailed Description of the Embodiments

Embodiment 1

[0016] The components of the electrolyte in this embodiment are as follows: 20% of NaF, 65.98% of AlF_3, 5.01% of LiF, 6.01% of KF and 3% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 0.6.

[0017] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 640°C.

[0018] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 720°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.7\Omega^{-1}\cdot cm^{-1}$, the density is about $2.03 g/cm^3$ and the saturation concentration of alumina is 5%.

Embodiment 2

[0019] The components of the electrolyte in this embodiment are as follows: 29.9% of NaF, 60.1 % of AlF3, 3% of LiF, 4% of KF and 3% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF3 is 0.995.

[0020] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 670°C.

[0021] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF3, LiF and KF, and heating the resultant mixture until the mixture is molten, and then adding the aforementioned amount of Al_2O_3 to obtain a melt; and

(2) raising the temperature of the melt prepared in step (1) to 760°C and then carrying out electrolysis, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.05 g/cm^3$ and the saturation concentration of alumina is 6%.

Embodiment 3

[0022] The components of the electrolyte in this embodiment are as follows: 20% of NaF, 66% of AlF_3, 4% of LiF, 4% of KF and 6% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 0.6.

[0023] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 640°C.

[0024] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 730°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.6\Omega^{-1}\cdot cm^{-1}$, the density is about $2.03 g/cm^3$ and the saturation concentration of alumina is 5%.

Embodiment 4

[0025] The components of the electrolyte in this embodiment are as follows: 21% of NaF, 60.1% of AlF_3, 10% of LiF, 5.9% of KF and 3% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 0.7.

[0026] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 640°C.

[0027] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 750°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.04 g/cm^3$ and the saturation concentration of alumina is 6%.

Embodiment 5

[0028] The components of the electrolyte in this embodiment are as follows: 20% of NaF, 60.1% of AlF_3, 3% of LiF, 13.9% of KF and 3% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 0.67.

[0029] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 620°C.

[0030] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 720°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.6\Omega^{-1}\cdot cm^{-1}$, the density is about $2.03g/cm^3$ and the saturation concentration of alumina is 5%.

Embodiment 6

[0031] The components of the electrolyte in this embodiment are as follows: 20% of NaF, 61 % of AlF_3, 9% of LiF, 4% of KF and 6% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 0.65.

[0032] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 670°C.

[0033] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 760°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.05g/cm^3$ and the saturation concentration of alumina is 6%.

Embodiment 7

[0034] The components of the electrolyte in this embodiment are as follows: 13% of NaF, 60% of AlF_3, 10% of LiF, 12% of KF and 5% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 0.43. The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 660°C.

[0035] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 760°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.05g/cm^3$ and the saturation concentration of alumina is 6%.

Embodiment 8

[0036] The components of the electrolyte in this embodiment are as follows: 32% of NaF, 57% of AlF_3, 3% of LiF, 4% of KF and 4% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 1.12.

[0037] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 640°C.

[0038] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 720°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.7\Omega^{-1}\cdot cm^{-1}$, the density is about $2.03g/cm^3$ and the saturation concentration of alumina is 5%.

Embodiment 9

[0039] The components of the electrolyte in this embodiment are as follows: 38% of NaF, 50% of AlF_3, 2% of LiF, 5% of KF and 5% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 1.52.

[0040] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 670°C.

[0041] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF and KF, and heating the resultant mixture until the mixture is molten, and then adding the aforementioned amount of Al_2O_3 to obtain a melt; and

(2) raising the temperature of the melt prepared in step (1) to 760°C and then carrying out electrolysis, wherein in the electrolysis process, the electric con-

ductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.05g/cm^3$ and the saturation concentration of alumina is 6%.

Embodiment 10

[0042] The components of the electrolyte in this embodiment are as follows: 32% of NaF, 57% of AlF_3, 3% of LiF, 4% of KF and 4% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 1.12.

[0043] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 640°C.

[0044] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in the step (1) to 730°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.6\Omega^{-1}\cdot cm^{-1}$, the density is about $2.03g/cm^3$ and the saturation concentration of alumina is 5%.

Embodiment 11

[0045] The components of the electrolyte in this embodiment are as follows: 32% of NaF, 57% of AIF3, 3% of LiF, 4% of KF and 4% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AIF3 is 1.12.

[0046] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 640°C.

[0047] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AIF3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 750°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.04g/cm^3$ and the saturation concentration of alumina is 6%.

Embodiment 12

[0048] The components of the electrolyte in this embodiment are as follows: 30% of NaF, 60% of AIF3, 1% of LiF, 6% of KF and 3% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AIF3 is 1.0.

[0049] The performances of the electrolyte in this embodiment are measured and the measurement result is that: the liquidus temperature of the electrolyte in this embodiment is 620°C.

[0050] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 720°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.6\Omega^{-1}\cdot cm^{-1}$, the density is about $2.03g/cm^3$ and the saturation concentration of alumina is 5%.

Embodiment 13

[0051] The components of the electrolyte in this embodiment are as follows: 38% of NaF, 54% of AlF_3, 4% of LiF, 1 % of KF and 3% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AlF_3 is 1.4.

[0052] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 670°C.

[0053] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in step (1) to 760°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.05g/cm^3$ and the saturation concentration of alumina is 6%.

Embodiment 14

[0054] The components of the electrolyte in this embodiment are as follows: 34% of NaF, 49% of AlF_3, 5% of LiF, 6% of KF and 6% of Al_2O_3, wherein the molar ratio of NaF to aluminum fluoride AIF3 is 1.39.

