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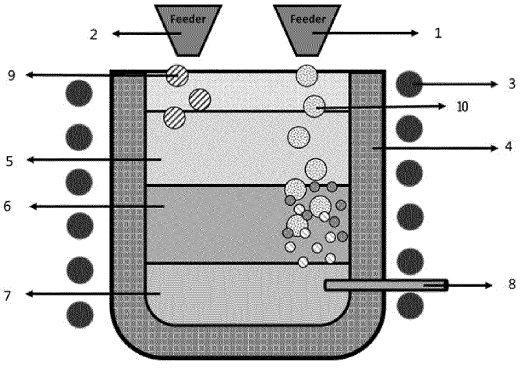
(54) REDUCTION METHOD AND SYSTEM FOR HIGH-MELTING-POINT METAL OXIDE, USING FLUORIDE-BASED ELECTROLYTES

(57) The present disclosure relates to a metal oxide reduction method and, specifically, to a metal oxide reduction method which, in producing a high-grade alloy metal using a metal oxide as a raw material, enables operation in the atmosphere by moving away from an existing production process in an inert gas atmosphere, and is easy to commercialize and can maximize efficiency, as an eco-friendly method is used.

Fig. 1



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Description

[Technical field]

[0001] The present disclosure relates to a reduction method for a high-melting-point metal oxide, and specifically, to a reduction method and system for a metal oxide in which an operation is enabled in an atmosphere without using an existing production process in an inert gas atmosphere and the efficiency thereof can be maximized and the easy commercialization thereof is provided using an eco-friendly method..

[Background Art]

[0002] When a metal typically known in the art is referred to as any metal "M", the metal M may be obtained by reducing a raw material such as an oxide or halide. Among the methods for producing the desired metal M, the relatively well-known and most widely used method in the art is a so-called Kroll process.

[0003] Typically, the Kroll process may be summarized as a process in which molten magnesium is used as a reducing agent and a chloride of the desired metal M, such as titanium chloride or zirconium chloride, is input thereto to reduce titanium or zirconium. In this regard, more details of the Kroll process may be found in US Registration Patent No. 5,035,404.

[0004] Since this Kroll process is a process using chloride as a raw material, chlorine gas and magnesium chloride are produced as by-products during the process. Among these by-products, the chlorine gas is regarded as a representative matter of the Kroll process as an environmental matter that causes fatal matters to the a human body, and in the case of magnesium chloride, it causes a matter in the process of quickly corroding a reaction vessel, which is called an cell, a melting furnace, or a crucible.

[0005] As such, the Kroll process requires an additional device to resolve environmentally acceptable regulations, and is accompanied by frequent replacement of the reaction vessel, resulting in high cost for operating the process.

[0006] On the other hand, in the Kroll process, the obtained metal is produced in the form of a sponge including a large number of pores, so that it is very difficult to control oxygen that may present in the metal. In other words, the Kroll process has limitations in obtaining high-purity metals.

[0007] An electrolytic refining process is being researched to replace these existing processes, the process has the advantage of being simpler than an existing process without generating chlorine gas by directly reducing the metal oxide, but has a matter in that the form of recovered metal is limited to powder and a particle size of the powder is also limited, making it difficult to control an oxygen concentration in the metal after the process. In order to overcome this, although the specific surface area of the recovered metal must be lowered by producing an ingot using a process such as vacuum arc melting while the recovered metal powder produced by a refining process is not exposed to the atmosphere, in this case, large-scale industrial facilities are difficult and realistic difficulties are present in terms of cost.

[0008] On the other hand, the present inventors proposed that, a liquid copper-aided electrolysis (LCE) process (see Patent Documents 1 to 3) to solve the matters of the preceding process involves a method of producing a target metal as an alloy through an electrolytic reduction process using a reducing agent, and then refining a high-purity target metal through electrolytic refining. However, even in this electrolytic reduction process, a chlorine-based flux with a high volatilization rate is used, causing rapid corrosion of equipment and matters in terms of cost, and generation of chlorine gas, which requires operation in a closed system in an argon gas atmosphere.

[Disclosure]

[Technical Problem]

[Patent Documents]

[0009]

(Patent Document 1) US Registration Patent No. 5,035,404
(Patent Document 2) Korean Patent Registration No. 10-1757626
(Patent Document 3) Korean Patent Registration No. 10-1793471
(Patent Document 4) Korean Patent Registration No. 10-1878652

[Non-Patent Document]

[0010] (Non-Patent Document 1) Antoine Allanore, Journal of The Electrochemical Society, 162 (1) (2015) E13-E22

[0011] The present disclosure has been proposed to solve the matters of the prior art as described above, and the present disclosure is for the purposed of reducing a high-melting point metal oxide in an environmentally friendly and highly-efficient atmospheric environment using a fluoride-based flux to produce a high-grade alloy metal. The present disclosure is for the purpose of providing a method and system for doing so.

[0012] The present disclosure is characterized by producing a liquid metal alloy of metal M^1 and metal M^2 forming an eutectic phase with each other. Since a melting point of metal M^1 is lowered by a eutectic reaction, reduction may be effectively performed at a relatively low temperature, which may significantly save energy and lead to cost reduction. In addition, the present disclosure is obtained in a liquid alloy state (liquid metal alloy of M^1 and M^2) by the eutectic reaction, so that the metal alloy itself may be used as a final product. In addition, the metal M^1 may be obtained by electrorefining of the obtained metal alloy. The liquid alloy thus obtained may be thoroughly separated from an environment in which oxygen may present, and thus contamination by oxygen may be significantly prevented. That is, it is possible to obtain a high-purity metal alloy and metal M^1 according to the above aspects.

[0013] The present disclosure is directed to providing an alloy metal reduction method that may increase a high-grade production rate of final products compared to the related art and has high energy efficiency and is advantageous for commercialization.

[Technical Solution]

[0014] According to the present disclosure, a method of reducing metal M^1 from a metal oxide is provided.

[0015] According to the present disclosure, the method of reducing the metal M^1 from the metal oxide includes:

forming a molten salt of a fluoride-based flux in an cell;
putting, into the cell, a metal M^2 forming an eutectic phase with the metal M^1, and a reducing agent including a metal M^3 to produce an eutectic composition of the metal M^2 and the metal M^3; and
reducing the metal M^1 by reacting the metal oxide with the eutectic composition and forming a liquid metal alloy with the reduced metal M^1 and M^2.

[0016] In the method of reducing the metal M^1 from the metal oxide, the molten salt of the fluoride-based flux may be smaller than a density of the eutectic composition of the metal M^2 and the metal M^3 and the metal oxide.

[0017] According to the present disclosure, a molten salt of the fluoride-based flux has a volatilization rate of 10% by weight or less, specifically 5% by weight or less, and more specifically 2% by weight or less for 10 hours at 1,600 °C.

[0018] According to the present disclosure, the fluoride-based flux may be one or more selected from the group consisting of MgF_2, CaF_2, SrF_2, and BaF_2, and specifically may be CaF_2.

[0019] According to the present disclosure, the metal M^1 may be one or more selected from the group consisting of Ti, Zr, Hf, W, Fe, Ni, Zn, Co, Mn, Cr, Ta, Ga, Nb, Sn, Ag, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, and No.

[0020] According to the present disclosure, the metal M^2 may be one or more selected from the group consisting of Cu, Ni, Sn, Zn, Pb, Bi, Cd, and alloys thereof, and specifically may be Cu.

[0021] According to the present disclosure, the metal M^3 may be one or more selected from the group consisting of Ca, Mg, Al, and alloys thereof, and specifically may be Mg.

[0022] According to the present disclosure, the metal oxide may include one or more selected from the group consisting of $M^1_xO_z$ and $M^1_xM^3_yO_z$, where x and y are real numbers of 1 to 3, respectively, and z is a real number of 1 to 4.

[0023] According to the present disclosure, a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition may be performed in air or in fluoride.

