

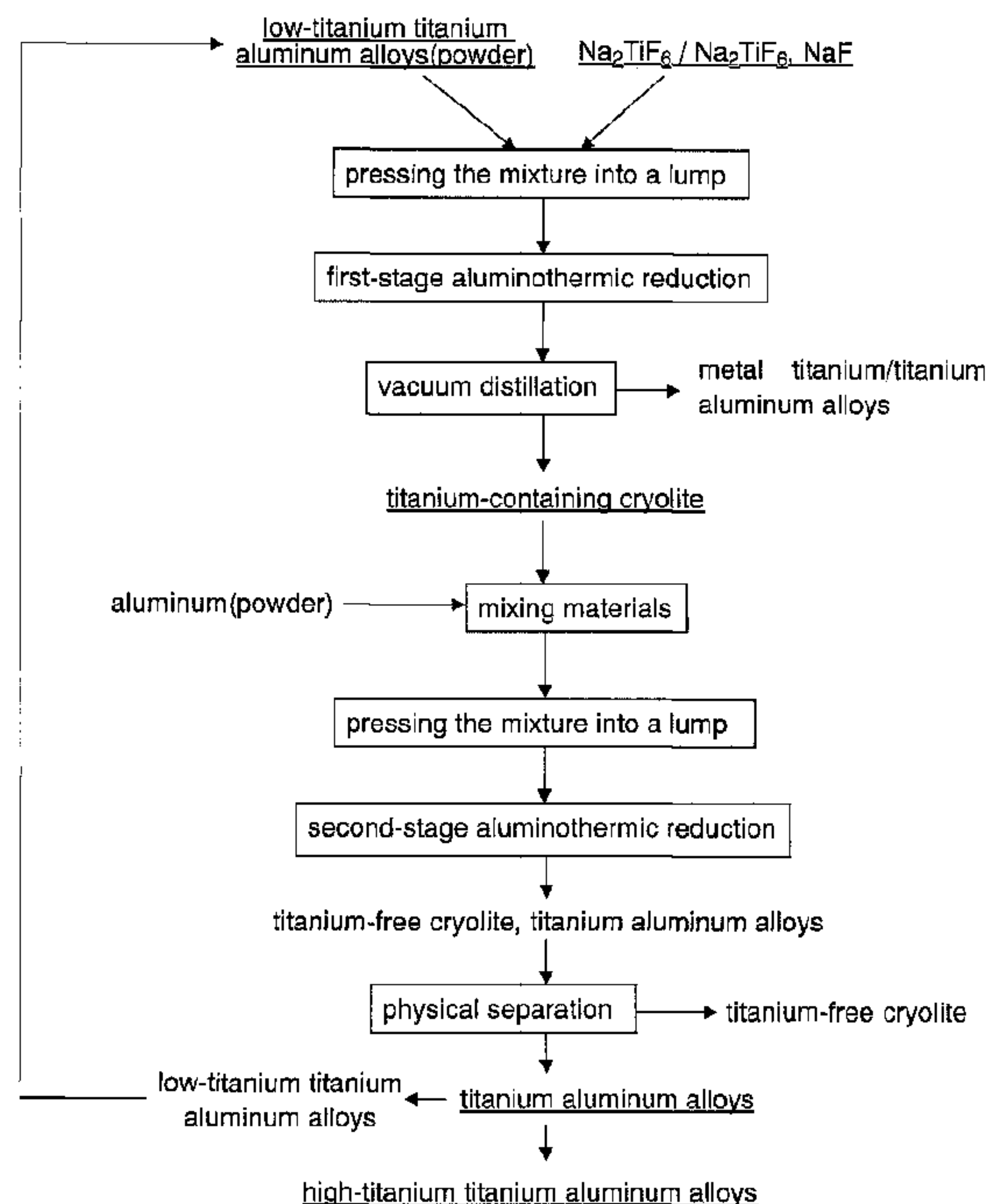


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(54) Titre : METHODE DE PRODUCTION DE TITANE OU D'ALLIAGES DE TITANE ET ALUMINIUM PARREDUCTION ALUMINOTHERMIQUE A DEUX ETAGES ET OBTENTION DE CRYOLITE EXEMPTDE TITANE COMME SOUS-PRODUITS

(54) Title: METHOD FOR PRODUCING TITANIUM OR TITANIUM ALUMINUM ALLOYS THROUGH TWO-STAGE ALUMINOTHERMIC REDUCTION AND OBTAINING TITANIUM-FREE CRYOLITE AS BYPRODUCTS



(57) Abrégé/Abstract:

The present invention relates to a method for preparing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts, and belongs to the technical field of metallurgy. The method

(57) Abrégé(suite)/Abstract(continued):

comprises the following steps: (1) using sodium fluoride and sodium fluotitanate as raw materials, or using sodium fluotitanate as raw materials, and using titanium aluminum alloy powder as a reducing agent; (2) mixing the raw materials with the reducing agent, pressing the mixture into a lump, and performing first-stage aluminothermic reduction and vacuum distillation on the lump; (3) after titanium-containing cryolite is taken out, grinding the titanium-containing cryolite, mixing the grinded titanium-containing cryolite with the reducing agent, pressing the mixture into a lump and performing second-stage aluminothermic reduction on the lump; and (4) separating low-titanium titanium aluminum alloys from high-titanium titanium aluminum alloys, making the low-titanium titanium aluminum alloys and the high-titanium titanium aluminum alloys into powder and returning to the two-stage aluminothermic reduction as the reducing agent; or after the alloys are molten, making the alloys into powder for the two-stage aluminothermic reduction. The method has the advantages that a reaction process is easy to control, the production cost is low, titanium elements can be recycled to the maximum extent, and the high-purity cryolite can be produced as the byproducts.

ABSTRACT OF THE DISCLOSURE

The present invention relates to a method for preparing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts, and belongs to the technical field of metallurgy. The method comprises the following steps: (1) using sodium fluoride and sodium fluotitanate as raw materials, or using sodium fluotitanate as raw materials, and using titanium aluminum alloy powder as a reducing agent; (2) mixing the raw materials with the reducing agent, pressing the mixture into a lump, and performing first-stage aluminothermic reduction and vacuum distillation on the lump; (3) after titanium-containing cryolite is taken out, grinding the titanium-containing cryolite, mixing the grinded titanium-containing cryolite with the reducing agent, pressing the mixture into a lump and performing second-stage aluminothermic reduction on the lump; and (4) separating low-titanium titanium aluminum alloys from high-titanium titanium aluminum alloys, making the low-titanium titanium aluminum alloys and the high-titanium titanium aluminum alloys into powder and returning to the two-stage aluminothermic reduction as the reducing agent; or after the alloys are molten, making the alloys into powder for the two-stage aluminothermic reduction. The method has the advantages that a reaction process is easy to control, the production cost is low, titanium elements can be recycled to the maximum extent, and the high-purity cryolite can be produced as the byproducts.

METHOD FOR PRODUCING TITANIUM OR TITANIUM ALUMINUM ALLOYS THROUGH TWO-STAGE ALUMINOTHERMIC REDUCTION AND OBTAINING TITANIUM-FREE CRYOLITE AS BYPRODUCTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention belongs to the technical field of metallurgy and particularly relates to a method for producing titanium and titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts.

2. The Prior Arts

[0002] Titanium is a light rare metal material and is widely applied in the technical fields of aviation, aerospace and chemical engineering. At present, titanium is produced by a method for reducing titanium tetrachloride (TiCl_4) with magnesium at high temperature, and the titanium produced by the method is spongy. The titanium can also be produced by a method for reducing titanium tetrachloride (TiCl_4) with sodium at high temperature. The method for producing titanium by reducing the titanium tetrachloride (TiCl_4) with the magnesium or the sodium is high in cost. In addition, Cl_2 is a raw material during production of the TiCl_4 , and the byproduct in reduction process is chloride. Since Cl_2 and the chloride are strong corrosive to equipment, the operation conditions are complicated and extreme. Therefore, people also continuously explore other smelting methods for producing titanium, such as fused salt electrolysis of TiCl_4 , and electro-deoxidization fused salt electrolysis of TiO_2 which is used as a negative pole, but the methods are still in a laboratory research stage and do not succeed in the industry. Additionally, methods for producing the titanium by using sodium fluotitanate or potassium fluotitanate or titanium trifluoride as a raw material and using Al-Zn, Al-Mg, and Al-Zn-Mg alloys as well as pure Al, pure Mg and pure Na as reducing agents, also exist (see US2010/0173170A1,

CN102534263A, CN102560153A and CN102534260A). According to the methods of producing titanium, the purity of titanium can be 70.7% or above, and the maximum purity can be 99.5%.

[0003] The reduction reactions are all performed at the temperature of 900-1000 °C, but the methods still cannot be applied in the industry. The methods have the disadvantages and problems as follows:

[0004] 1. The reduction process is comparatively complicated; in the methods disclosed by the patents, the reducing agents are mixed and fused firstly, and then the mixed and fused compound reducing agents are added or dropped into the raw material needed to reduce; and the reaction material needs to be stirred in the reaction process, and finally products should be separated out;

[0005] 2. when the reduction agent is Al-Zn alloys, Zn does not participate in the reduction reaction, so that Zn needs to be separated out the purification technology is complicated, and the production cost is greatly increased; and

[0006] 3. in the technical methods disclosed by the patents, the byproducts mainly Na_3AlF_6 and AlF_3 separated out from products are black or grey-black and contain a lot of titanium compounds, so that the loss of titanium is caused.

[0007] With the development of aviation and aerospace techniques and requirements for some high-temperature corrosion-resistant materials in the chemical engineering field, the development of Ti-Al alloys or Ti-Al-based high-performance alloys doped with some other metal elements is extensively concerned in various countries of the world. However, raw metals of the alloys are all produced by the method of smelting pure metal aluminum and sponge titanium which are produced by magnesiothermic reduction for TiCl_4 , and the production technology is comparatively complicated.

