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(54) Title: PRODUCTION METHOD FOR SCANDIUM METAL AND AL-SC ALLOYS VIA ELECTROLYSIS OF FLUORINATED SCANDIUM SALTS OBTAINED BY THE CALCINATION OF SCANDIUM COMPOUND IN THE FORM OF $(NH_4)_2NASCF_6$

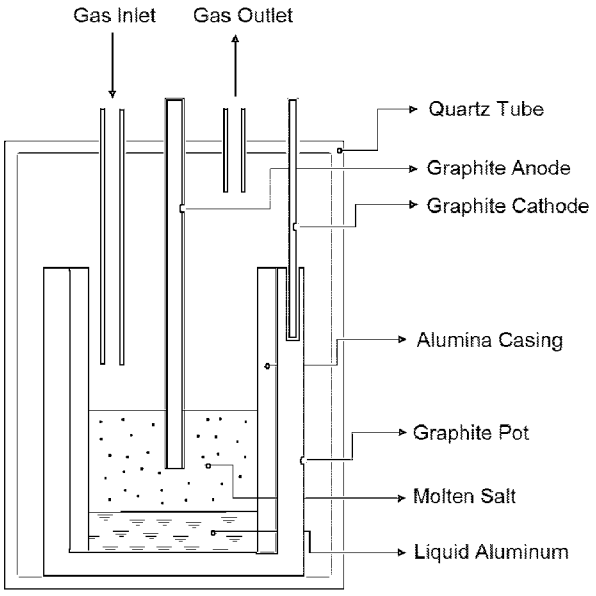


Figure 2

(57) Abstract: The invention relates to scandium metal obtained in its pure or alloy form, by removing (NH_4) form via calcining the initial scandium compound in $(NH_4)_2NaScF_6$ form and via molten salt electrolysis of fluorinated scandium compounds in $NaScF_4$ and Na_3ScF_6 forms that resulted after the calcination process.

[Continued on next page]

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Production Method for Scandium Metal and Al-Sc Alloys via Electrolysis of Fluorinated Scandium Salts Obtained by the Calcination of Scandium Compound in the form of $(NH_4)_2NaScF_6$

Technical Field

The invention relates to scandium metal in its pure or alloy form obtained by removing the NH_4 form present in the scandium compound which is initially in its $(NH_4)_2NaScF_6$ form, by calcination first and then with molten salt electrolysis of fluorinated scandium compounds in $NaScF_4$ and Na_3ScF_6 forms that resulted after the calcination process.

State of the Art

Scandium is one of the transition metals, which belongs to the 3B group of the periodic table, and known as one of the rare earth elements, which is rarely enriched in nature. Scarcity of the ores which has sufficient grade of scandium for feasible processing, constitutes a great obstacle against production and the usage of this metal in various industries. Until today, scandium has been found in trace amounts among uranium, tin, iron, tungsten, tantalum, zirconium, titanium and other rare earth element ores that are economically processed, within the content of more than 100 minerals; it has been obtained as a byproduct during the production of these metals. Other than this, the presence of substantial amounts of scandium element in lateritic nickel-cobalt ores have brought the possibility of producing scandium as a byproduct during the processing of these resources and consequently various studies about this subject have recently been conducted. An example of these studies is provided by patent application no. TR201308682 titled 'High pressure acid leaching of refractory lateritic ores containing nickel, cobalt and scandium and recovery of scandium from the pregnant leach solution loaded with metals and purification precipitates' claimed by 'Meta Nikel Kobalt Madencilik Sanayi ve Ticaret Anonim Şirketi'. Another one is the patent application titled 'Recovering scandium and its derivatives from leach solutions loaded with metals, which are obtained by leaching lateritic ores containing nickel, cobalt and scandium, and secondary sources containing scandium', claimed by 'Meta Nikel Kobalt Madencilik Sanayi ve Ticaret Anonim Şirketi' as well. The aforementioned applications are related to scandium recovery which is present in lateritic nickel-cobalt ores.

Another of them is given by the US application no. US3111467. Mentioned application requires pure NaF, ScF_3 and Sc_2O_3 salts in order to conduct the electrolysis process. First, NaF and ScF_3 salts are mixed and melted at 800 ℃, and then Sc_2O_3 salt is dissolved inside this melt.

One of the most important areas of scandium element usage is in aluminum-scandium alloys which is obtained by adding 0.2-0.8% scandium into aluminum for applications which require high strength, corrosion resistance and weldability. These alloys are generally obtained via adding pure scandium metal or master alloy containing 1-20% scandium, into molten aluminum metal.

One of the methods used for obtaining pure scandium metal is based on metallothermic reduction of pure Sc_2O_3 compound with gaseous calcium metal at high temperature. However, since the compound is a highly stable compound during the reduction, the reduction process may not be complete and some amount of scandium metal is lost in the form of $CaSc_2O_4$.