[0024] According to the present disclosure, a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition may be performed in a range of 900 to 1,600 °C

[0025] According to the present disclosure, a method of reducing the metal M^1 from the metal oxide may further include forming slags of the molten salt and a by-product generated in a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition by adding a slag-forming additive, and specifically the slag-forming additive may include one or more selected from the group consisting of MgO, CaO, FeO, BaO, SiO_2, and Al_2O_3.

[0026] According to the present disclosure, the method includes: forming a layer in which the liquid metal alloy is positioned at a bottom of the cell and separated from the eutectic composition, and continuously obtaining the liquid metal alloy through a lower portion of the cell; and
forming a distinct layer on top of the eutectic composition using the slag, and continuously removing the slag through a top of the cell.

[0027] According to the present disclosure, the method may further include electrorefining the liquid metal alloy to produce the metal M^1.

[0028] A metal alloy or metal according to the present disclosure may be one obtained by any method disclosed herein or a combination thereof, and may be a metal alloy having a residual content of 0.1% by weight or less, specifically 0.01% by weight or less, and more specifically 0.001% by weight or less, and an oxygen content of 1,800 ppm or less, specifically 1,500 ppm or less, and more specifically 1,200 ppm or less.

[0029] A system for reducing metal M^1 from a metal oxide according to the present disclosure may include:

an cell;
a molten salt of a fluoride-based flux positioned in the cell;
a eutectic composition of metal M^2 and metal M^3 positioned at a lower portion of the molten salt; and
a liquid metal alloy of the metal M^1 and the metal M^2 positioned below the eutectic composition;
wherein a density of the molten salt may be smaller than a density of the metal oxide,
the metal oxide and the metal M^3 may react to reduce the metal M^1, and
the metal M^2 may form an eutectic phase with the metal M^1.

[Advantageous Effects]

[0030] The present disclosure provides a system optimized for obtaining the desired metal from a metal oxide without using a metal chloride or chloride at all as a flux, and a method for producing this metal. Therefore, the present disclosure may solve the above-mentioned environmental matters of a Kroll process and cost matters due to corrosion of a cell.

[0031] The present disclosure is characterized by producing a liquid metal alloy of metal M^1 and metal M^2 forming an eutectic phase with each other. Since a melting point of metal M^1 is lowered by a eutectic reaction, reduction may be effectively performed at a relatively low temperature, which may significantly save energy and lead to cost reduction.

[0032] The present disclosure is obtained in a liquid alloy state (liquid metal alloy of metal M^1 and metal M^2) by the eutectic reaction, so that the metal alloy itself may be used as a final product. In addition, the metal M^1 may be obtained by electrorefining of the obtained metal alloy. The liquid alloy thus obtained may be thoroughly separated from an environment in which oxygen may present, and thus contamination by oxygen may be significantly prevented. That is, it is possible to obtain a high-purity metal alloy and metal M^1 according to the above aspects.

[0033] In addition, according to the present disclosure, it is easy to adjust the ratio of the target alloy, and a high-purity metal may be produced through an electrorefining technique using a finally produced alloy metal.

[0034] In the present disclosure, a recovery rate of high-grade metal M^1 is high, and the separation of a final product and a reaction product is easy, so that continuous operation is possible.

[Brief Description of Drawings]

[0035]

FIG. 1 shows a process chart showing a process for reducing metal M^1 from a metal oxide according to an embodiment of the present disclosure.
FIG. 2 shows a diagram illustrating a process procedure of a method of reducing metal M^1 from the metal oxide according to an embodiment of the present disclosure.
FIG. 3 shows a diagram and a result table showing a difference in a volatilization rate between a fluoride-based flux and a chloride-based flux.
FIG. 4 shows a diagram showing the vapor pressure of a fluoride-based flux and a chloride-based flux according to temperature.
FIG. 5 shows a photograph of a metal alloy produced according to an embodiment of the present disclosure.
FIG. 6 shows a diagram and a result table of elements analyzed using an energy dispersive spectrometer (EDS) after cutting the metal alloy produced according to an embodiment of the present disclosure.
FIG. 7 shows a result table of measuring a oxygen content present in the metal alloy produced according to Example 2 of the present disclosure using ELTRA ONH2000.

[Modes of the Invention]

[0036] Hereinafter, the intention, operation, and effect of the present disclosure will be described in detail through the embodiments of the present disclosure and specific descriptions, and examples to aid understanding and practice thereof, However, the following description and embodiments are presented as examples to aid understanding of the present disclosure as described above, and the scope of the invention disclosure is not limited or limited thereto.

[0037] Prior to the detailed description of the present disclosure, the terms or words used in the specification and claims should not be interpreted as limiting in a sense in the related art or a preliminary sense, and the inventor should be interpreted in a sense and a concept that are consistent with the technical concept of the present disclosure given the principle that the concepts of the terms may be appropriately defined in order to explain its own invention in its best mode.

[0038] Accordingly, it should be understood that the configuration of the embodiments described herein are only preferred embodiments of the present disclosure and are not intended to vary all of the spirit of the invention, and that there may be various equivalents and modifications that may be substituted for them at the time of this application.

[0039] In this specification, the singular expression includes the plural expression unless the context clearly dictates otherwise. In this specification, the terms "comprises," "includes," or "has" and the like are intended to designate the presence of the features, numbers, steps, components, or combinations thereof that are implemented, and are not to be understood as precluding the possibility of the presence or addition of one or more other features or numbers, steps, components or combinations thereof.

[0040] As used herein, the term "loading" may be used interchangeably with "put", "introduction", "inflow", and "injection" in this specification, and may be understood to mean bringing or putting any material, such as a raw material, into a place where it is needed.

[0041] Hereinafter, the present disclosure will be described in detail in the order of reduction method of metal M^1, a reduction system, and examples.

1. Reduction method of metal M^1

[0042] A method of reducing metal M^1 from a metal oxide according to the present disclosure may include:

forming a molten salt of a fluoride-based flux in an cell;
putting, into the cell, a metal M^2 forming an eutectic phase with the metal M^1, and a reducing agent including a metal M^3 to produce an eutectic composition of the metal M^2 and the metal M^3; and
reducing the metal M^1 by reacting the metal oxide with the eutectic composition and forming a liquid metal alloy with the reduced metal M^1 and M^2.

[0043] In the method of the present disclosure, the molten salt of the fluoride-based flux may be smaller than a density of the eutectic composition of the metal M^2 and the metal M^3 and the metal oxide.

[0044] In the method of the present disclosure, a molten salt of the fluoride-based flux has a volatilization rate of 10% by weight or less, specifically 5% by weight or less, and more specifically 2% by weight or less for 10 hours at 1,600 °C

[0045] By using the molten salt of the fluoride-based flux, there is an environmental advantage in that toxic chlorine gas is not generated, and since its volatilization rate is low, loss of the flux during the process is small, and it is advantageous in terms of maintenance cost. In particular, when compared with a chloride-based flux, such as $CaCl_2$, which has a volatilization rate of about 74% by weight (FIG. 3) at 1,600 °C for 10 hours, the advantage of this fluoride-based flux may be more clearly understood. Here, the volatilization rate may be measured by leaving for a certain time at a specific temperature and comparing the weight before and after leaving, but Other methods well known to those skilled in the art may be used, and numerical values in the case of using other methods may be appropriately converted from the numerical values in the present disclosure. However, since the flux of the present disclosure is used in a process of reducing a metal by reacting a metal oxide with a eutectic composition, the volatilization rate should be measured within a process temperature (900 to 1600 °C) according to the present disclosure. In particular, since the volatilization rate is higher at higher temperatures, it may be desirable to measure the volatilization rate at 1600 °C, which is the highest among allowable process temperatures, to ensure process stability.