SUMMARY OF THE INVENTION

[0008] For the problems existing in the production technique of titanium, the present invention provides a method for producing titanium and titanium aluminum alloys through two-stage aluminothermic reduction and producing titanium-free cryolite as byproducts; the titanium-free cryolite

containing the extremely low content of titanium can be used for electrolytic aluminum industry. The two-stage aluminothermic reduction method consists of a first-stage aluminothermic reduction process and a second-stage aluminothermic reduction process. In the first-stage aluminothermic reduction process, the titanium or the titanium aluminum alloys are the to-be-produced products, and sodium fluoride and sodium fluotitanate are used as raw materials, or sodium fluotitanate is used as raw material, and powder made of the Al-Ti alloys produced by the second-stage aluminothermic reduction process is used as reducing agent. The titanium or the titanium aluminum alloys are produced by the first-stage aluminothermic reduction. In the first-stage aluminothermic reduction process, the materials and the reducing agent participating in the reduction reaction are mixed and pressed into lumps, and the lumps are heated to 900-1300 °C under the vacuum or argon protection condition for aluminothermic reduction. Then, the reduction product is separated through vacuum distillation at the temperature of 900-1300 °C, so as to obtain titanium-containing cryolite and the titanium or the titanium aluminum alloys. In the second-stage aluminothermic reduction process, the titanium-containing cryolite produced by the first-stage aluminothermic reduction is used as a raw material, and aluminum powder is used as reducing agent. The titanium-containing cryolite and the reducing agent are mixed and pressed into lumps, and the lumps are reduced under the argon protection condition at the temperature of 900-1300 °C, so as to obtain the titanium-free cryolite and the aluminum titanium alloys. In the second-stage aluminothermic reduction process, the feeding quantity of the reducing agent follows a rule that the melting point of the aluminum titanium alloys produced after the second-stage reduction process is lower than the temperature of the reduction reaction. In the second-stage aluminothermic reduction process, the aluminum titanium alloys and the titanium-free cryolite are mutually insoluble, so that the aluminum titanium alloy melt and the titanium-free cryolite melt can be well separated out in the molten state. the titanium in the aluminum titanium alloys produced by the second-stage aluminothermic reduction mainly exist in the form of TiAl_3 metallic compound, and most of TiAl_3 metallic compound settle at the bottom of the alloy melt in a slow cooling process, therefore,

low-titanium aluminum titanium alloys with lower content of titanium are formed at the upper part, and high-titanium aluminum titanium alloys with higher content of titanium are formed at the lower part. When the second-stage reduction reaction completed and the reduction product cooled, the solid titanium-free cryolite can be separated from the aluminum titanium alloys. The aluminum titanium alloys separated out in the second-stage aluminothermic reduction process are remolten and made into powder to be used as the reducing agent of the first-stage aluminothermic reduction. The aluminum titanium alloys produced in the second-stage aluminothermic reduction can also be separated out by adopting one of the following two methods: 1, separating the low-titanium aluminum titanium alloys from the high-titanium Al-Ti alloys by a mechanical method. 2, putting the aluminum titanium alloys obtained by the second-stage aluminothermic reduction into a tiltable induction furnace for remelting, after standing for a period of time, firstly pouring out the low-titanium aluminum titanium alloys at the upper part, and then digging out the high-titanium aluminum titanium alloys at the bottom, so that the purpose of separating the high-titanium aluminum titanium alloys from the low-titanium aluminum titanium alloys is realized. The low-titanium aluminum titanium alloys which are divided out or separated are made into powder, and the powder is used as the reducing agent of the first-stage aluminothermic reduction, and the high-titanium aluminum titanium alloys with higher content of titanium are sold as commodities.

[0009] The method provided by the present invention comprises the following steps:

[0010] 1. using sodium fluotitanate as the raw material, or using sodium fluoride and sodium fluotitanate as the raw materials. when the titanium and the titanium aluminum alloys are produced and manufactured, using the aluminum titanium alloy powder produced in the second-stage aluminothermic reduction as the reducing agent. In addition, designing the proportion of all the materials according to the to-be-produced product, wherein the reaction formulas of the production proportion are shown as follows:



or,



[0011] 2. uniformly mixing the raw materials with the reducing agent to obtain a mixture, pressing the mixture into lumps, placing the lumps into a vacuum reduction furnace, heating the placed lumps to 900-1300 °C under the vacuum condition or in the argon atmosphere, performing the first-stage aluminothermic reduction, and separating the reduction product by vacuum distillation at the temperature of 900-1300 °C; coagulating the titanium-containing cryolite distilled out on a crystallizer at the low-temperature end of the vacuum reduction furnace, wherein the product mainly comprises Na_3AlF_6 , $\text{Na}_5\text{Al}_3\text{F}_{14}$, AlF_3 and titanium-containing sub-fluoride, the residual product which is not distilled out in the vacuum reduction furnace is the metal Ti or the titanium aluminum alloys.

[0012] Because of containing some unreacted sodium fluotitanate and titanium-containing sub-fluoride produced by a side reaction, the product distilled out after the first-stage aluminothermic reduction is black-grey, so that the product distilled out is called the titanium-containing cryolite;

[0013] 3. taking out the titanium-containing cryolite, grinding it until the particle size is less than 1.0mm, using the aluminum powder as the reducing agent, uniformly mixing the grinded titanium-containing cryolite with the aluminum powder to obtain a mixture, and pressing the mixture into lumps, wherein the feeding amount of the aluminum powder follows the rule that the melting point of the aluminum titanium alloys produced by the second-stage aluminothermic reduction is less than or equal to the temperature of the second-stage reduction reaction; placing the lumps in the vacuum reduction furnace, heating the placed lumps to 900-1300 °C in the argon atmosphere and preserving the temperature for 0.5-2h for the second-stage aluminothermic reduction, wherein when the reduction

reaction completed and the temperature in the furnace reduced to normal temperature, white easily-broken titanium-free cryolite is formed at the upper parts of the product and the aluminum titanium alloys are formed at the bottom of the product, wherein the low-titanium aluminum titanium alloys with low content of titanium are formed at the upper parts of the aluminum titanium alloys, which are called the low-titanium aluminum titanium alloys, and the aluminum titanium alloys with comparatively high content of titanium are formed at the lower parts of the aluminum titanium alloys, which are called the high-titanium aluminum titanium alloys; and

[0014] 4. remelting the aluminum titanium alloys produced by the second-stage aluminothermic reduction, making the aluminum titanium alloys into powder and returning the powder back to the first-stage aluminothermic reduction by using as the reducing agent, which are shown as in the flow diagram of Fig. 1; or, separating the low-titanium aluminum titanium alloys from the high-titanium aluminum titanium alloys by a mechanical division method, or a remelting and dumping method in the induction furnace, then making the low-titanium aluminum titanium alloys into powder as the reducing agent of the first-stage aluminothermic reduction, and selling the high-titanium aluminum titanium alloys as the commodities, which are shown in the flow diagram of Fig. 2.

[0015] In the method, when the first-stage aluminothermic reduction is performed for the first time, the metal aluminum powder is used as the reducing agent if no available aluminum titanium alloys are used as the reducing agent, and the dosage of the reducing agent in step 1 is designed according to the to-be-produced product, and the reaction formulas of the production proportion are respectively shown in (1), (2) or (3), (4).

[0016] In the method, the titanium-containing cryolite in step 2 mainly comprises Na_3AlF_6 , $\text{Na}_5\text{Al}_3\text{F}_{14}$, AlF_3 and titanium-containing sub-fluoride, wherein the titanium mainly exists in the form of Na_3TiF_6 , TiF_3 and a small amount of Ti. Since the content of AlF_3 , TiF_3 and titanium powder are small in the mixture, they are possibly not obvious in an XRD (x-ray diffraction) analysis result of the product.

[0017] In the method, the argon condition in step 2 and step 3 refers to that the vacuum reduction furnace is vacuumized to 10Pa or below, and then argon is inflated to realize normal pressure.

[0018] In the method, the vacuum distillation refers to that distillation is performed for 1h or above under the condition that the vacuum of the vacuum reduction furnace is 10Pa or below, and the temperature is 900-1300 °C.

[0019] The method provided by the present invention is simple to operate, lower corrosion to the equipment, and high in purity of obtained cryolite, titanium and titanium aluminum alloys. The method also does not need complicated equipment. The reaction process of the method and the contents of Ti and Al in the alloys are easy to control, and the production cost is low, and the reduction rate of titanium and the utilization rate of aluminum are 100%. The byproduct namely the cryolite obtained by the method is high in purity and can be used in the aluminum electrolysis industry.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Fig. 1 is a flow diagram of the method for producing titanium or titanium aluminum alloys by two-stage aluminothermic reduction process and producing titanium-free cryolite as byproducts in the second-stage aluminothermic reduction process, wherein the aluminum titanium alloys produced in the second-stage aluminothermic reduction are remolten and then made into alloy powder, and the alloy powder is used as a reducing agent in the first-stage aluminothermic reduction process;

[0021] Fig. 2 is a flow diagram of the method for producing titanium or titanium aluminum alloys by two-stage aluminothermic reduction process and producing titanium-free cryolite as byproducts in the second-stage aluminothermic reduction process, wherein the aluminum titanium alloys produced in the second-stage aluminothermic reduction are divided into two parts of low-titanium aluminum titanium alloys and high-titanium aluminum titanium alloys, the high-titanium aluminum titanium alloys are sold as commodities, and the low-titanium aluminum titanium alloys are used as the reducing agent in the first-stage aluminothermic reduction process;

[0022] Fig. 3 is an XRD phase analysis diagram of a Ti_3Al alloy product obtained in an embodiment 1 of the present invention;

[0023] Fig. 4 is an XRD phase analysis diagram of titanium-containing cryolite in an embodiment 1 of the present invention;

[0024] Fig. 5 is an XRD phase analysis diagram of a distillation product obtained in an embodiment 2 of the present invention;

[0025] Fig. 6 is an XRD phase analysis diagram of a TiAl_3 alloy product obtained in an embodiment 3 of the present invention;

[0026] Fig. 7 is an XRD phase analysis diagram of a TiAl alloy product obtained in an embodiment 5 of the present invention;

[0027] Fig. 8 is an XRD phase analysis diagram of a metal Ti product obtained in an embodiment 7 of the present invention;

[0028] Fig. 9 is an XRD phase analysis diagram of titanium-free cryolite(Na_3AlF_6) obtained in an embodiment 9 of the present invention;

[0029] Fig. 10 is an SEM (scanning electron microscope) morphology analysis diagram of a layered interface of an aluminum titanium alloy product obtained in an embodiment 9 of the present invention; and

[0030] Fig. 11 is an EDS (energy dispersive spectrum) detection result diagram of the aluminum titanium alloy product obtained in the embodiment 9 of the present invention, wherein an upper diagram and a lower diagram respectively correspond to the position A and the position B of Fig. 10.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0031] XRD phase analysis equipment adopted in an embodiment of the present invention is an X'Pert Pro type X-ray diffractometer.

[0032] SEM morphology analysis equipment adopted in an embodiment of the present invention is an S-4800 type cold field emission scanning electron microscope.

[0033] EDS detection equipment adopted in an embodiment of the present invention is an accessory X-ray energy spectrometer of the S-4800 type scanning electron microscope.

[0034] Metal aluminum powder adopted in an embodiment of the present invention is a product purchased on the market, and the purity of the metal aluminum powder is greater than or equal to 99%.

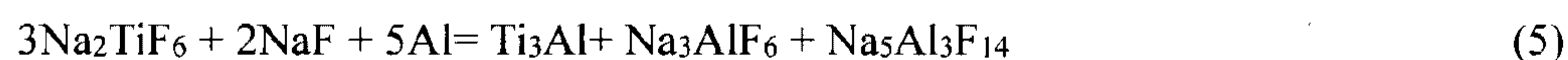
[0035] Sodium fluoride adopted in an embodiment of the present invention is a powder product purchased on the market, and the purity of the sodium fluoride is greater than or equal to 98%.

[0036] Sodium fluotitanate adopted in an embodiment of the present invention is a powder product purchased on the market, and the purity of the sodium fluotitanate is greater than or equal to 98%.

[0037] A reduction furnace adopted in an embodiment of the present invention is a vacuum reduction furnace with a crystallizer.