Another method for obtaining pure scandium metal is that converting Sc_2O_3 compound into relatively less stable ScF_3 form via using HF gas at high temperature and metallothermic reduction with calcium metal at high temperature. However, HF gas used in converting the Sc_2O_3 compound into ScF_3 form, is an extremely environmentally hazardous and corrosive compound, thus technically it makes the process very difficult. At the end of the reaction CaF_2 compound is produced along with the scandium metal, leading into the problem of separating scandium from this compound. Furthermore, impurity problem is caused by the tantalum pots where the reduction process takes place during the applied process, and the calcium metal used in the reaction, thus additional operational costs occur because of the vacuum distillation method used in order to overcome the impurity problem. In order to overcome these problems, it has been proposed to perform the reduction process of pure Sc_2O_3 or ScF_3 compound with calcium in the presence of aluminum metal, so recovering scandium aluminum alloy instead of pure scandium metal is proposed. The reduction process has been claimed to become easier and more efficient by dissolving the scandium metal, which has been reduced to metallic form, in molten aluminum metal.

However on the other hand; impurity problems during the reduction process at high temperatures due to tantalum pots and calcium metal, generation of Al_4Ca phase in

processes where Sc_2O_3 compound is used as the initial compound, and the requirement of using HF gas in processes where ScF_3 compound is used as the initial compound still constitute the technical problems which should be overcome during these processes.

It has been proposed that it may be possible to obtain scandium metal alternatively by using molten salt electrolysis method in order to overcome the problems encountered during metallothermic reduction methods realized at high temperatures with calcium metal [1]. The basic principle of the molten salt method is to dissolve the compound of the desired metal, inside an appropriate salt mixture at high temperature and separate it into its ions, and during the process, reduction of the desired element ions and selectively collect it at the cathode may be achieved by applying electric current to the molten salt mixture. Salts that may be used in this process, are fluoride, chloride, bromide and iodide and among them fluoride, chloride and mixtures thereof have been the most preferred alternatives [2]. Molten salts containing chloride and fluoride, fluoride containing salts are the most preferred ones due to having higher stability at high temperatures, absence of humidity absorption problem (not being hydroscopic) in contrast to chloride, and having high current efficiency [3].

As a result, aforementioned disadvantages and lack of adequate solutions in the background art have made it necessary to make a development in the technical field related to scandium metal production.

Objectives of the Invention

The present invention relates to a production method for scandium metal and Al-Sc alloys from scandium compounds obtained by the calcination of scandium compound in $(NH_4)_2NaScF_6$ form, via molten salt electrolysis method, which meets the aforementioned requirements while overcoming all disadvantages and providing further advantages.

The primary objective of the invention is the production of pure scandium metal, directly obtaining aluminum-scandium alloys containing 0.2-0.8% scandium and obtaining aluminum-scandium master alloys containing 1-20% scandium.

Another objective of the invention is to obtain scandium metal by using molten salt method, in order to overcome the technical problems associated with metallothermic reduction method. It is also obtaining fluoride containing salts in order to achieve this.

Another objective of the invention is the calcination of the scandium compound in $(NH_4)_2NaScF_6$, form at a temperature between 350-400 ℃; and after the calcination process, by removing the (NH_4) form from the structure, obtaining fluorinated scandium salts having the forms of $NaScF_4$ and Na_3ScF_6, in order to be used in molten salt electrolysis method.

A similar objective of the invention is to prevent the use of various high purity salts required to form the molten salt mixture.

In order to achieve aforementioned objectives, a production method of pure scandium metal, wherein, it comprises;

a) obtaining fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms from the scandium compound in $(NH_4)_2NaScF_6$ form via calcination process,

b) electrolysis process of the obtained fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms via molten salt electrolysis method,

process steps.

Structural and characteristic features of the invention with all its advantages shall become apparent with the detailed description given below and the appended drawings, therefore, assessment should be based on these drawings and the detailed description.

Brief Description of the Drawings

Figure 1: View of the cell system that is used to obtain pure scandium metal

Figure 2: View of the cell system that is used to obtain aluminum-scandium metal

Figure 3: Graphical representation of DTA/TGA analysis results which is conducted to determine the calcination temperature of $(NH_4)_2NaScF_6$ compound

Figure 4: XRD graph of $(NH_4)_2NaScF_6$ compound which has been calcined between 350-400 ℃ for 1 hour

Figure 5: XRD graph of the Al-Sc alloy obtained by electrolysis

Figure 6: Optical microscope image of the Al-Sc alloy obtained by electrolysis (x190 magnification)

Figure 7: Optical microscope image of the Al-Sc alloy obtained by electrolysis (x190 magnification) and micro-hardness measurement of Al and Al_3Sc phases

Drawings may not be scaled and the details that are not essential for understanding the present invention may have been omitted. Moreover, at least substantially identical elements or elements with at least substantially identical functions are denoted with same numbers.

Explanation of the Parts Presented in the Drawings

1. Gas inlet

2. Gas outlet

3. Quartz Tube

4. Graphite anode

5. Graphite cathode

6. Alumina Casing

7. Graphite pot

8. Molten salt

9. Reduced metallic scandium powder (solid)

10. Liquid aluminum

Detailed Description of the Invention

In this detailed description, the preferred embodiments of the production method for scandium metal and Al-Sc alloys from scandium compounds obtained via calcination of a scandium compound in $(NH_4)_2NaScF_6$ form, via molten salt electrolysis method, are described without any limiting effect for a better understanding of the subject.

The invention relates to production method for scandium metal in its pure or alloy form. The scandium production method of the invention comprises two steps. In the first step; removing the (NH_4) form by applying calcination process to scandium compound in $(NH_4)_2NaScF_6$ form for a duration of 1-3 hours (preferably 1 hour) at 350-400 ℃

temperature, after the calcination process obtaining a fluorinated scandium salt mixture in the forms of $NaScF_4$ and Na_3ScF_6. The second step is the use of fluorinated scandium salt mixture in the $NaScF_4$ and Na_3ScF_6 forms, in molten salt electrolysis method in order to obtain pure scandium metal.