[0046] In the method of the present disclosure, the fluoride-based flux may be a fluoride-based flux of one or more metals selected from the group of alkali metals and alkaline earth metals, and determined by considering the relative density difference, a volatilization rate, convenience and safety of operation, and the like according to the target metal M^1 and the reducing agent used. The fluoride-based flux may, for example, be one or more selected from the group consisting of MgF_2, CaF_2, SrF_2, and BaF_2, and specifically may be CaF_2.

[0047] In the method of the present disclosure, by using an eutectic composition of metal M^2 and metal M^3 and a fluoride-based flux molten salt having a density lower than that of the metal oxide, In the step in which the metal oxide reacts with the eutectic composition to reduce the metal M^1 and form a liquid metal alloy between the reduced metal M^1 and the metal M^2, and since the molten salt of the fluoride-based flux is positioned at the top of the cell, the eutectic composition and the metal oxide may not be exposed to an external environment, and inflow of oxygen from the outside may be prevented. Accordingly, a reduction process of the metal M^1 is possible even in a normal air atmosphere other than an inert gas atmosphere.

[0048] In addition, by using a fluoride-based flux with a low volatilization rate, it is advantageous for large-scale industrialization because it allows harmful gases to be disloaded in an acceptable amount even in a normal air atmosphere, thereby increasing the convenience and safety of operation, and significantly lowering a degree of corrosion of equipment than used fluxes in the related art.

[0049] The metal M^1 is not particularly limited, but specifically may be one selected from the group consisting of Ti, Zr, Hf, W, Fe, Ni, Zn, Co, Mn, Cr, Ta, Ga, Nb, Sn, Ag, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, and No, more specifically, one selected from the group consisting of Ti, Zr, W, Fe, Ni, Zn, Co, Mn, Cr, Ta, Er, and No, and even more specifically, one selected from the group consisting of Ti, Zr, W, Fe, Ni, Zn, Co, Mn, and Cr, and in particular, Ti, Zr, or W.

[0050] In the method of the present disclosure, the metal M^2 is not limited as long as it may form an eutectic phase with the metal M^1, for example, the metal M^2 may be one or more selected from the group consisting of Cu, Ni, Sn, Zn, Pb, Bi, Cd, and alloys thereof, and specifically, Cu.

[0051] In the method of the present disclosure, a reducing agent including the metal M^3 is not limited as long as it may reduce the metal oxide including the metal M^1, for example, the metal M^3 may be one or more selected from the group consisting of Ca, Mg, Al, and alloys thereof. Specifically, the metal M^3 may be Mg.

[0052] In the method of the present disclosure, the metal oxide may include one or more selected from the group consisting of $M^1_xO_z$ and $M^1_xM^3_yO_z$, where x and y are real numbers of 1 to 3, respectively, and z is a real number of 1 to 4.

[0053] Non-limiting examples of the above metal oxides for ease of understanding may include one selected from the group consisting of ZrO_2, TiO_2, $MgTiO_3$, HfO_2, Nb_2O_5, Dy_2O_3, Tb_4O_7, WO_3, Co_3O_4, MnO, Cr_2O_3, MgO, CaO, Al_2O_3, Ta_2O_5, Ga_2O_3, Pb_3O_4, SnO, NbO, and Ag_2O, or a combination of two or more of these.

[0054] When a composite oxide ($M^1_xM^3_yO_z$) of the metal M^1 and the metal M^3 is used as the metal oxide, a process of reducing the metal M^1 by reacting with the eutectic composition of the metal M^2 and the metal M^3 may be faster. According to the findings of the present disclosure, in the case of using the complex oxide ($M^1_xM^3_yO_z$), the time required for reduction may be reduced by at least 1/3 to 1/10 compared to the case of using $M^1_xO_z$. That is, when the composite oxide of the metal M^1 and the metal M^3 is used as the metal oxide, a reaction rate between the metal oxide and the eutectic composition may be faster than when only the oxide of the metal M^1 is used. In addition, in the case of using $M^1_xM^3_yO_z$, there is an advantage in that a ratio of M^1 and M^2 in the liquid metal alloy produced according to the present disclosure may be more widely adjusted. Moreover, when $M^1_xM^3_yO_z$ is used, a required amount of M^3 used as a reducing agent is significantly reduced compared to the case of using $M^1_xO_z$. For example, when Ti is used as the metal M^1 and Ca is used as the metal M^3, oxide of the metal M^1 may be TiO^2, and the composite oxide of the metal M^1 and the metal M^3 may be $CaTiO_3$.

[0055] Unlike the Kroll process in the related art, the method according to the present disclosure is different in that it uses a metal oxide instead of a metal chloride as a raw material. A raw material usually found in nature includes an oxide of the metal M^1, and a pre-treatment process of substituting the metal oxide with a chloride is involved in order to use the oxide in the Kroll process. When such a pre-treatment process is performed, it itself causes an increase in process cost. Moreover, hydrochloric acid is used in the pre-treatment process of replacing metal oxide with chloride, and this process promotes corrosion of manufacturing equipment due to strong acidity, and toxic chlorine gas may be generated during the process, which may cause environmental matters. Since the method according to the present disclosure does not require a pre-treatment process for substituting the metal oxide with chloride, process cost is lower than that of the Kroll process and there are advantages in not causing environmental matters.

[0056] In the method of the present disclosure, a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition may be performed in air or in fluoride. Since a density of the molten salt of the fluoride-based flux is lower than that of the eutectic composition and the metal oxide, the molten salt of the fluoride-based flux is positioned at the top of the cell, and the eutectic composition and the input metal oxide are positioned below the molten salt of the fluoride-based flux. Due to this, since the eutectic composition and the introduced metal oxide can present in a state that is not exposed to an external environment due to the molten salt of the fluoride-based flux and the cell, a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition may be performed even in a normal atmosphere other than an inert gas atmosphere. Moreover, since a volatilization rate of the molten salt of the fluoride-based flux is relatively low, even when the process is performed in an atmospheric atmosphere, the generation of toxic gases is reduced, and the corrosion of equipment used in the process is significantly reduced, a harmful environment is not created for operators, and large-scale industrialization can be achieved.

[0057] In the method of the present disclosure, a method of reducing the metal M^1 may be performed at least a temperature at which the fluoride-based flux can be melted, the eutectic composition can be produced, and a process of reducing metal M^1 by reacting the metal oxide with the eutectic composition can be performed. For example, a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition may be performed at 900 °C or more. In addition, he method can be performed at a temperature below which the molten salt of the fluoride-based flux does not evaporate excessively, and considering the energy efficiency according to the heating of the furnace, the method may be performed at 1800 °C or less, 1700 °C or less, 1600 °C or less, or 1600 °C or less. Accordingly, a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition may be performed in the range of 900 to 1600 °C.

[0058] As an example, when the metal M^1 is Ti, the metal oxide ($M^1_xO_z$) is TiO^2, the metal M^2 is Cu, and the metal M^3 is Ca, the metal Ti is reduced according to the following Scheme 1-1 and Scheme 1-2, and a metal M^3 oxide ($M^3_aO_b$)

can then be separated while the liquid metal alloy CuTi is obtained. Here, a and b are a real number from 1 to 3, respectively.

[Scheme 1-1] $2Ca + TiO_2 \rightarrow Ti + 2CaO$

[Scheme 1-2] $Ti + Cu + 2CaO \rightarrow CuTi$ (Alloy) + $2CaO$ (separation)

[0059] As another example, when the metal M^1 is Ti, the metal oxide ($M^1_xM^3_yO_z$) is $CaTiO_3$, the metal M^2 is Cu, and the metal M^3 is Ca, the metal Ti is reduced according to the following Scheme 1-1 and Scheme 1-2, and a metal M^3 oxide ($M^3_aO_b$) can then be separated while the liquid metal alloy CuTi is obtained.