Embodiment 1

[0038] 1. Sodium fluoride and sodium fluotitanate are used as raw materials, and 100g of aluminum titanium alloy powder containing 4.21wt% of titanium is used as reducing agent; when Ti_3Al alloys ($x=1/3$ in the formula (1)) are produced, the reaction formulas of the production proportion of all the materials are shown as follows:



according to the chemical reaction formulas (5) and (6), it can be obtained that 100g of the reducing agent (aluminum titanium alloy powder) contains 4.21g of Ti, namely the content of Ti_3Al is 5g, Al powder participating into the reduction reaction is 95g, the content of Na_2TiF_6 required by the reaction is 439.11g, and the content of NaF required by the reaction is 59.11g; therefore, the actual

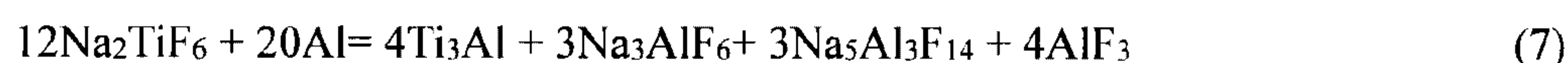
production materials of the embodiment comprise 439.11g of Na_2TiF_6 , 59.11g of NaF and 100g of the aluminum titanium alloy powder containing 4.21wt% of titanium;

[0039] 2. the production materials are uniformly mixed and then are pressed into lumps, the lumps are placed into a vacuum reduction furnace, the vacuum reduction furnace is vacuumized to 10Pa or below, argon is inflated into the vacuum reduction furnace to realize normal pressure, and the vacuum reduction furnace is heated to 1100 °C under the argon atmosphere condition, so that a first-stage aluminothermic reduction reaction is completed; and

[0040] 3. after the reduction reaction is ended, the vacuum reduction furnace is vacuumized to 10Pa or below, a product of the reduction reaction is distilled for 2h under the vacuum condition at the temperature of 1100 °C, a distillation product on a crystallizer at the low-temperature end in the vacuum reduction furnace is titanium-containing cryolite, and an alloy product is reserved in a reactor in a loose spongy form; an XRD phase analysis result of the alloy product is shown in Fig. 3, and an XRD phase analysis result of the titanium-containing cryolite is shown in Fig. 4.

Embodiment 2

[0041] 1. Sodium fluotitanate is used as raw materials, and 100g of titanium aluminum alloy powder containing 4.21wt% of titanium is used as reducing agent; when the produced product is Ti_3Al alloys ($x=1/3$ in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:



according to the chemical reaction formulas (7) and (8), it can be obtained that 100g of the reducing agent (titanium aluminum alloy powder) contains 4.21g of Ti, namely the content of Ti_3Al is 5g, Al powder participating into the reduction reaction is 95g, and the content of Na_2TiF_6 required by

the reaction is 439.11g; therefore, the actual production materials of the embodiment comprise 439.11g of Na_2TiF_6 and 100g of the titanium aluminum alloy powder containing 4.21wt% of titanium;

[0042] 2. the production materials are uniformly mixed and then are pressed into lumps, the lumps are placed into a vacuum reduction furnace, the vacuum reduction furnace is vacuumized to 10Pa or below, and the vacuum reduction furnace is heated to 1100 °C under the argon atmosphere condition, so that a first-stage aluminothermic reduction reaction is completed; and

[0043] 3. after the reduction reaction is ended, the vacuum reduction furnace is vacuumized to 10Pa or below, a product of the reduction reaction is distilled for 2h under the vacuum condition at the temperature of 1100 °C, the distillation product on the crystallizer at the low-temperature end in the vacuum reduction furnace is a mixture of the titanium-containing cryolite and aluminium fluoride, and an alloy product is reserved in a reactor in a loose spongy form; an XRD phase analysis result of the alloys is shown in embodiment 1; and an XRD phase analysis result of the distillation product is shown in Fig. 5.

Embodiment 3

[0044] A method in an embodiment 3 is the same as the method in the embodiment 1, but differs from it in that 100g of aluminum titanium alloy powder containing 1.86wt% of titanium is used as reducing agent for production of TiAl_3 alloys:

[0045] 1. according to the produced product TiAl_3 ($x=3$ in the formula (1)), the reaction formulas of the production proportion of all the materials are shown as follows:



according to the chemical reaction formulas (9) and (10), it can be obtained that 100g of the reducing agent (titanium aluminum alloy powder) contains 1.86g of Ti, namely the content of TiAl_3 is

5g, Al powder participating in the reduction reaction is 95g, the content of Na_2TiF_6 required by the reaction is 168.89g, and the mass of NaF required by the reaction is 22.74g; therefore, the actual production materials of the embodiment 3 comprise 168.89g of Na_2TiF_6 , 22.74g of NaF and 100g of titanium aluminum alloy powder containing 1.86wt% of titanium;

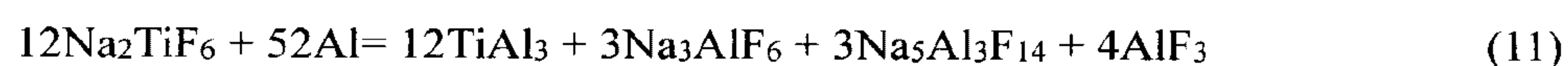
[0046] 2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and

[0047] 3. distillation is performed for 2h at the temperature of 1100 °C; after cooling, the residual metal in a reduction furnace is the TiAl_3 alloys, and an XRD phase analysis result of the TiAl_3 alloys is shown in Fig. 6.

Embodiment 4

[0048] A method in an embodiment 4 is the same as the method in the embodiment 2 and differs from it in that 100g of aluminum titanium alloy powder containing 1.86wt% of titanium is used as reducing agent for production of TiAl_3 alloys:

[0049] 1. according to the produced product TiAl_3 ($x=3$ in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:



and therefore, it can be obtained that from the reaction equations (11) and (12) the actual production materials of the embodiment comprise 168.89 g of Na_2TiF_6 and 100g of aluminum titanium alloy powder containing 1.86wt% of titanium;

[0050] 2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for the first-stage aluminothermic reduction; and

[0051] 3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in a reduction furnace is the TiAl₃ alloys, and an XRD phase analysis result of the TiAl₃ alloys is the same as that in embodiment 3.

Embodiment 5

[0052] A method in an embodiment 5 is the same as the method in the embodiment 1 and differs from it in that 100g of titanium aluminum alloy powder containing 3.2wt% of titanium is used as reducing agent for production of TiAl alloys.

[0053] 1. according to the produced product TiAl (x=1 in the formula (1)), the reaction formulas of the production proportion of all the materials are shown as follows:



according to the chemical reaction formulas (13) and (14), it can be obtained that 100g of the reducing agent (aluminum titanium alloy powder) contains 3.2g of Ti, namely the content of TiAl is 5g, Al powder participating in the reduction reaction is 95g, the content of Na₂TiF₆ required by the reaction is 313.65g, and the content of NaF required is 42.22g; therefore, the actual production materials of the embodiment 5 comprise 313.65g of Na₂TiF₆, 42.22g of NaF and 100g of aluminum titanium alloy powder containing 3.2wt% of titanium;

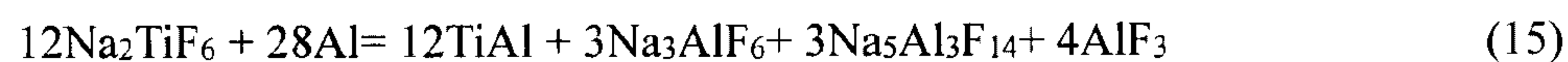
[0054] 2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and

[0055] 3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in the vacuum reduction furnace is the TiAl alloys, and an XRD phase analysis result of the TiAl alloys is shown in Fig. 7.

Embodiment 6

[0056] A method in an embodiment 6 is the same as the method in the embodiment 2 and differs from the embodiment 2 in that 100g of aluminum titanium alloy powder containing 3.2wt% of titanium is used as reducing agent for production of TiAl alloys.

[0057] 1. according to the produced product TiAl(x=1 in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:



and therefore, it can be obtained that from the reaction equations (15) and (16) the actual production materials of the embodiment comprise 313.65 g of Na_2TiF_6 and 100g of the aluminum titanium alloy powder containing 3.2 wt% of titanium;

[0058] 2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and

[0059] 3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in a reduction furnace is the TiAl alloys, and an XRD phase analysis result of the TiAl alloys is shown in embodiment 5.

Embodiment 7

[0060] A method in an embodiment 7 is the same as the method in the embodiment 1 and differs from the embodiment 1 in that 100g of titanium aluminum alloy powder containing 3wt% of titanium is used as reducing agent for production of pure titanium:

[0061] 1. according to the produced product Ti (x=0 in the formula (1)), the reaction formulas of the production proportion of all the materials are shown as follows:



according to the chemical reaction formula (17), it can be obtained that 100g of the reducing

agent(aluminum titanium alloy powder contains 3g of Ti), Al powder participating in the reduction reaction is 97g, the content of Na_2TiF_6 required by the reaction is 560.44g, and the content of NaF added is 75.44g; therefore, the actual production materials of the embodiment 7 comprise 560.44g of Na_2TiF_6 , 75.44g of NaF and 100g of aluminum titanium alloy powder containing 3wt% of titanium;

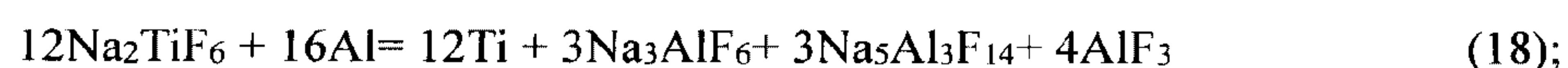
[0062] 2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and

[0063] 3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in the vacuum reduction furnace is the Ti, and an XRD phase analysis result of the Ti is shown in Fig. 8.

Embodiment 8

[0064] A method in an embodiment 8 is the same as the method in the embodiment 2 and differs from the embodiment 2 in that 100g of aluminum titanium alloy powder containing 3wt% of titanium is used as reducing agent for production of pure titanium:

[0065] 1. according to the produced product Ti ($x=0$ in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:



It can be obtained through the chemical reaction formula (18), the actual production materials of the embodiment comprise 560.44g of Na_2TiF_6 and 100g of the aluminum titanium alloy powder containing 3wt% of titanium;

[0066] 2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and

[0067] 3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in the vacuum reduction furnace is the metal Ti, and an XRD phase analysis result of the Ti is shown in embodiment 7.

Embodiment 9

[0068] A method in an embodiment 9 is the same as the method in the embodiment 1 and differs from the embodiment 1 in that 100g of aluminum titanium alloy powder containing 2.13wt% of titanium is used as reducing agent for production of titanium aluminum alloys containing 42.55% of titanium.