In Figure 1, a cell system that is used to obtain pure scandium metal is shown. The calcined fluorinated salt mixture is used directly in order to obtain pure scandium metal. It is desired to maintain the salts, which are used in molten salt electrolysis, in molten phase during the process. Therefore, the obtained salt mixture is desired to have a relatively lower melting temperature. It has been observed that the fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms, obtained by calcination, melts at about 600 ℃. Therefore, in this process the temperature duri ng the molten salt electrolysis method should be over 600 ℃.

Over this temperature Na, Sc and F elements are in ionic states, generally in Na^+, Sc^{+3} and F^- forms. Therefore, when an electric current is applied through the molten mixture at a certain potential, positively charged Na^+, Sc^{+3} ions will be attracted by the cathode, while negatively charged F^- ions will be attracted by the anode. Depending on the relative stability of these ions with respect to each other, the applied potential will result in electrochemical oxidation and reduction reactions at the anode and the cathode regions.

Mentioned salt mixture is heated until it reaches 600-1100 ℃ as shown in the example drawing of Figure 1. Depending on the composition of the salt mixture, the preferred temperature should be 10-15 ℃ above the melting te mperature of the salt.

The circuit is supplied with electric current to maintain 2-8 volts of potential difference. The current density applied to the circuit should be stabilized preferentially between 0.5-1.0 A/cm^2. Due to the relatively lower applied potential, Na^+ ions are prevented to react, while only Sc^{3+} ions are reduced at the cathode (5) and collected on the electrolysis cell in a metallic form. Therefore, limiting the potential applied to the circuit below 3 volts will prevent the Na contamination problem. Whereas, due to the oxidation reactions at the anode, F^- ions will react with the graphite anode (4) and leave the cell as various fluorocarbon gases. These gases leaving the anode are environmentally undesired and hence may be collected and neutralized later. The scope of this study does not cover disposal of these gases. If preferred, in order to provide easier disposal of these gases,

instead of the graphite anode (4) more stable anode materials which does not react with fluorine may be used, resulting only fluorine gas output at the anode. These residual gases may be converted into more stable and less hazardous fluoride compounds using a gas collector unit. When fluorine gas outlet (2) is not preferred in the circuit after the reduction reactions, Sc_2O_3 compound may be added to the system no more than 10% by weight in the total salt bath and this compound may be dissolved into Sc^{+3} and O^{-2} ions inside the molten salt (8) phase. Since O^{-2} ions are oxidized with lower potentials in comparison to F^- ions, F^- ions may be prevented to react by adjusting the potential difference applied to the circuit. In order to meet this criterion, the potential difference applied to the circuit should not exceed 6 volts. Thereby, carbon monoxide and carbon dioxide gases, which are environmentally easier to dispose of, may be the gas outlet (2) as a result of the carbon and oxygen reactions at the graphite anode (4). Alternatively, oxygen gas which does not possess any environmental risks may be obtained at by using more stable anode materials which does not react with oxygen, When the oxidation and reduction reactions at the anode and the cathode terminate, the Sc^{+3} ions inside the molten salt is reduced and separated from the salt mixture so pure scandium metal (9) can be obtained at the bottom of the cell.

If it is desired to obtain an aluminum-scandium alloy containing 0.2-0.8% scandium or an aluminum-scandium master alloy containing 1-20% scandium via molten salt electrolysis method; then pure aluminum metal is added to the bottom of the cell before the reaction as shown in Figure 2. Subsequently, fluoride salt mixture of $NaScF_4$ and Na_3ScF_6 obtained from the calcination process is added on top of the Al metal.

Thereafter, both phases are melted by increasing the temperature of the cell over a value where the aluminum and the fluoride salt mixtures are in their molten states (preferably 700-1100 ℃). When melting is completed , liquid aluminum (10) is collected at the bottom of the cell due to the density difference, while fluoride salt mixture (8) is collected on top of the liquid aluminum (10).

A current may be applied to the circuit in order to create a potential difference between 2 and 8 volts. Applying relatively lower potentials preferably not exceeding 3 volts prevents Na^+ ions to react, ensuring only Sc^{3+} ions to be reduced at the cathode (5) and to be dissolved in the liquid aluminum (10), collected at the bottom of the electrolysis cell in molten state. Due to oxidation reactions occurred at anode, by reacting with the graphite anode (4), F^- ions may leave the cell in the form of various fluorocarbon gases.