[Scheme 2-1] $2Ca + CaTiO_3 \rightarrow Ti + 3CaO$

[Scheme 2-2] $Ti + Cu + 3CaO \rightarrow CuTi$ (alloy) + $3CaO$ (separation)

[0060] The metal M^3 oxide ($M^3_aO_b$) produced according to the above reaction is a kind of by-product, and it is necessary to continuously remove the by-products in order to enable a continuous process. The by-products may not be completely soluble in the molten salt and it may not be easy to remove the by-products or run the process continuously. The method of the present disclosure may further include forming slags of by-products generated in the process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition and the molten salt of the fluoride-based flux by putting a slag-forming additive. When slags are formed, viscosity is relatively reduced compared to the case where by-products and the molten salt of the fluoride-based flux are present, fluidity is increased, continuous removal of slags including by-products is possible, and furthermore, a continuous process can be made possible.

[0061] Examples of the slag-forming additive to achieve the above effect may include one or more selected from the group consisting of MgO, CaO, FeO, BaO, SiO_2, and Al_2O_3, but are not limited thereto.

[0062] A method of reducing metal M^1 from a metal oxide according to the present disclosure may further include forming a layer in which the liquid metal alloy is positioned at a bottom of the cell and separated from the eutectic composition, and continuously obtaining the liquid metal alloy through a lower portion of the cell; and forming a distinct layer on top of the eutectic composition using the slags, and continuously removing the slags through a top of the cell. By forming a layer in which the liquid metal alloy is positioned at a bottom of the cell and separated from the eutectic composition, a liquid metal alloy may be continuously tapped from a lower portion of the cell. In addition, input of the slag-forming additive causes the slag to form as a distinct layer on an upper portion of the eutectic composition, and the slag is continuously removed through the upper portion of the cell, so that by-products generated in the reduction process of metal oxides can be continuously removed. Accordingly, by continuously removing the reaction product formed when the metal oxide is input to the eutectic composition from the cell, after inputting an amount of the metal oxide, the liquid metal alloy of the metal M^1 and the metal M^2 may be obtained without interruption of the process by continuously inputting the metal oxide rather than all reactions being terminated. At this time, a method known to those skilled in the art may be used for continuously obtaining a liquid metal alloy through the lower portion of the cell or continuously removing slags through the upper portion of the cell.

[0063] After the slags are removed through removing the slags and the fluoride-based flux through the upper portion of the cell, the fluoride-based flux is supplemented during a process operation to maintain the balance of a reaction system and enable a continuous process. At this time, the fluoride-based flux may be continuously separated from the removed slags, and the separated fluoride-based flux may be input into the cell again.

[0064] Cooling for solidification of the obtained liquid metal alloy may be performed. Since the liquid metal alloy is in a state in which the metal M^1 and the metal M^2 are homogeneously mixed, the structure of the alloy obtained after solidification is greatly affected by a cooling rate of the liquid metal alloy. The cooling rate can stably form an intermetallic compound phase, in the temperature range in which the process according to the present disclosure is performed, it may be slowly cooled to room temperature at a rate of 20 °C/min, so that a tissue structure in which the intermetallic compound phases of M^1 and M^2 are continuously connected to each other can be produced. When the cooling rate is excessively fast outside a suggested range, a structure in which a large amount of fine intermetallic compound particles are dispersed and incorporated into the metal M^1 matrix is obtained, and thus there is a risk that a continuous and rapid mass transfer path of metal M^1 may not be formed. When the cooling is excessively slow, the microstructural benefit is negligible, but as the time required for the process becomes excessively long, the cooling rate may be substantially 1 °C/min or more, and more substantially 5 °C/min or more.

[0065] The method according to the present disclosure may further include obtaining an alloy including the metal M^1 and the metal M^2, and then electrolytically refining the obtained alloy including the metal M^1 and the metal M^2 to obtain the metal M^1.

[0066] Obtaining the metal M^1 by performing the electrorefining may be solidifying the obtained liquid metal alloy to obtain a solid alloy, electrolytically refining the solid alloy, and recovering the metal M^1 from the alloy.

[0067] In some cases, prior to electrorefining the solidified alloy, the flux that may remain in the liquid metal alloy may be removed, this can be achieved, for example, by heat treating the liquid metal alloy in a vacuum or inert gas atmosphere to cause the flux to distill off. A distillation temperature (heat treatment temperature) is not particularly limited as long as the temperature is higher than a boiling point of the flux used in the system of the present disclosure, for example, the temperature may be 2,500 °C or more, and reduced pressure may be performed to lower the distillation temperature and increase efficiency. In order to effectively prevent the liquid metal alloy from being oxidized again, it may be advantageous to perform the distillation in a vacuum atmosphere and under an inert gas.

[0068] The present disclosure provides a metal alloy of the metal M^1 and the metal M^2 obtained by any method or combination thereof described in the specification of the present disclosure. For example, the metal alloy of the metal M^1 and the metal M^2 can be obtained by a method of reducing metal M^1 from a metal oxide, including: forming a molten salt of a fluoride-based flux in an cell; putting, into the cell, a reducing agent including a metal M^2 forming an eutectic phase with the metal M^1, and a metal M^3 to produce an eutectic composition of the metal M^2 and the metal M^3; and reducing the metal M^1 by reacting the metal oxide with the eutectic composition and forming a liquid metal alloy with the reduced metal M^1 and M^2. For example, the metal alloy of the metal M^1 and the metal M^2 may be made in an atmosphere or obtained from a process performed in a range of 900 to 1600 °C. For example, the metal alloy of the metal M^1 and the metal M^2 may be obtained by a method including forming slags of the molten salt and a by-product generated in a process of reducing the metal M^1 by adding a slag-forming additive to react the metal oxide with the eutectic composition. In addition, the metal alloy of the metal M^1 and the metal M^2 of the present disclosure may be obtained by any method or a combination thereof described in the specification of the present disclosure.

[0069] In one embodiment, the metal alloy of the metal M^1 and the metal M^2 is a high-grade metal alloy with a residual content of 0.1% by weight or less, specifically 0.01% by weight or less, and more specifically 0.001% by weight or less, based on a total weight of the metal alloy. In addition, the metal alloy of the metal M^1 and the metal M^2 is a high-grade metal alloy with an oxygen content of 1,800 ppm or less, specifically 1,500 ppm or less, and more specifically 1,200 ppm or less.

[0070] In addition, in a liquid alloy (M^1 and M^2 are liquid metal alloys) obtained according to the method of the present disclosure, the metal alloy itself may be used as a final product. M^1 is often used industrially in the form of an alloy, and when M^1 can be produced with only a single metal, as in the Kroll process in the related art, a post-processing process for forming an alloy with another metal may be required. However, the present disclosure has high process efficiency in that a final product may be obtained in the form of a metal alloy of M^1 and M^2 simultaneously with reduction without such a post-treatment process. Moreover, the reduced metal produced through the Kroll process in the related art has a low production of high grade (grade 1) metal having a low oxygen content and a relatively high residual oxygen content. Therefore, even when a metal alloy is produced using the reduced metal produced by the Kroll process, there is a limit in that the residual oxygen content is high. On the other hand, most of the metal alloys produced according to the present disclosure have a very low oxygen content and are of high quality grade. For example, when M^1 is Ti, the method according to the present disclosure yields a high-grade metal as high as 98% or more, but it is known that the crawl process in the related art yields less than 50% of high-grade metal, and through this, superiority of the present disclosure can be more clearly understood.

2. System for reducing M^1

[0071] A system for reducing metal M^1 from a metal oxide according to the present disclosure may include:

an cell;
a molten salt of a fluoride-based flux positioned in the cell;
an eutectic composition of metal M^2 and metal M^3 positioned at a lower portion of the molten salt; and
a liquid metal alloy of the metal M^1 and the metal M^2 positioned below the eutectic composition;
wherein a density of the molten salt may be smaller than a density of the metal oxide,
the metal oxide and the metal M^3 may react to reduce the metal M^1, and
the metal M^2 may form an eutectic phase with the metal M^1.