[0069] 1. The titanium aluminum alloys containing 42.55wt% of titanium are the same as the product $\text{TiAl}_{2.4}$ alloys ($x=2.4$ in the formula (1)), and therefore, the reaction formulas of the production proportion of all the materials in the embodiment 9 are shown as follows:



according to the chemical reaction formulas (19) and (20), it can be obtained that 100g of the reducing agent (aluminum titanium alloy powder) contains 2.13g of Ti, namely the content of $\text{TiAl}_{2.4}$ is 5g, Al powder participating in the reduction reaction is 95g, the content of Na_2TiF_6 required by the reaction is 196.03g, and the mass of NaF added is 26.39g; therefore, the actual production materials of the embodiment 9 comprise 196.03g of Na_2TiF_6 , 26.39g of NaF and 100g of aluminum titanium alloy powder containing 2.13 wt% of titanium;

[0070] 2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and

[0071] 3. distillation is performed for 2h at the temperature of 1100 °C; after cooling, the residual metal in a reduction furnace is the $\text{TiAl}_{2.4}$ alloys, and an chemical component analysis result of the $\text{TiAl}_{2.4}$ alloys is shown in Table 1.

Table 1

Chemical components	Al	Ti	Ca	Si	Fe
Percentage by mass (%)	57.4963	42.0368	0.0537	0.0152	0.0044

Embodiment 10

[0072] Titanium-free cryolite and aluminum titanium alloys are produced through vacuum reduction by using the titanium-containing cryolite distilled out through the first-stage aluminothermic reduction in the embodiment 7 as a raw material and aluminum powder as reducing agent.

[0073] 1. after the first-stage aluminothermic reduction process, 427.78g of the titanium-containing cryolite is grinded until the particle size is lower than 1.0mm, wherein the content of titanium is 12.84g; 100g of aluminum powder is used as reducing agent; the grinded titanium-containing cryolite and the aluminum powder are uniformly mixed and then are pressed into lumps; the lumps are placed into the vacuum reduction furnace, the vacuum reduction furnace is vacuumized to 10Pa or below, argon is inflated into the vacuum reduction furnace to normal pressure, the lumps are heated to 1200 °C under the argon atmosphere condition, and the temperature is preserved for 2h for the second-stage aluminothermic reduction; and

[0074] 2. after the materials in the vacuum reduction furnace are cooled to normal temperature, a product is taken out and separated out, so as to obtain the white titanium-free cryolite and the aluminum titanium alloys with the forming amounts of 414.94g and 112.84g respectively in theory; the aluminum titanium alloys can be used as reducing agent for the next first-stage aluminothermic reduction process to produce metal titanium, and the cycle continues; an XRD phase analysis result of the white titanium-free cryolite is shown in Fig. 9, and an XRF component analysis result is listed in Table 2;

Table 2

Chemical components	F	Na	Al	Mg	Ca	Si	Fe	K	Ti
Percentage by mass(%)	59.8487	22.7601	16.6017	0.7133	0.0254	0.0177	0.0058	0.0043	<0.001

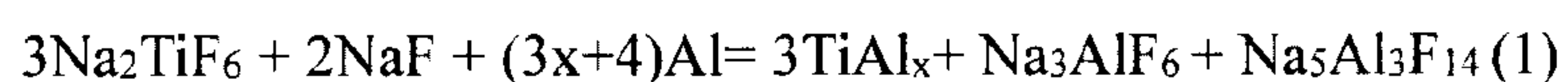
[0075] It can be seen from Table 2 that the cryolite produced in the embodiment 10 completely conforms with the Chinese national standard GB/T 4291-1999 ‘cryolite’ and can be directly applied in the aluminum electrolysis industry. Low-titanium aluminum titanium alloys are formed at the upper layer of the aluminum titanium alloy product, and high-titanium aluminum titanium alloys are formed at the lower layer of the aluminum titanium alloy product. An SEM image and an energy spectrum analysis result of the aluminum titanium alloy product are respectively shown in Fig. 10 and Fig. 11.

[0076] The titanium-containing cryolite obtained in the first-stage aluminothermic reduction of the embodiments 1-9 can be further treated by the method shown in the embodiment 10, the aluminum powder is adopted for performing the second-stage vacuum aluminothermic reduction, the obtained white titanium-free cryolite can be applied in the aluminum electrolysis industry, and the aluminum titanium alloys can fully returns to the next first-stage aluminothermic reduction process as the reducing agent.

WHAT IS CLAIMED IS:

1. A method for producing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts, comprising the following steps:

- (1) using sodium fluoride and sodium fluotitanate as raw materials, and using aluminum titanium alloy powder obtained through a second-stage aluminothermic reduction as a reducing agent, wherein the reaction formulas of the production proportion of all the materials are shown as follows:



wherein $x=0-10$;

- (2) uniformly mixing the raw materials with the reducing agent to obtain a mixture, pressing the mixture into lumps, placing the lumps into a vacuum reduction furnace, heating the placed lumps to 900-1300 °C under a vacuum condition or in an argon atmosphere, and performing a first-stage aluminothermic reduction and vacuum distillation; coagulating a titanium-containing cryolite distilled out on a crystallizer at a low-temperature end of the vacuum reduction furnace, wherein the titanium-containing cryolite on the crystallizer comprises Na_3AlF_6 , $\text{Na}_5\text{Al}_3\text{F}_{14}$, AlF_3 and titanium-containing sub-fluoride, and the residual product in the vacuum reduction furnace is TiAl_x ;
- (3) taking out the titanium-containing cryolite, grinding the titanium-containing cryolite until a particle size is lower than 1.0mm, using an aluminum powder as the reducing agent, uniformly mixing the grinded titanium-containing cryolite with the aluminum powder to obtain a mixture, and pressing the mixture into lumps, wherein the feeding amount of the aluminum powder follows the rule that a melting point of the Al-Ti alloys produced by the second-stage aluminothermic reduction is less than or equal to the temperature of the second-stage aluminothermic reduction; placing the lumps

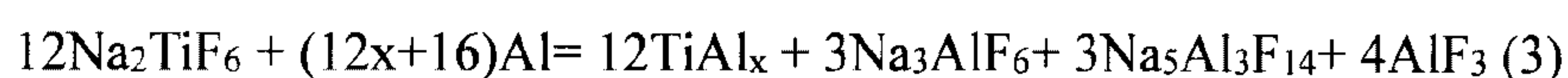
into the vacuum reduction furnace, heating the placed lumps to 900-1300 °C in the argon atmosphere and preserving the temperature for 0.5-2h for the second-stage aluminothermic reduction,

wherein according to the products obtained after the reduction reaction is ended and the temperature in a furnace body is reduced to normal temperature, white titanium-free cryolite is formed at upper parts of the products and the aluminum titanium alloys are formed at bottoms of the products, wherein alloys with low content of titanium are formed at the upper parts of the aluminum titanium alloys, which are called the low-titanium aluminum titanium alloys; the aluminum titanium alloys with comparatively high content of titanium are formed at the lower parts of the aluminum titanium alloys, which are called the high-titanium aluminum titanium alloys; and

(4) separating the low-titanium aluminum titanium alloys and the high-titanium aluminum titanium alloys with a mechanical division method or a remelting and dumping method of an induction furnace, making the low-titanium aluminum titanium alloys separated out or remelted into powder as the reducing agent of the first-stage aluminothermic reduction, and returning the powder back to the first-stage aluminothermic reduction as the reducing agent for use.

2. A method for producing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts, comprising the following steps:

(1) using sodium fluotitanate as raw materials, and using aluminum titanium alloy powder obtained through a second-stage aluminothermic reduction as a reducing agent, wherein the reaction formulas of the production proportion of all the materials are shown as follows:



wherein $x=0-10$;

- (2) uniformly mixing the raw materials with the reducing agent to obtain a mixture, pressing the mixture into lumps, placing the lumps into a vacuum reduction furnace, heating the placed lumps to 900-1300 °C under a vacuum condition or in an argon atmosphere, and performing a first-stage aluminothermic reduction and vacuum distillation; coagulating a titanium-containing cryolite distilled out on a crystallizer at a low-temperature end of the vacuum reduction furnace, wherein the titanium-containing cryolite on the crystallizer comprises Na_3AlF_6 , $\text{Na}_5\text{Al}_3\text{F}_{14}$, AlF_3 and titanium-containing sub-fluoride, the residual product in the vacuum reduction furnace is TiAl_x ;
- (3) taking out the titanium-containing cryolite, grinding the titanium-containing cryolite until a particle size is lower than 1.0mm, using an aluminum powder as the reducing agent, uniformly mixing the grinded titanium-containing cryolite with the aluminum powder to obtain a mixture, and pressing the mixture into lumps, wherein the feeding amount of the aluminum powder follows the rule that a melting point of the Al-Ti alloys produced by the second-stage aluminothermic reduction is less than or equal to the temperature of the second-stage aluminothermic reduction; placing the lumps in the vacuum reduction furnace, heating the placed lumps to 900-1300 °C in the argon atmosphere and preserving the temperature for 0.5-2h for the second-stage aluminothermic reduction, wherein according to the products obtained after the reduction reaction is ended and the temperature in a furnace body is reduced to normal temperature, white titanium-free cryolite is formed at upper parts of the products and the aluminum titanium alloys are formed at bottoms of the products, wherein alloys with low content of titanium are formed at the upper parts of the aluminum titanium alloys, which are called the low-titanium aluminum titanium alloys; the aluminum titanium alloys with comparatively high content of titanium are formed

at the lower parts of the aluminum titanium alloys, which are called the high-titanium aluminum titanium alloys; and

- (4) separating the low-titanium aluminum titanium alloys and the high-titanium aluminum titanium alloys with a mechanical division method or a remelting and dumping method of an induction furnace, making the low-titanium aluminum titanium alloys separated out or remelted into powder as the reducing agent of the first-stage aluminothermic reduction, and returning the powder back to the first-stage aluminothermic reduction as the reducing agent for use.
3. The method according to claim 1 or 2, wherein, when the first-stage aluminothermic reduction is performed for the first time, metal aluminum powder is used as a reducing agent, and the production proportion of the using dosage of the reducing agent is shown in the reaction formula in step (1).
4. The method according to claim 1 or 2, wherein, the vacuum distillation is conducted such that the vacuum reduction furnace is vacuumized to 10Pa or below, and distillation is performed for 1h or above under the condition that the temperature is 900-1300 °C.