Since these gases emitted at the anode are environmentally undesired, these gases may be collected and disposed of later. If it is preferred, more stable anode materials which does not react with fluorine gas may be used instead of the graphite anode (4), resulting in only fluorine gas output (2) at the anode, in order to provide easier disposal of these gases. These residual gases may be converted into more stable and less hazardous fluoride compounds via using a gas collector unit. When fluorine gas outlet (2) is not preferred in the circuit during the reduction reactions, Sc_2O_3 or Al_2O_3 compounds may be added to the system no more than 10% by weight in the salt mixture and scandium oxide may be dissolved into Sc^{+3} and O^{-2} ions, or the aluminum oxide may be dissolved into Al^{+3} and O^{-2} ions, inside the molten salt (8) phase. Since O^{-2} ions are oxidized with lower potentials in comparison to F^- ions, F^- ions may be prevented to react by adjusting the potential difference applied to the circuit. In order to meet this criterion, the potential difference applied to the circuit should not exceed 6 volts. Thereby, carbon monoxide and carbon dioxide gases, which are environmentally more easily disposable, may be emitted as a result of the carbon and oxygen reactions at the graphite anode (4). Alternatively, instead of graphite by using more stable anode materials which does not react with oxygen, only oxygen gas, which does not possess any environmental risks, may be emitted at the anode. While potential difference between 2-8 volts is applied, Sc^{3+} and Al^{+3} ions may be reduced simultaneously and dissolved in the liquid aluminum (10), collected at the bottom of the electrolysis cell in molten state. Applying 2-8 volts of potential difference to the cell in this way while the process is maintained until the desired scandium concentration; an aluminum-scandium alloy containing 0.2-0.8% scandium or, with longer electrolysis durations, an aluminum-scandium master alloy with 1-20% scandium may be obtained. After the electrolysis process, the aluminum-scandium alloy at the bottom of the cell in liquid state again, may be separated from the molten fluoride salt phase and an aluminum-scandium alloy may be obtained via this way.

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CLAIMS

1. A production method for pure scandium, wherein, it comprises;

a) obtaining fluorinated salt mixture of scandium in $NaScF_4$ and Na_3ScF_6 forms from the scandium compound in $(NH_4)_2NaScF_6$ form via calcination process,

b) electrolysis process of the obtained fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms via molten salt electrolysis method,

process steps.

2. The production method according to claim 1, wherein; the fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms, mentioned in process step a, is obtained by,

- removing the (NH_4) from the structure of the scandium compound in $(NH_4)_2NaScF_6$ form by calcination

process step.

3. The production method according to claim 2, wherein; the calcination process of the scandium compound in $(NH_4)_2NaScF_6$ form, is conducted at 350-400 ℃ for a duration of 1-3 hours.

4. The production method according to claim 1, wherein; the electrolysis process mentioned in step b comprises;

- heating the fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms, until it is molten to the temperature of 600-1100 ℃,
- applying an electrical current to the obtained molten salt bath through the anode and the cathode in order to maintain 2-8 volts of potential difference,
- obtaining pure scandium metal at the bottom of the electrolysis cell by reducing and separating the Sc^{+3} ions from the molten salt mixture via this applied electrical current and potential,

process steps.

5. The production method according to claim 4, wherein; when it is desired to obtain an aluminum-scandium alloy containing 0.2-0.8% scandium or an aluminum-scandium master alloy containing 1-20% scandium, it comprises;

a) adding aluminum to the bottom of the electrolysis cell,

b) adding fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms, on top of the aluminum metal,

c) heating the aluminum metal and the fluorinated scandium salt mixture in $NaScF_4$ and Na_3ScF_6 forms until it is molten, to the temperature of 700-1100℃,

d) applying an electrical current to the obtained molten salt bath through the anode and the cathode in order to maintain 2-8 volts of potential difference,

e) obtaining aluminum-scandium alloy by separating the molten aluminum-scandium alloy from the molten fluoride salt mixture via this electrical current,

process steps.

6. The production method according to claim 5, wherein; when the anode material mentioned in step d is graphite; fluorocarbon gas or carbon monoxide-carbon dioxide gases may be emitted.

7. The production method according to claim 6, wherein; when carbon monoxide-carbon dioxide gas emission is preferred; it comprises,

- adding Sc_2O_3 or Al_2O_3 compound no more than 10% by weight to the salt mixture and dissolving scandium oxide into Sc^{+3} and O^{-2} ions, or dissolving the aluminum oxide into Al^{+3} and O^{-2} ions, inside the molten salt phase,
- adjusting the potential difference applied to the circuit without exceeding 6 volts, in order to oxidize only O^{-2} ions,

process steps.

8. The production method according to claim 5, wherein; when the anode material mentioned in step d is a stable anode material which does not react with F^-, F_2 gas is emitted; and when it is a stable anode material which does not react with O^-, O_2 gas is emitted.

9. The production method according to claim 8, wherein; when emission of O_2 gas is preferred; it comprises,

- adding Sc_2O_3 or Al_2O_3 compound no more than 10% by weight to the salt mixture and dissolving scandium oxide into Sc^{+3} and O^{-2} ions, or dissolving the aluminum oxide into Al^{+3} and O^{-2} ions, inside the molten salt phase,
- adjusting the potential difference applied to the circuit without exceeding 6 volts, in order to oxidize only O^{-2} ions,

process steps.