[0072] In one embodiment, the cell may be an electrolytic reduction cell or the like, a high-frequency melting furnace may be used to achieve a desired temperature range, or an electric furnace may be used depending on a target metal alloy, but is not limited thereto. Considering a reaction temperature range, reactivity, and the like, all cells and furnaces that are easy for a person skilled in the art may be used.

[0073] In one embodiment, a mass ratio of the molten salt of the fluoride-based flux to the reaction by-product may be 5:1 to 2:1, preferably 3:1, but is not limited thereto, for smooth separation of the liquid metal alloy and the reaction by-product.

[0074] In one embodiment, the flux may further include an oxide of one or two or more metals selected from an alkali metal and an alkaline earth metal group as a reactive additive. A content of the reactive additive may be 0.1 to 25% by weight based on a total weight of the flux. The reactive additive may include, but are not limited to, LiO, NaO, SrO, CsO, KO, CaO, BaO, or mixtures thereof. The reactive additive contained in the flux may enable easier reduction of a metal oxide contained in a raw material module.

[0075] In one embodiment, a cell similar to that of FIG. 1 may be used to perform a production method an alloy metal of the present disclosure. For example, The fluoride-based flux is loaded into an cell 1 and melted to form a molten salt 5, and a reducing agent including metal M^2 forming an eutectic phase with metal M^1, and metal M^3 is input into an cell to produce an eutectic composition 6 of the metal M^2 and the metal M^3. Since the density of the molten salt of the fluoride-based flux is less than that of the eutectic composition, the molten salt 5 of the fluoride-based flux is positioned on the eutectic composition 6. Thereafter, a metal oxide 10 is loaded into the cell using the raw material input device 1, and the oxide is reacted with the eutectic composition 6 to prepare a liquid metal alloy 7 of the metal M^1 and the metal M^2, and after the reaction is completed, a slag-forming additive 9 is input into the reaction by-product positioned between the liquid metal alloy and the flux to slag the by-product. After that, the liquid metal alloy 7 is obtained through a tapping portion 8 connected to a lower portion of the cell through the lower portion of the cell. Since the slags are positioned at a upper portion of the cell, about 50-90% of the slags are removed by tilting the cell, and a new fluoride-based flux is input into about 10 to 50% of residual slags through an flux input device 2 to form a new flux layer. Thereafter, again, the metal oxide 10 is loaded into the cell using the raw material input device 1 and reacted with the eutectic composition 6, and a process of producing the liquid metal alloy 7 may be repeated. In all stages of the process, such as before removing slags or tilting the cell to remove slags, the liquid metal alloy 7 produced in the lower portion of the cell is continuously obtained through the tapping portion 8 in the lower portion of the cell. The cell may use, for example, a high-frequency melting furnace 3 to facilitate stirring, but is not limited thereto.

3. Examples

[0076] Hereinafter, examples will be described in detail, through which the action and effect of the present disclosure will be demonstrated. However, the following examples are only presented as examples of the invention disclosure, and the scope of the invention disclosure is not determined thereby.

<Example 1>

[0077] A system as shown in FIG. 1 was used and proceeded according to a process sequence of FIG. 2. Flux CaF_2 (40.8 g) was weighed in a resistance heating furnace, input into an cell, and then heated to about 1415 °C to produce a molten salt of a fluoride-based flux (FIG. 2A).

[0078] 52.8 g and 72.3 g of Cu(s) and Ca(s) were weighed, input into an cell, and melted to produce an eutectic composition (FIG. 2B).

[0079] 72.1 g of TiO_2 (average particle size of 100 μm) as a metal oxide was weighed and reacted for 10 hours (FIGS. 2c and 2d).

[0080] In order to remove by-products, 200 g of Al_2O_3 powder and 100 g of CaO as slag-forming additives were input to slags (FIG. 2E), and then slowly cooled in the furnace. The process was performed in an air atmosphere.

<Example 2>

[0081] A system as shown in FIG. 1 was used and proceeded according to a process sequence of FIG. 2. Flux CaF_2 (40.8 g) was weighed in a resistance heating furnace, input into an cell, and then heated to about 1415 °C to produce a molten salt of a fluoride-based flux (FIG. 2A).

[0082] 60 g and 65.5 g of Cu(s) and Ca(s) were weighed, input into a cell, and melted to produce an eutectic composition (FIG. 2B).

[0083] 111 g of $CaTiO_3$ as a metal oxide was weighed and reacted for 2 hours (FIG. 2c and 2d).

[0084] In order to remove by-products, 200 g of Al_2O_3 powder and 100 g of CaO as slag-forming additives were input to slags (FIG. 2E), and then slowly cooled in the furnace. The process was performed in an air atmosphere.

<Experimental Example 1>

[0085] A volatilization rate of a fluoride-based flux and a chloride-based flux were measured. 500 g of each flux (weight before loading) was weighed and input into a crucible, and weight (weight after loading) of the flux after loading the crucible to a melting furnace and leaving the flux at 1,600 °C for 10 hours was measured. The volatilization rate was evaluated using the following method.

- Volatilization rate:

(weight before loading - weight after loading) / (weight before loading) x 100%

[0086] As a result, it was confirmed that CaF_2 used as the fluoride-based flux showed a low volatilization rate of 1.8% by weight, but $CaCl_2$, a chloride-based flux, showed a high volatilization rate of about 74% by weight (FIG. 3).

[0087] Regarding a volatilization rate of CaF_2, a fluoride-based flux, and a volatilization rate of $CaCl_2$, a chloride-based flux, measured in each temperature range, it may be seen that a vapor pressure of the fluoride-based flux is remarkably low based on a process temperature at which this process is performed (FIG. 4), indicating that the volatilization rate in the process of the fluoride-based flux is remarkably low.

[0088] From this, it is preferable to use a fluoride-based flux having a low volatilization rate for an efficient process as described above.

<Experimental Example 2>

[0089] The properties of the alloys obtained in Examples 1 and 2 were evaluated using the following method.
- Recovery rate: 100 - {(1st weight - 2nd weight)/2nd weight x 100%}
- Residual impurity content: The produced alloy was cut and the inside of the alloy was confirmed using an energy dispersion spectrum.
- Oxygen content: The oxygen content present in the alloy was measured using an ELTRA ONH2000.

[Table 1]

	1st weight	2nd weight	Recovery rate (%)	Results of energy dispersion spectrum		Oxygen content (ppm)
				Ti (% by weight)	Cu (% by weight)	
Example 1	96	83.9	87.4	27.3	72.7	1162.69
Example 2	99.16	95.86	96.7	40.81	59.19	1126.08
*1st weight: Total amount of Cu put into the initial electrolytic bath + Chemical theoretical reduction amount of Ti included in metal oxide. ** 1st weight: Total amount of CuTi obtained						

[0090] From the results of Table 1, it may be seen that the alloys of Examples produced according to the present disclosure showed a high recovery rate, and that a high-purity alloy was obtained that was substantially free of metal or oxygen used as a reducing agent. That is, it was confirmed that, unlike a presenting process, which was possible only in an inert gas atmosphere as above, even though the process proceeded in an air atmosphere, the recovery rate of the target metal was better and the oxygen content was significantly lower.

[0091] Although the present disclosure has been described with reference to embodiments, those skilled in the art will be able to make various applications and modifications within the scope of the present disclosure based on the above information.

Claims

1. A method of reducing metal M^1 from a metal oxide, comprising:

forming a molten salt of a fluoride-based flux in an cell;
putting, into the cell, a metal M^2 forming an eutectic phase with the metal M^1, and a reducing agent including a metal M^3 to produce an eutectic composition of the metal M^2 and the metal M^3; and
reducing the metal M^1 by reacting the metal oxide with the eutectic composition and forming a liquid metal alloy with the reduced metal M^1 and M^2,
wherein density of the molten salt is less than density of the eutectic composition and the metal oxide.

2. The method of claim 1, wherein the molten salt has a volatilization rate of 10% by weight or less at 1,600 °C for 10 hours.

3. The method of claim 1, wherein the fluoride-based flux is one or more selected from the group consisting of MgF_2, CaF_2, SrF_2, and BaF_2.