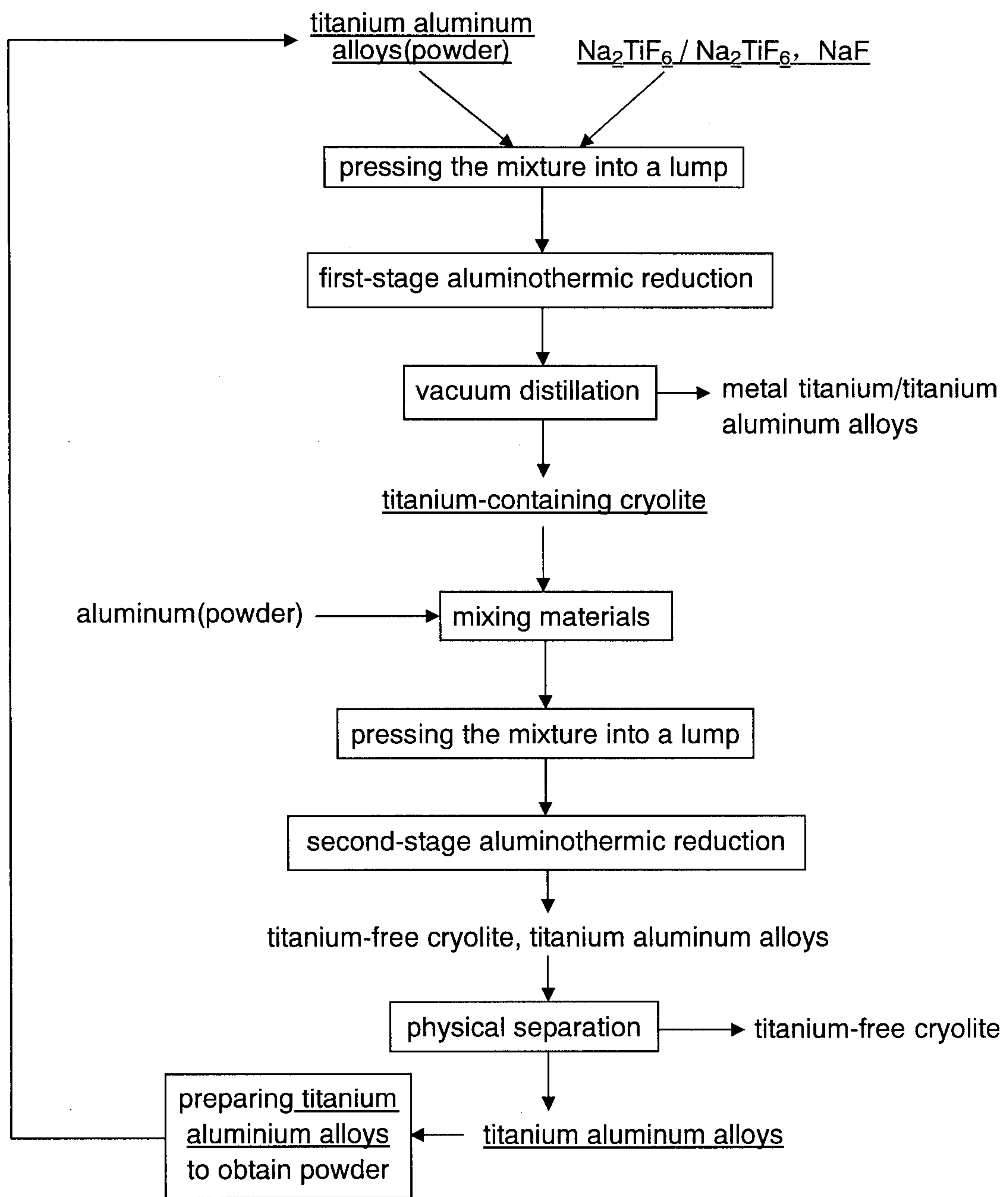


Fig. 1

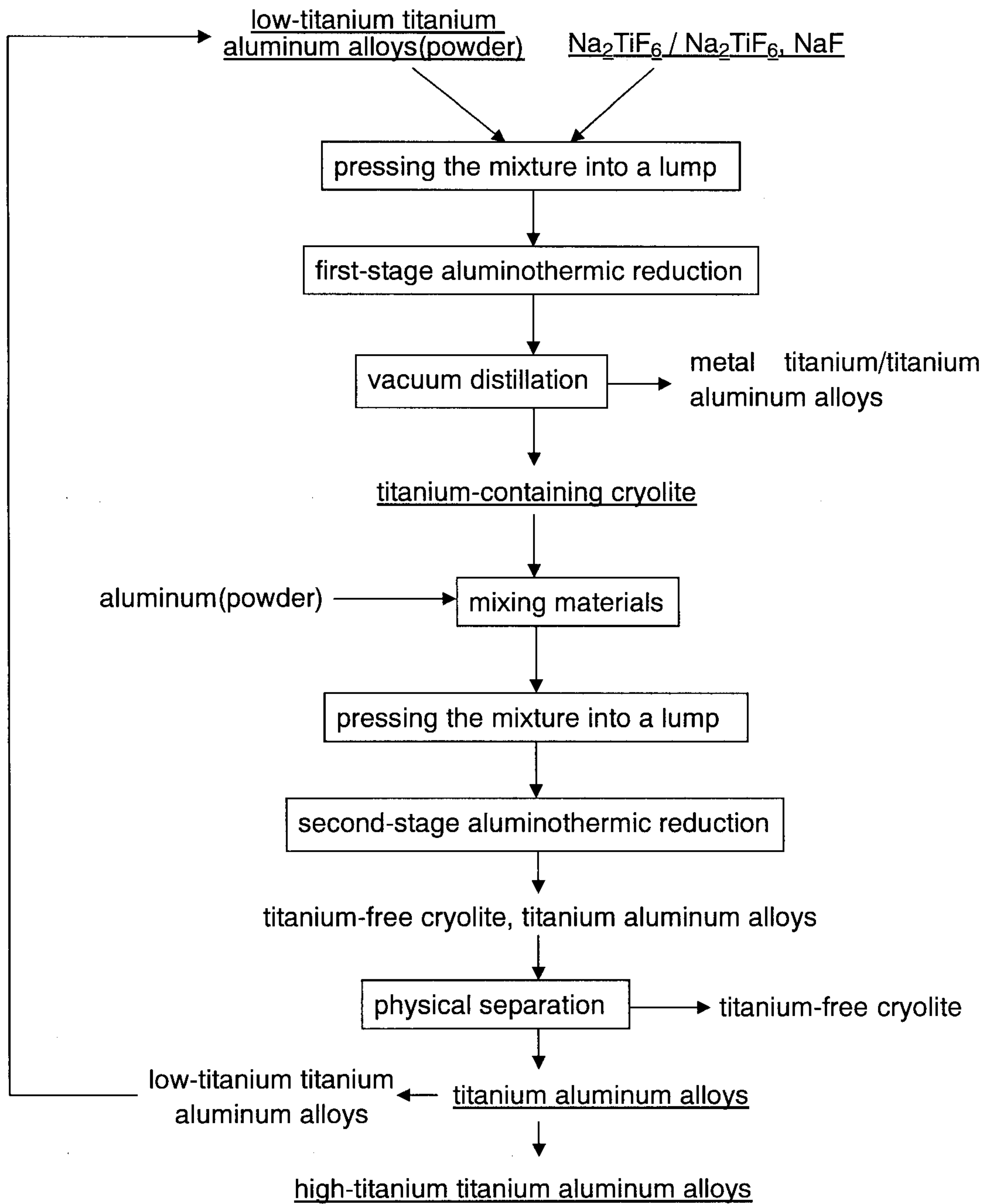
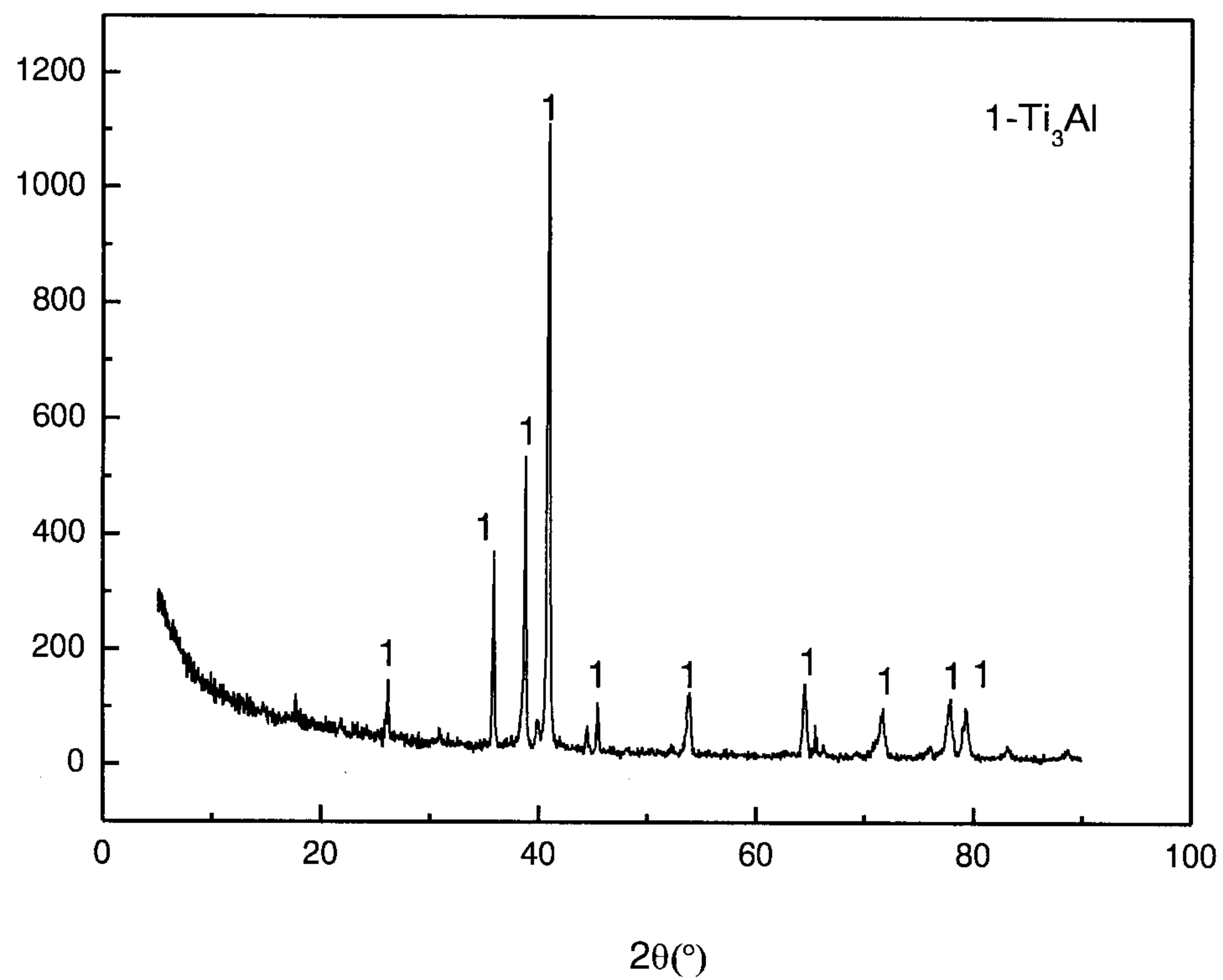