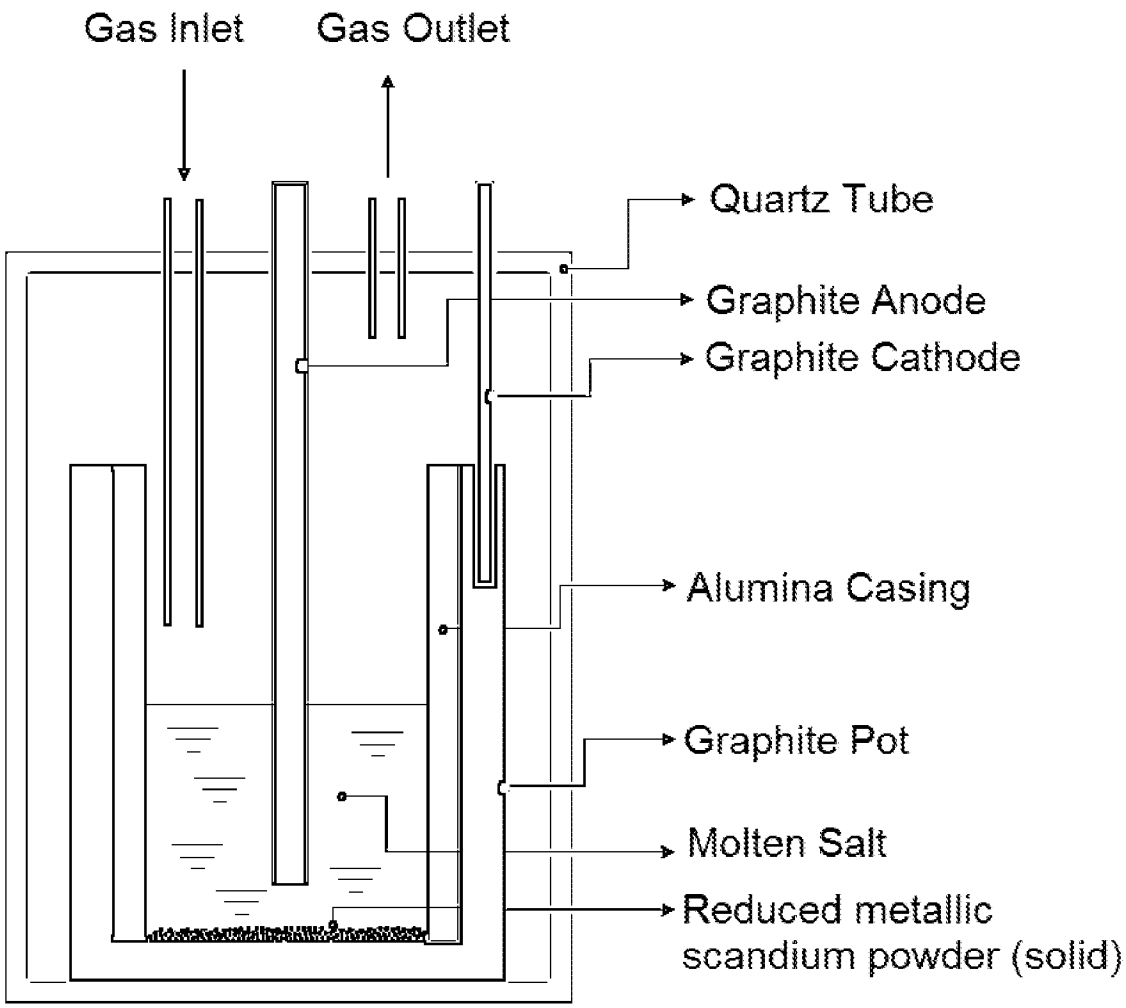

Gas Inlet
Gas Outlet
Quartz Tube
Graphite Anode
Graphite Cathode
Alumina Casing
Graphite Pot
Molten Salt
Reduced metallic scandium powder (solid)