4. The method of claim 3, wherein the fluoride-based flux is CaF_2.

5. The method of claim 1, wherein the metal M^1 is one or more selected from the group consisting of Ti, Zr, Hf, W, Fe, Ni, Zn, Co, Mn, Cr, Ta, Ga, Nb, Sn, Ag, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, and No.

6. The method of claim 1, wherein the metal M^2 is one or more selected from the group consisting of Cu, Ni, Sn, Zn, Pb, Bi, Cd, and alloys thereof.

7. The method of claim 6, wherein the metal M^2 is Cu.

8. The method of claim 1, wherein the metal M^3 is one or more selected from the group consisting of Ca, Mg, Al, and alloys thereof.

9. The method of claim 1, wherein the metal oxide includes one or more selected from the group consisting of $M^1_xO_z$, and $M^1_xM^3_yO_z$:
wherein x and y are a real number from 1 to 3, respectively, and z is a real number from 1 to 4.

10. The method of claim 1, wherein a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition is performed in air or in fluoride.

11. The method of claim 1, wherein a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition is performed in a range of 900 to 1,600 °C

12. The method of claim 1, further comprising forming slags of the molten salt and a by-product generated in a process of reducing the metal M^1 by reacting the metal oxide with the eutectic composition by adding a slag-forming additive.

13. The method of claim 12, wherein the slag-forming additive comprises one or more selected from the group consisting of MgO, CaO, FeO, BaO, SiO_2, and Al_2O_3.

14. The method of claim 12, further comprising:

forming a layer in which the liquid metal alloy is positioned at a bottom of the cell and separated from the eutectic composition, and continuously obtaining the liquid metal alloy through a lower portion of the cell; and
forming a distinct layer on top of the eutectic composition using the slags, and continuously removing the slags through a top of the cell.

15. The method of claim 1, further comprising electrorefining the liquid metal alloy to produce the metal M^1.

16. A metal obtained by the method of claim 15.

17. A metal alloy obtained by the method of claim 1.

18. The method of claim 17, wherein a residual content of the metal M^3 is 0.1% by weight or less based on the total weight of the metal alloy, and a oxygen content is 1,800 ppm or less.

19. A system for reducing metal M^1 from a metal oxide, comprising:

an cell;
a molten salt of a fluoride-based flux positioned in the cell;
an eutectic composition of metal M^2 and metal M^3 positioned at a lower portion of the molten salt; and
a liquid metal alloy of the metal M^1 and the metal M^2 positioned below the eutectic composition;
wherein a density of the molten salt is smaller than a density of the metal oxide,

the metal oxide and the metal M^3 react to reduce the metal M^1, and the metal M^2 forms an eutectic phase with the metal M^1.

Fig. 1

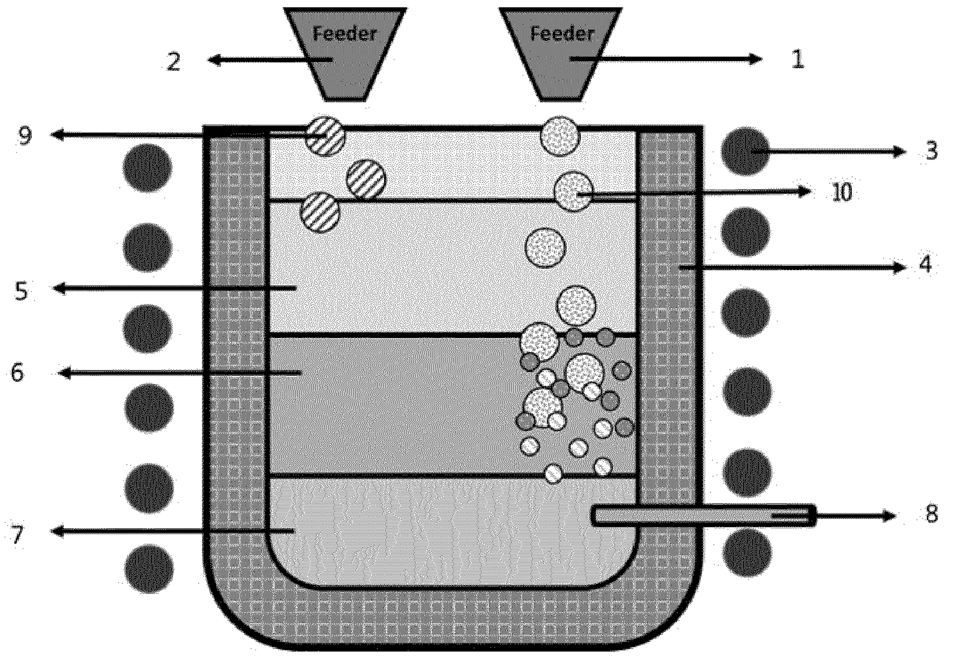


Fig. 2

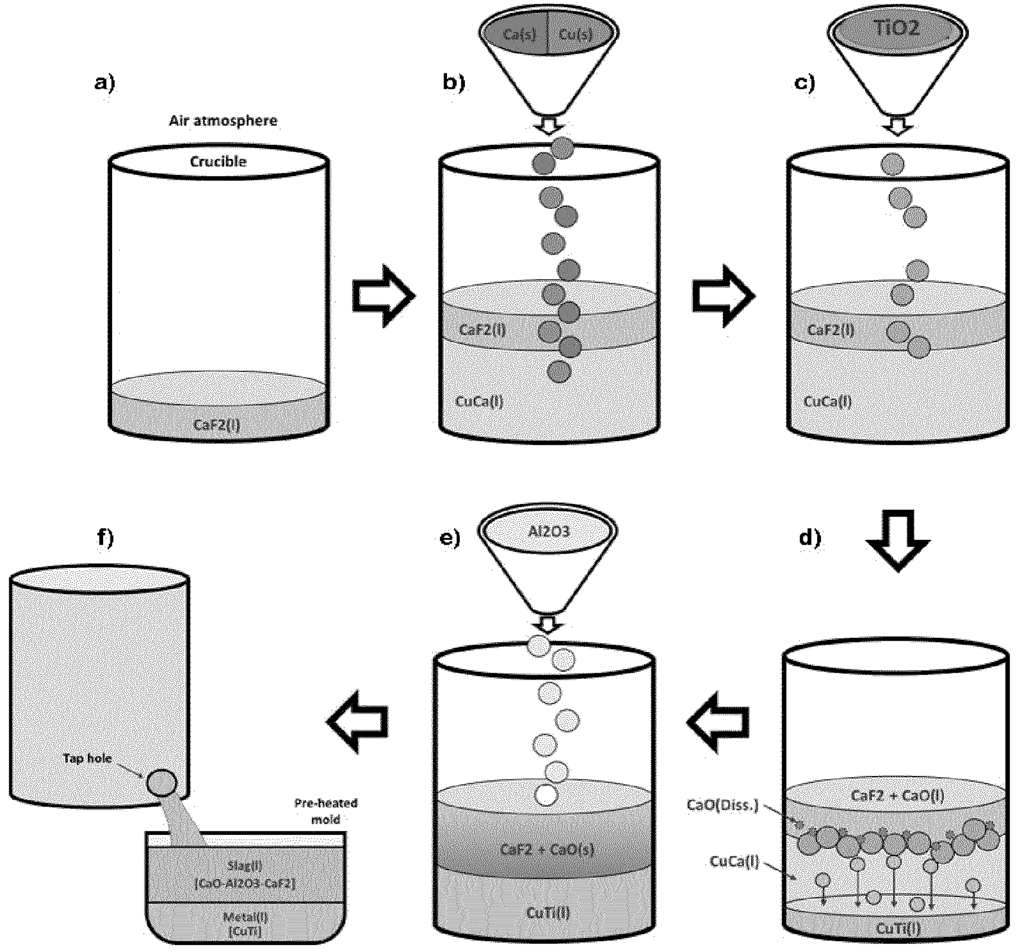
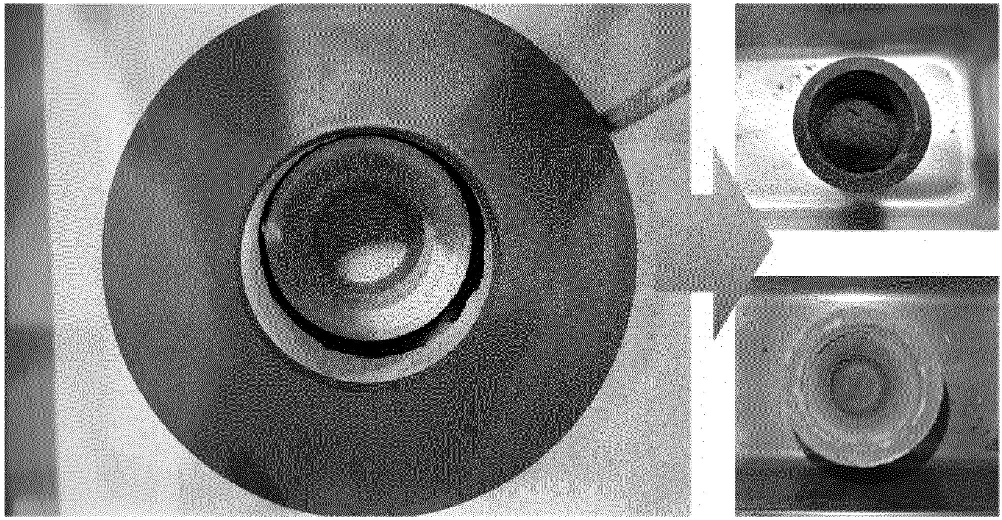