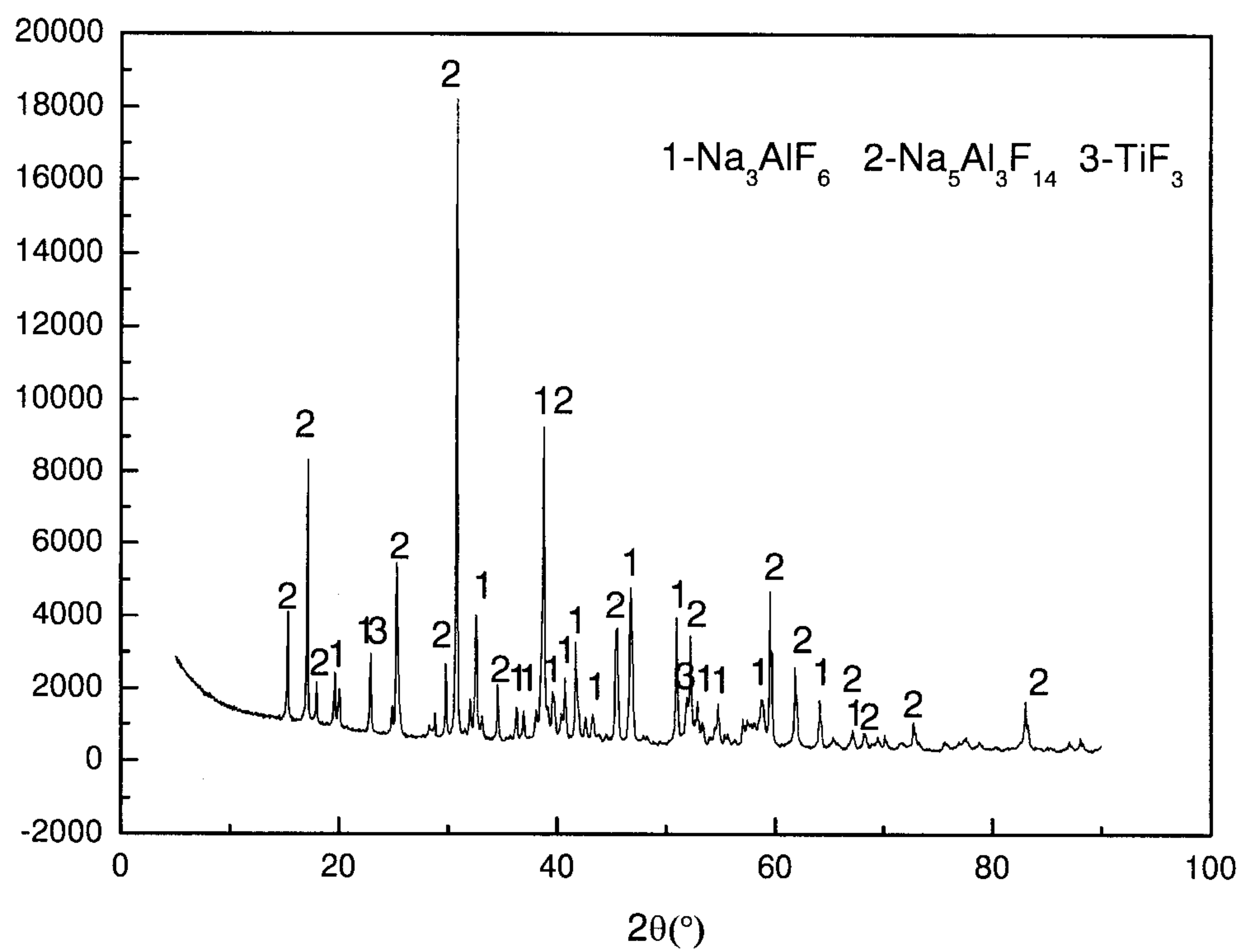
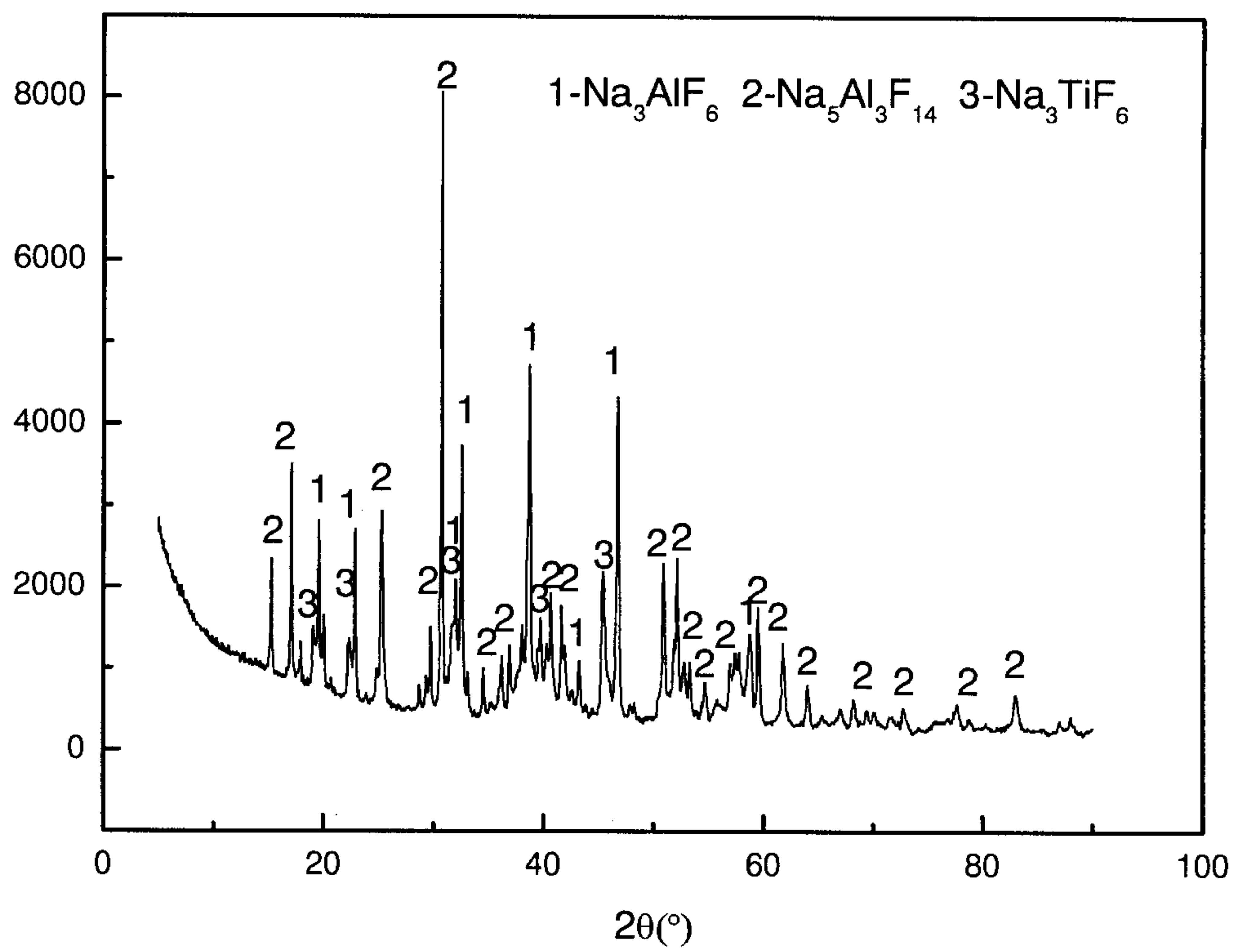
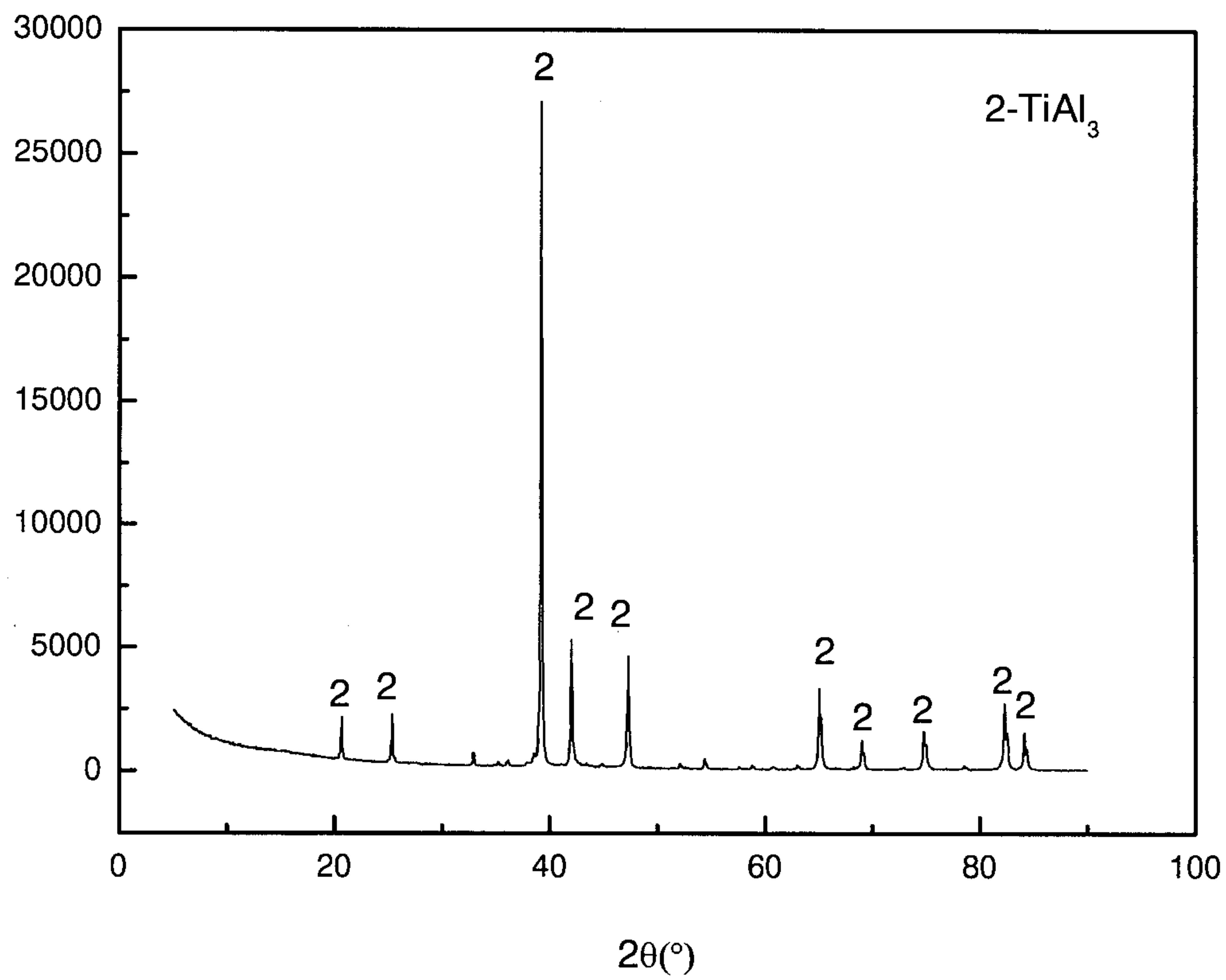
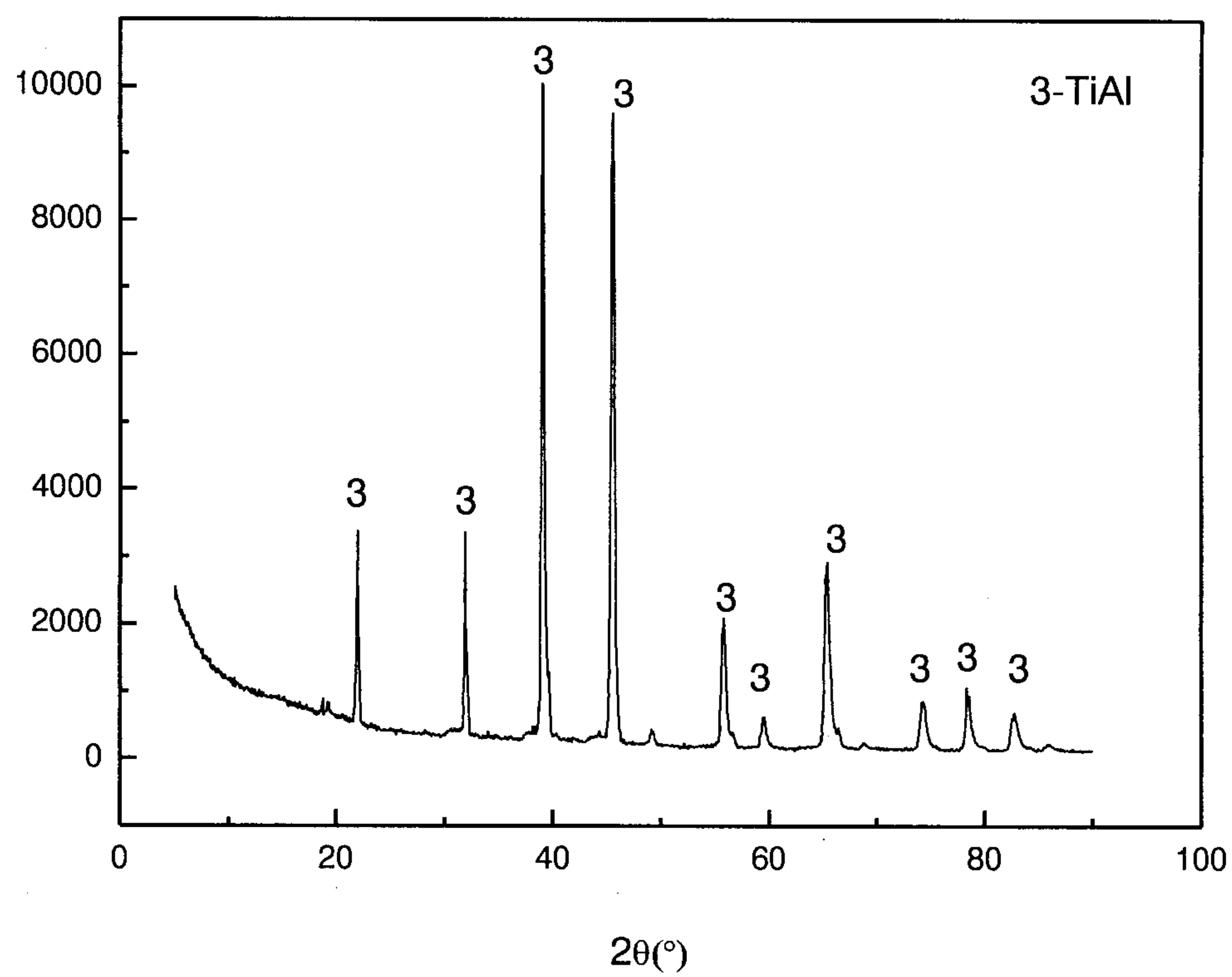