Figure 1

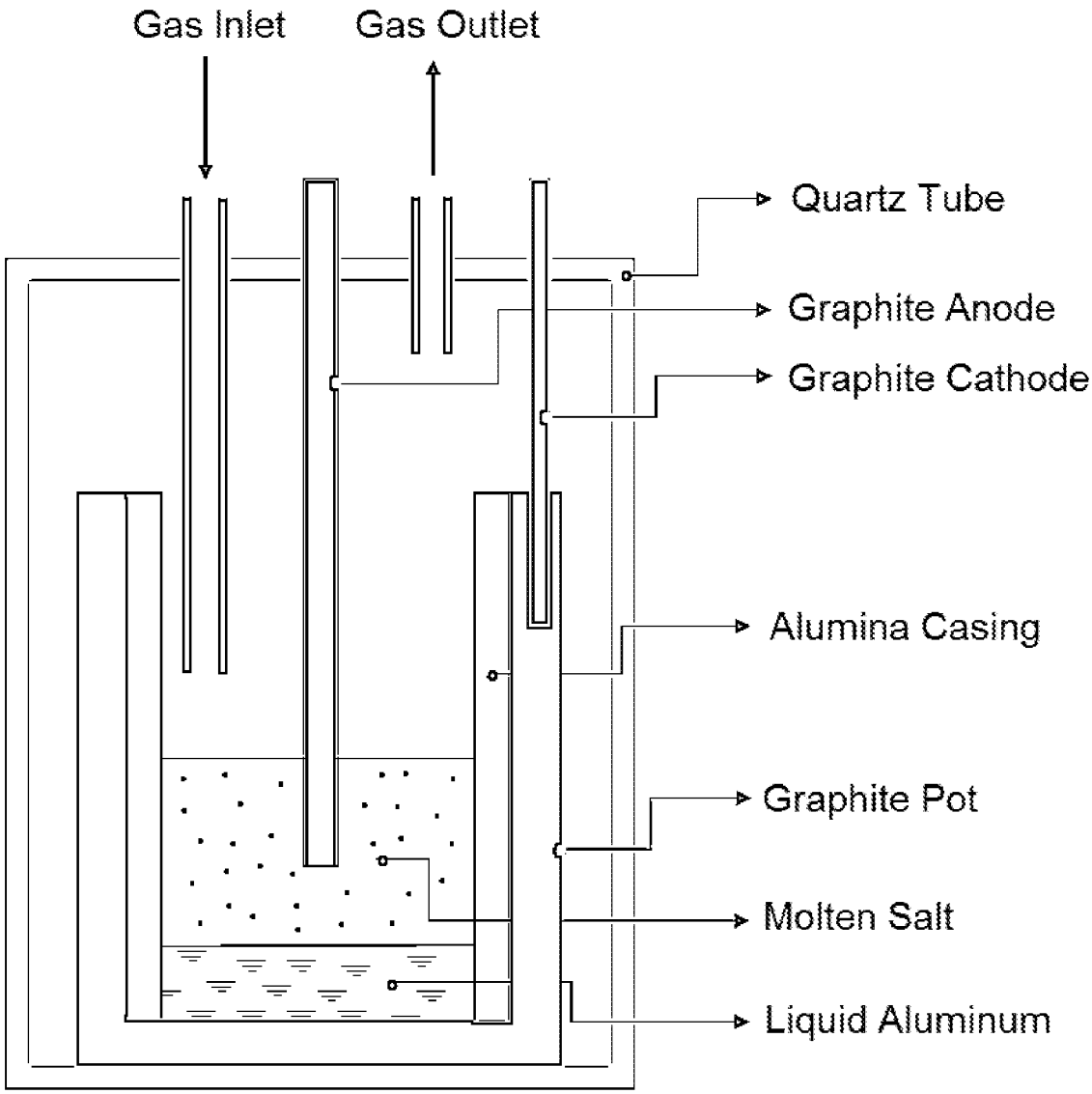

Gas Inlet
Gas Outlet
Quartz Tube
Graphite Anode
Graphite Cathode
Alumina Casing
Graphite Pot
Molten Salt
Liquid Aluminum