a)
Air atmosphere
Crucible
CaF2(l)
b)
Ca(s)
Cu(s)
CaF2(l)
CuCa(l)
c)
TiO2
CaF2(l)
CuCa(l)
d)
CaO(Diss.)
CuCa(l)
CaF2 + CaO(l)
CuTi(l)
e)
Al2O3
CaF2 + CaO(s)
CuTi(l)
f)
Tap hole
Pre-heated mold
Slag(l)
[CaO-Al2O3-CaF2]
Metal(l)
[CuTi]

Fig. 3



	$CaCl_2$	CaF_2
Before Loading(g)	500	500
After Loading(g)	131	491
Volatilization rate (w%)	73.8	1.8

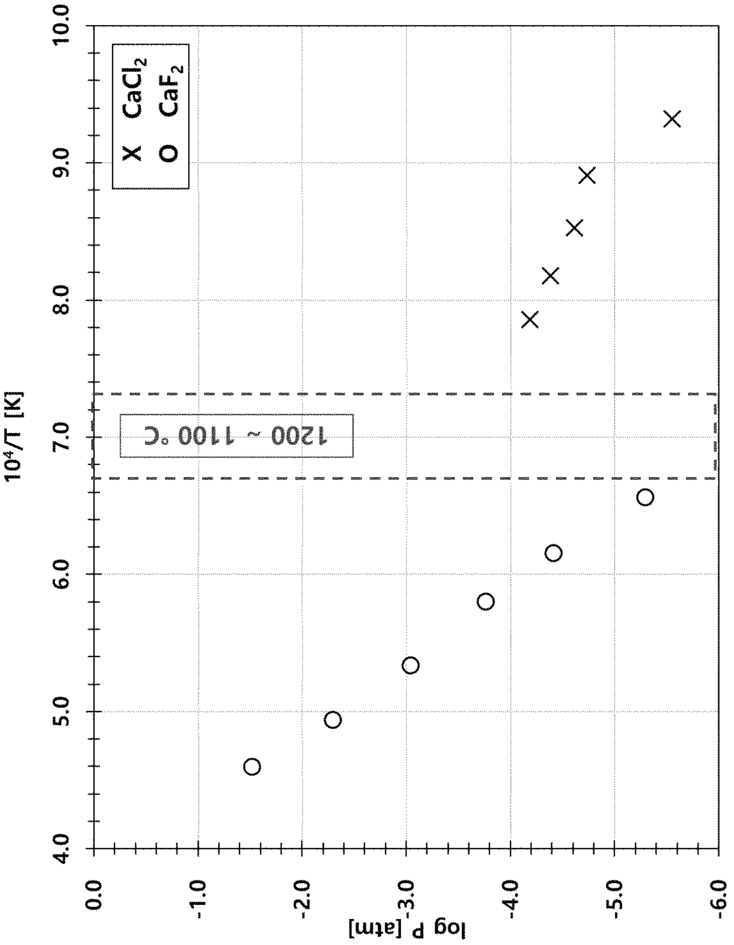

X CaCl$_2$
O CaF$_2$
1200 ~ 1100 °C
10^4/T [K]
4.0
5.0
6.0
7.0
8.0
9.0
10.0
log P [atm]
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0

Fig. 4

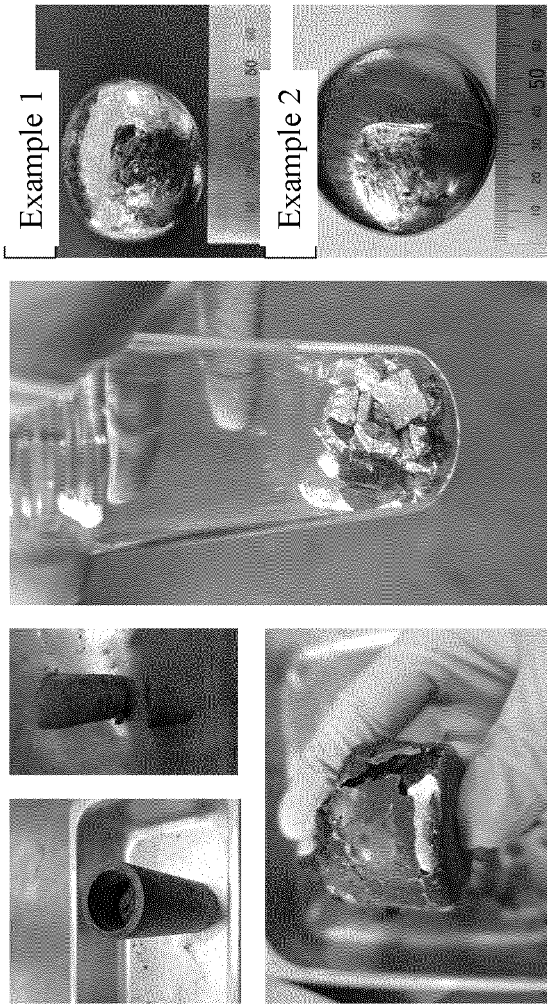
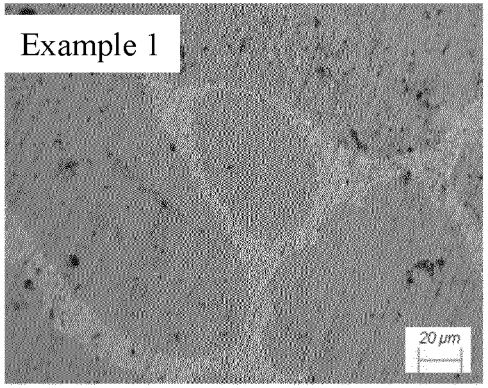