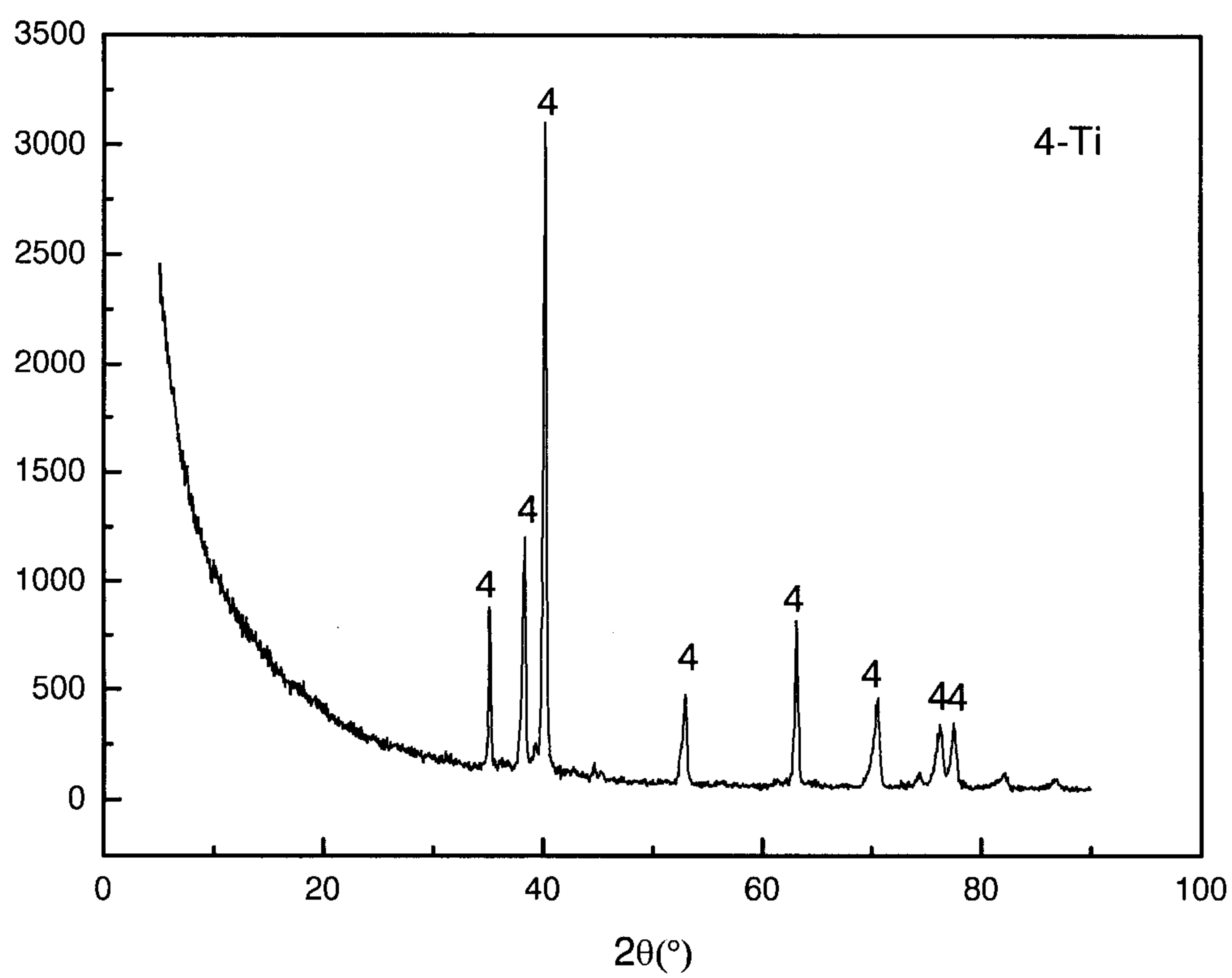
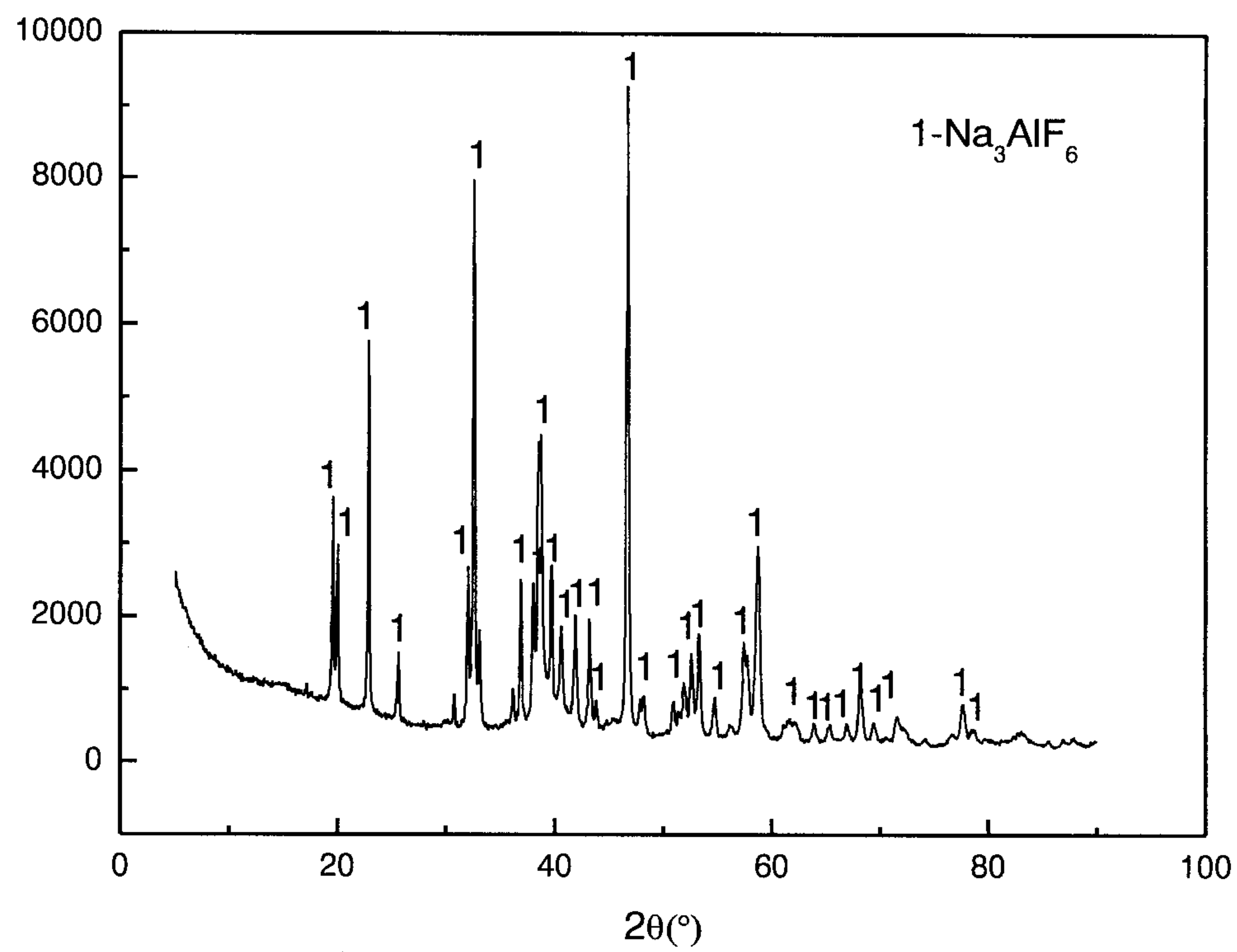
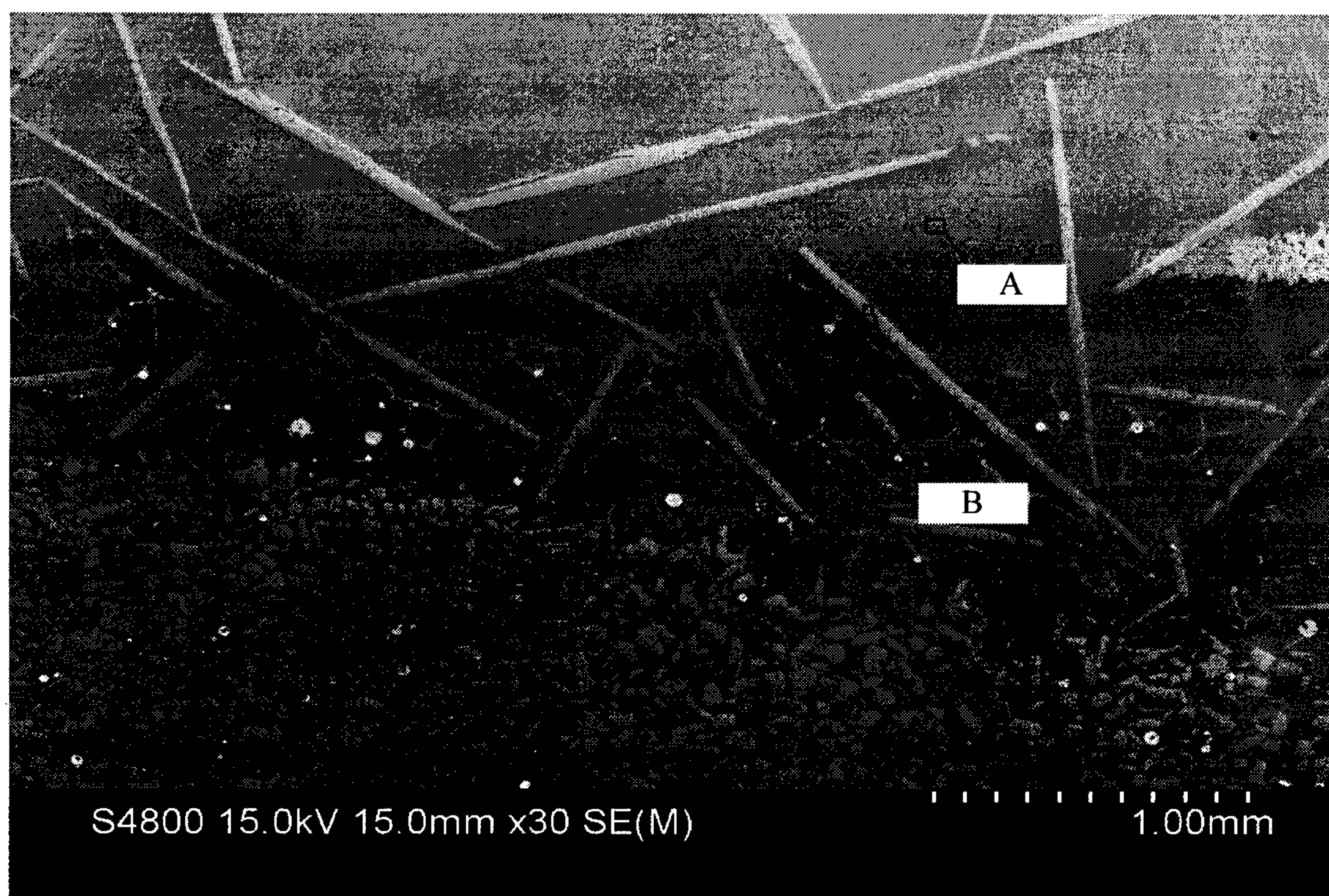