Figure 2

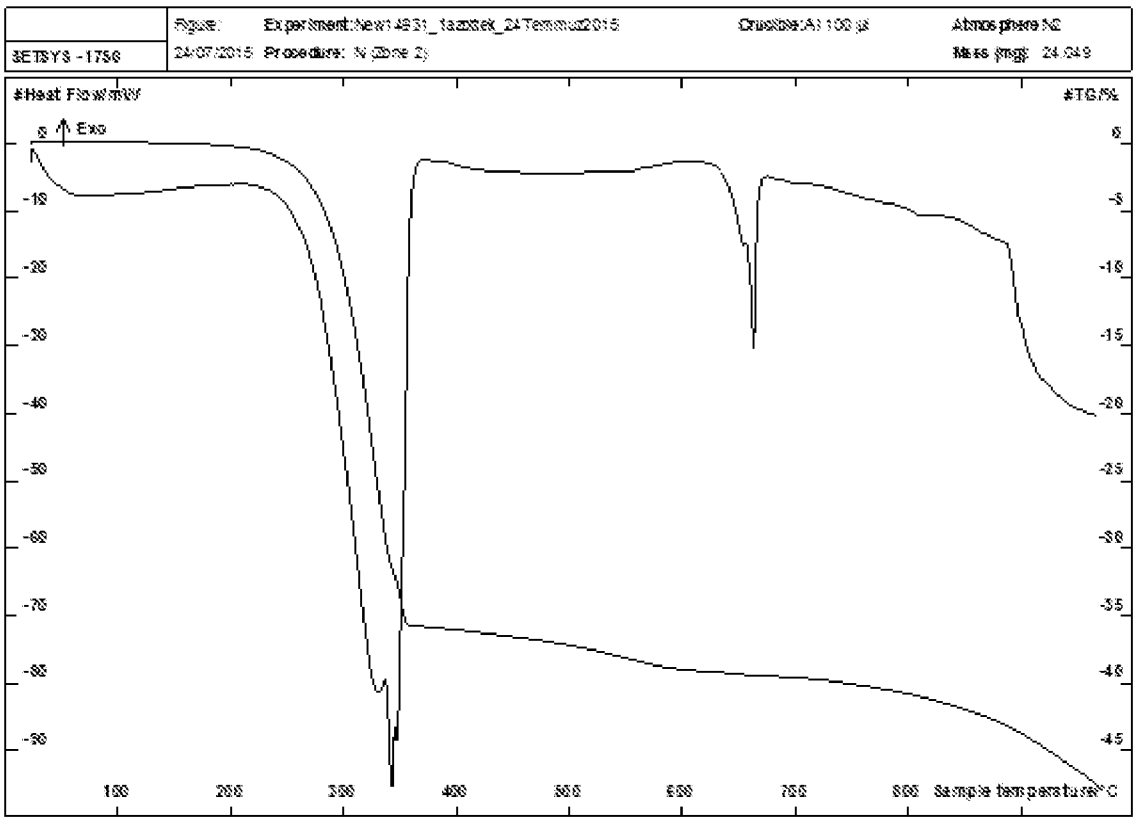


Figure 3

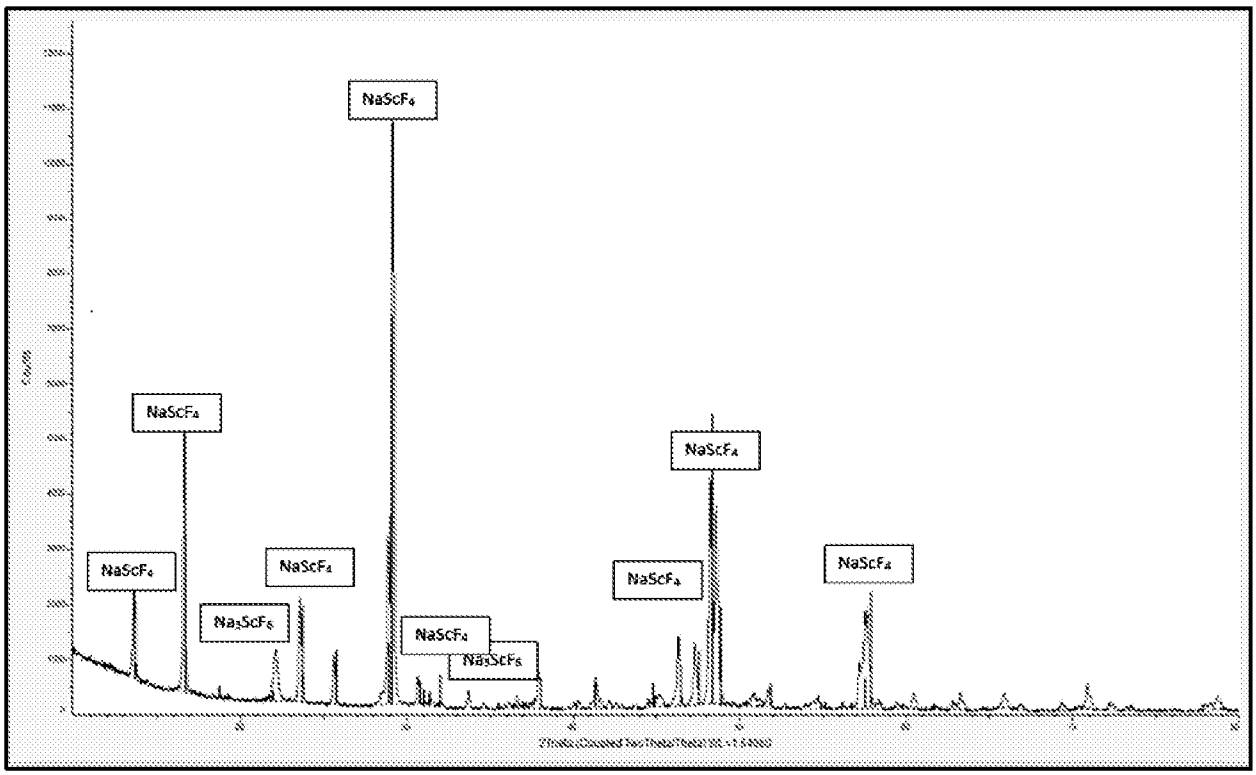

NaScF4
NaScF4
NaScF4
Na3ScF6
NaScF4
NaScF4
Na3ScF6
NaScF4
NaScF4
NaScF4

Figure 4

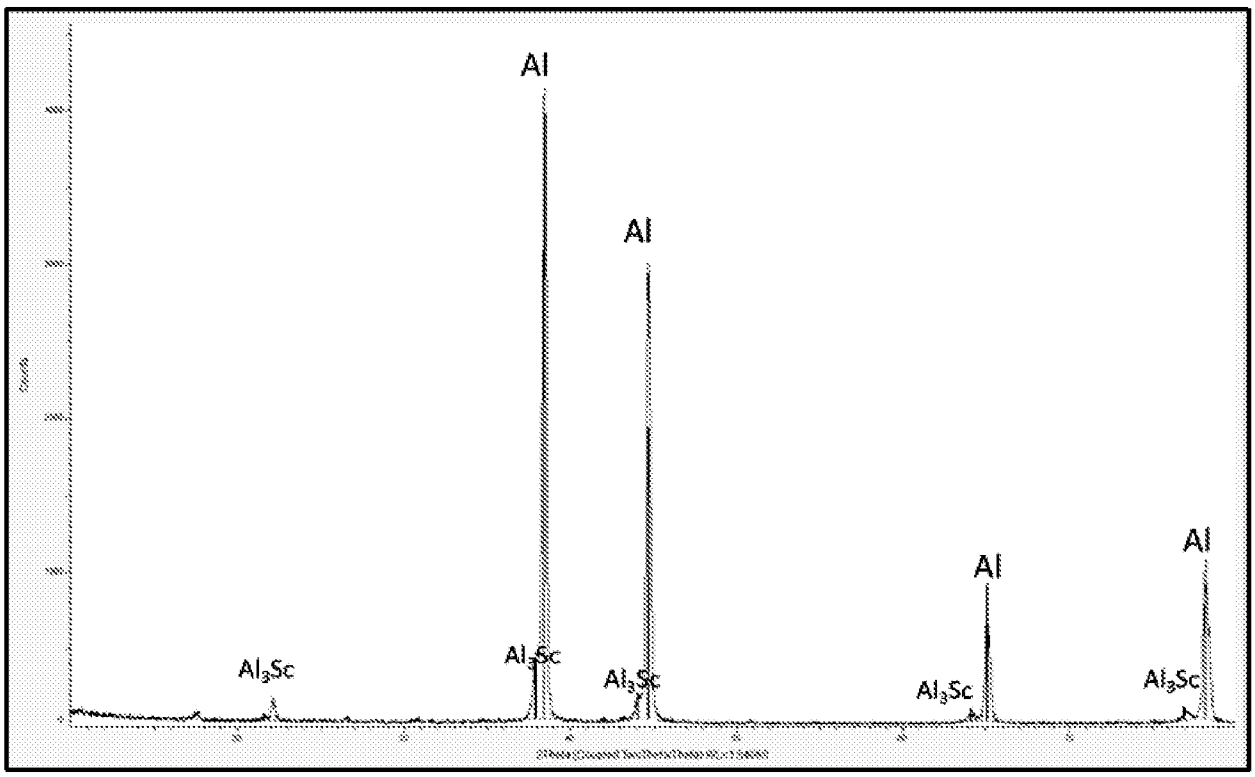


Figure 5