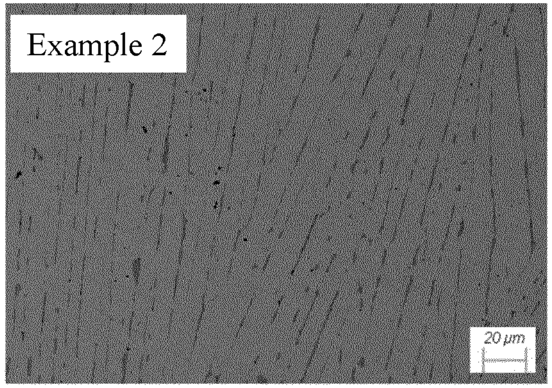
Fig. 5

Fig. 6



Example 1

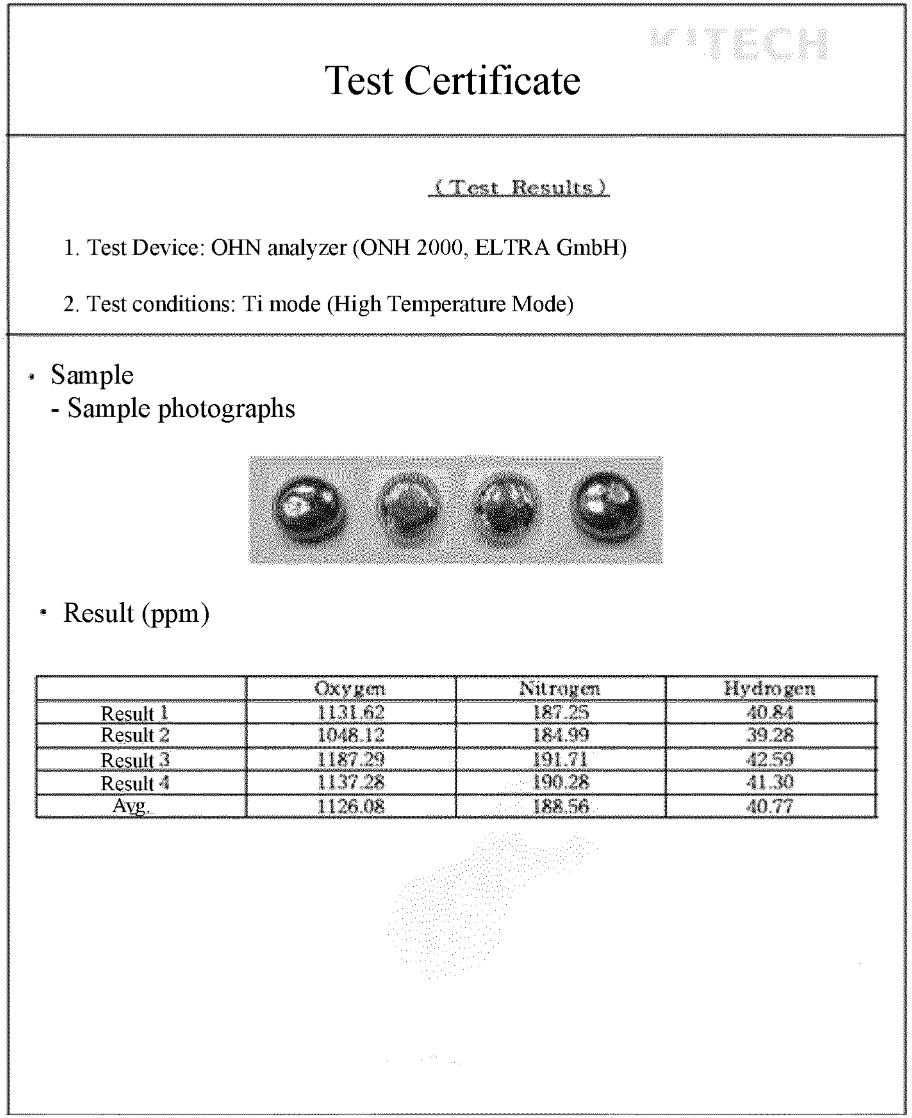
Element	Line Type	Wt%	Atomic %
Ti	K series	27.3	27.3
Cu	L series	72.7	72.7
Total:		100.00	100.00



Example 2

Element	Line Type	Wt%	Atomic %
Ti	K series	40.81	47.77
Cu	L series	59.19	52.23
Total:		100.00	100.00

Fig. 7



Test Certificate

（Test Results）

1. Test Device: OHN analyzer (ONH 2000, ELTRA GmbH)
2. Test conditions: Ti mode (High Temperature Mode)

- Sample
  - Sample photographs
- Result (ppm)

	Oxygen	Nitrogen	Hydrogen
Result 1	1131.62	187.25	40.84
Result 2	1048.12	184.99	39.28
Result 3	1187.29	191.71	42.59
Result 4	1137.28	190.28	41.30
Avg.	1126.08	188.56	40.77

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2021/003849

A. CLASSIFICATION OF SUBJECT MATTER

C25C 7/00(2006.01)i; **C25C 7/06**(2006.01)i; **C25C 3/36**(2006.01)i; **C22B 5/04**(2006.01)i; **C22B 9/10**(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)

C25C 7/00(2006.01); B22D 21/06(2006.01); B22D 23/10(2006.01); C22C 9/05(2006.01); C23C 14/34(2006.01); C25C 3/04(2006.01); C25C 3/26(2006.01); C25C 3/34(2006.01); C25C 3/36(2006.01); C25C 7/06(2006.01); C25C 7/08(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 액상금속(molten metal), 금속산화물(metal oxide), 불소(fluoride), 환원(reduction), 용융염(molten salt), 공융상(eutectic phase)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2004920 B1 (KOREA INSTITUTE OF GEOSCIENCE AND MINERAL RESOURCES(KIGAM)) 29 July 2019 (2019-07-29) See abstract, paragraphs [0014], [0028], [0033]-[0035], [0037]-[0041] and [0047] and figures 1-2.	1-17,19
A		18
X	KR 10-2009-0031508 A (NIPPON MINING & METALS CO., LTD.) 26 March 2009 (2009-03-26) See paragraphs [0003] and [0011] and claims 1-5.	16-18
A	JP 06-146049 A (KOBE STEEL LTD.) 27 May 1994 (1994-05-27) See paragraphs [0017]-[0035] and figure 1.	1-19
A	JP 11-071694 A (MITSUBISHI MATERIALS CORP.) 16 March 1999 (1999-03-16) See paragraph [0017] and claim 1.	1-19

☑ 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
“D”	document cited by the applicant in the international application
“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 **13 August 2021**	Date of mailing of the international search report **13 August 2021**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2021/003849

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-199354 A (GENERAL ELECTRIC CO. <GE>) 28 July 2005 (2005-07-28) See paragraph [0031].	1-19

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2021/003849

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2004920 B1	29 July 2019	WO 2020-159043 A1	06 August 2020
KR 10-2009-0031508 A	26 March 2009	CN 101473059 A	01 July 2009
		CN 101473059 B	20 March 2013
		EP 2014787 A1	14 January 2009
		EP 2014787 B1	06 September 2017
		JP 2012-149346 A	09 August 2012
		JP 4955008 B2	20 June 2012
		JP 5420685 B2	19 February 2014
		JP WO2008-041535 A1	04 February 2010
		KR 10-1070185 B1	05 October 2011
		TW 200821401 A	16 May 2008
		TW I368660 B	21 July 2012
		US 2010-0013096 A1	21 January 2010
		WO 2008-041535 A1	10 April 2008
JP 06-146049 A	27 May 1994	None	
JP 11-071694 A	16 March 1999	None	
JP 2005-199354 A	28 July 2005	DE 102004063817 A1	28 July 2005
		IT MI20042438 A1	21 March 2005
		JP 4744872 B2	10 August 2011
		RU 2004139197 A	20 June 2006
		RU 2383636 C2	10 March 2010
		UA 93651 C2	10 March 2011
		US 2005-0145065 A1	07 July 2005
		US 7381366 B2	03 June 2008

Form PCT/ISA/210 (patent family annex) (July 2019)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 5035404 A **[0003] [0009]**
- KR 101757626 **[0009]**
- KR 101793471 **[0009]**
- KR 101878652 **[0009]**

Non-patent literature cited in the description

- **ANTOINE ALLANORE.** *Journal of The Electrochemical Society,* 2015, vol. 162 (1), E13-E22 **[0010]**