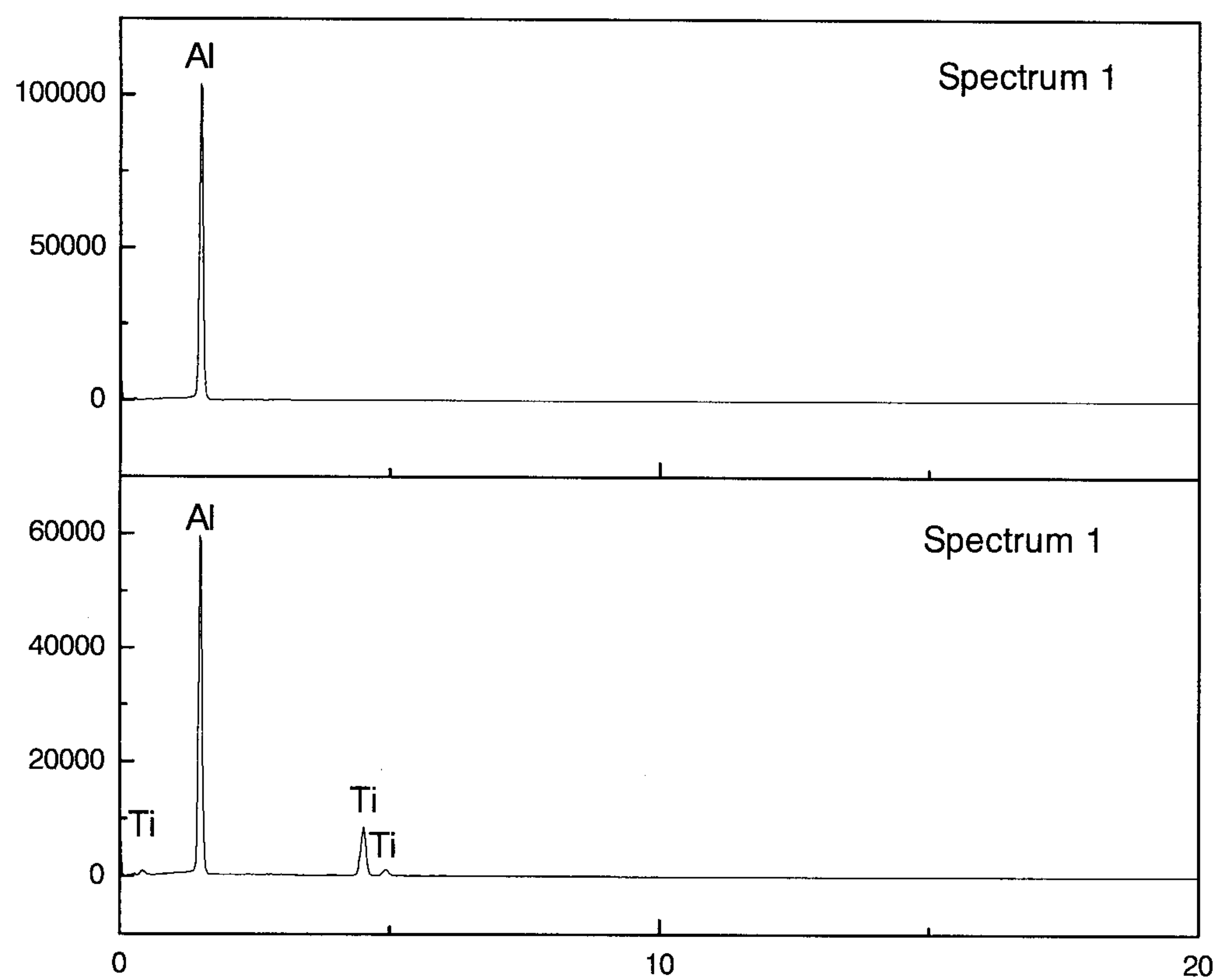
Fig. 2

**Fig. 3****Fig. 4**

**Fig. 5****Fig. 6**

**Fig. 7****Fig. 8**

**Fig. 9****Fig. 10**

**Fig. 11**

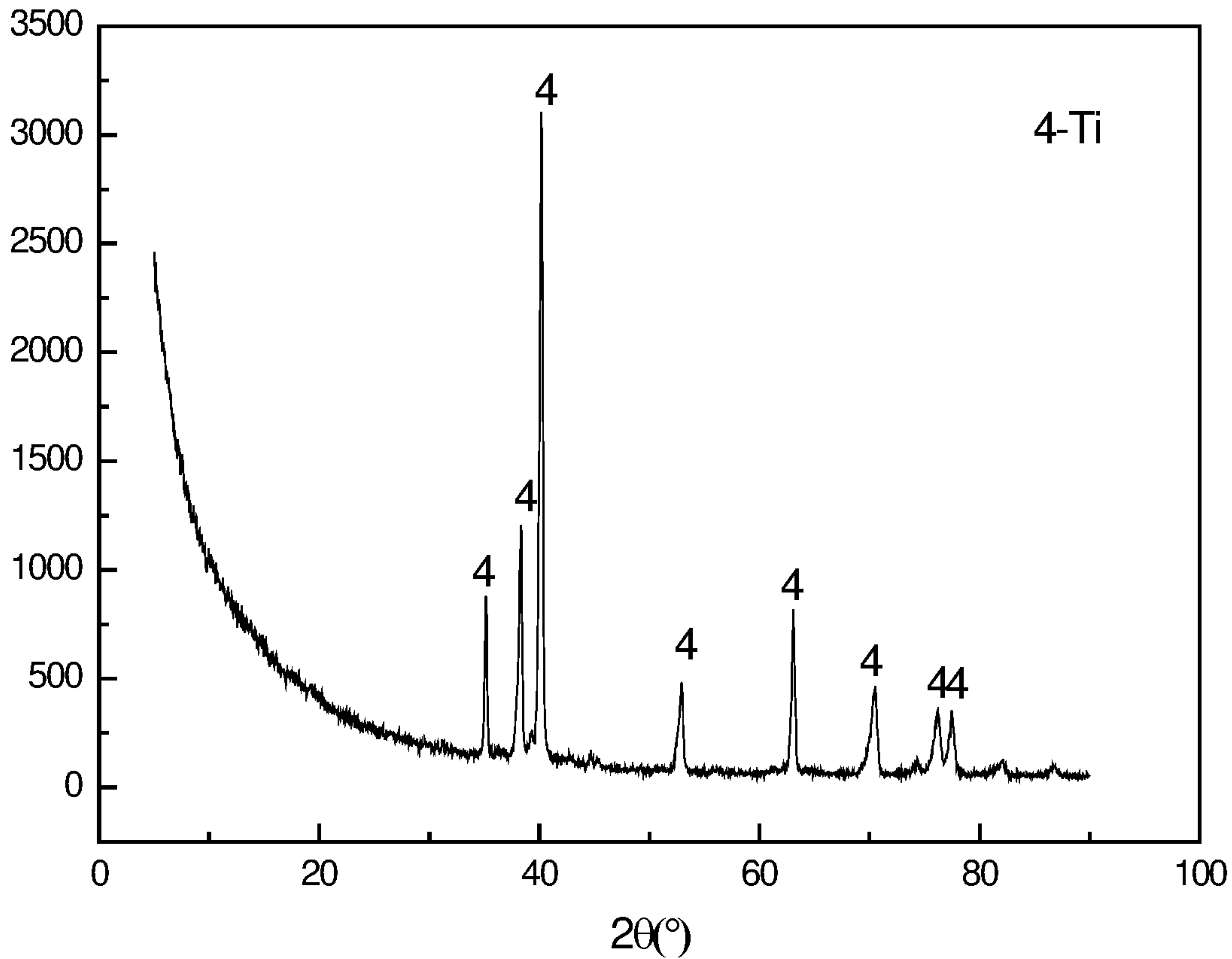


图 8