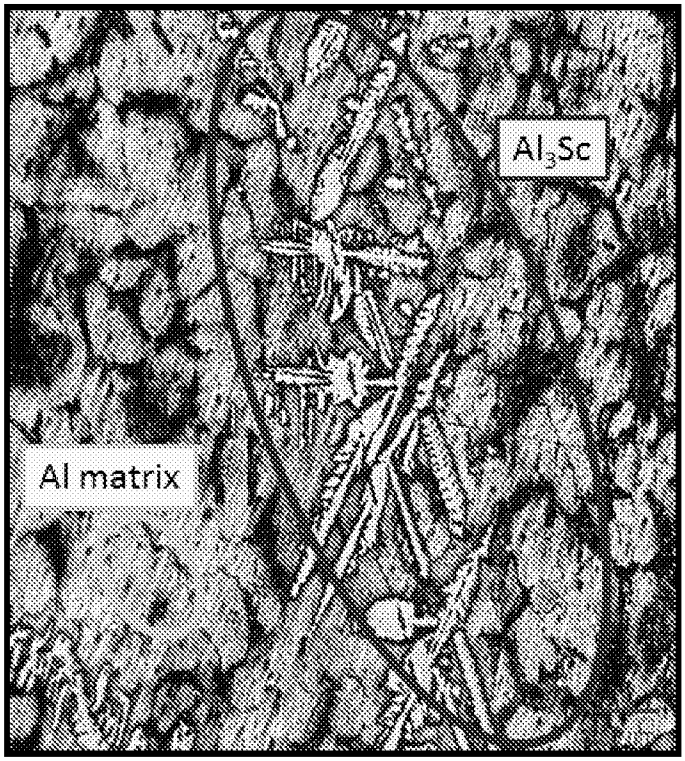


Figure 6

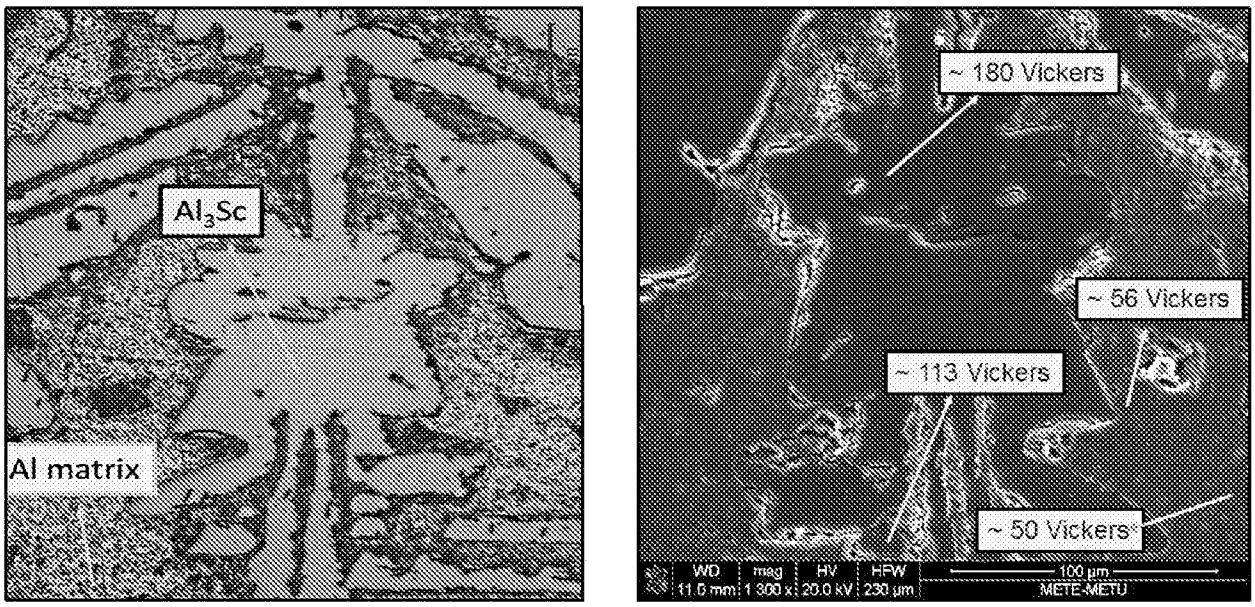

Al_3Sc
Al matrix
~ 180 Vickers
~ 56 Vickers
~ 113 Vickers
~ 50 Vickers
WD mag HV HFW
11.6 mm 1 300 x 20.0 kV 230 µm
100 µm
METE-METU

Figure 7