[0055] The performances of the electrolyte in this embodiment are measured and the measurement result is that the liquidus temperature of the electrolyte in this embodiment is 660°C.

[0056] The electrolysis process using the electrolyte in this embodiment is as follows:

(1) mixing the aforementioned amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; and

(2) raising the temperature of the melt prepared in the step (1) to 760°C and then carrying out electrolysis, and quantitatively supplying Al_2O_3 in the electrolysis process, wherein in the electrolysis process, the electric conductivity of the electrolyte is about $1.8\Omega^{-1}\cdot cm^{-1}$, the density is about $2.05 g/cm^3$ and the saturation concentration of alumina is 6%.

[0057] The electrolytic cells used in the electrolysis processes in the aforementioned embodiments are continuous pre-baked anode electrolytic cells having an anode current density of $0.8 A\cdot cm^{-2}$. The electrolyte described in the present invention is applicable to any electrolytic cell in the prior art.

[0058] Detailed description has been made to the specific contents of the present invention in the aforementioned embodiments, and it should be understood by those skilled in this art that improvements and detail variations in any form based upon the present invention pertain to the contents that the present invention seeks to protect.

Claims

1. An electrolyte for aluminum electrolysis,
being composed of the following components by mass percent: 20-29.9% of NaF, 60.1-66% of AlF_3, 3-10% of LiF, 4-13.9% of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 0.6-0.995; or being composed of the following components by mass percent: 30-38% of NaF, 49-60% of AlF_3, 1-5% of LiF, 1-6% of KF and 3-6% of Al_2O_3, wherein the molar ratio of NaF to AlF_3 is 1.0-1.52.

2. The electrolyte according to claim 1, **characterized in that** the molar ratio of NaF to AlF_3 is 0.6-0.7 or 1.12-1.52.

3. The electrolyte according to claim 1 or 2, **characterized in that** the liquidus temperature of the electrolyte ranges from 620 to 670°C.

4. The electrolyte according to claim 3, **characterized in that**, the liquidus temperature of the electrolyte ranges from 640 to 670°C.

5. The electrolyte according to any of claims 1-4, **characterized in that**, the electrolysis temperature of the electrolyte ranges from 720 to 760°C.

6. An electrolysis process using the electrolyte for aluminum electrolysis according to any of claims 1-5, comprising the steps of:

   (1) mixing specified amounts of NaF, AlF_3, LiF, KF and Al_2O_3, and heating the resultant mixture to form a melt; or mixing specified amounts of NaF, AlF_3, LiF and KF, heating the resultant mixture until the mixture is molten, and then adding Al_2O_3 to obtain a melt; and
   (2) raising the temperature of the melt prepared in step (1) to 720-760°C and then carrying out electrolysis.

7. The electrolysis process using the electrolyte for aluminum electrolysis according to claim 6, **characterized in that** the melt prepared in step (1) is electrolyzed at 730-750°C.

8. The electrolysis process using the electrolyte for aluminum electrolysis according to claim 6 or 7, **characterized in that** Al_2O_3 is quantitatively supplied in the electrolysis process.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2013/076442

A. CLASSIFICATION OF SUBJECT MATTER

C25C 3/18 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C25C 3/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, CNPAT: aluminum, electrolytic, electrolyte, sodium fluoride, aluminum fluoride

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5284562 A (ELECTROCHEMICAL TECHNOLOGY CORP., et al.) 08 February 1994 (08.02.1994) description, column 3, lines 43-49, column 4, lines 33-47, column 6, lines 22-25, and column 7, lines 58-59	1-8
X	US 5006209 A (ELECTROCHEMICAL TECHNOLOGY CORP., et al.) 09 April 1991 (09.04.1991) description, column 4, lines 21-52, and column 7, lines 34-38	1-8
A	CN 101671835 A (BEIJING NON-FERROUS METAL INS.) 17 March 2010 (17.03.2010) description, page 2, paragraphs [0003]-[0009]	1-8
A	CN 101709487 A (CHINA ALUMINIUM IND. CORP.) 19 May 2010 (19.05.2010) description, page 2, paragraphs [0005]-[0012]	1-8
A	GB 891369 A (HARVEY LESTER SLATIN) 14 March 1962 (14.03.1962) examples 1-2	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 August 2013 (06.08.2013)	05 September 2013 (05.09.2013)

Name and mailing address of the ISA	Authorized officer
State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No. (86-10) 62019451	WANG, Xiaoming Telephone No. (86-10) 82245733

Form PCT/ISA /210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2013/076442

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
US 5284562 A	08.02.1994	NO 940181 A	19.07.1995
		AU 5385694 A	03.08.1995
		CA 2113696 A	19.07.1995
		BR 9400328 A	17.10.1995
		AU 669407 B	06.06.1996
		CA 2113696 C	14.12.1999
		NO 309284 B1	08.01.2001
US 5006209 A	09.04.1991	WO 9112357 A	22.08.1991
		AU 7259891 A	03.09.1991
		NO 923150 A	12.08.1992
		BR 9106039 A	02.02.1993
		AU 646434 B	24.02.1994
		CA 2075892 C	18.08.1998
		NO 315713 B1	13.10.2003
CN 101671835 A	17.03.2010	None	
CN 101709487 A	19.05.2010	WO 2011072546 A1	23.06.2011
GB 891369 A	14.03.1962	None	

Form PCT/ISA /210 (patent family annex) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 101671835 A **[0003]**