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(54) **SURFACE PROCESSING METHOD FOR TANTALUM SPINNING HEAD**

(57) The present invention relates to a surface treatment method of tantalum spinneret, wherein the method comprises the following steps: (a) forming a layer of Ta<sub>2</sub>O<sub>5</sub> film on the tantalum spinneret; (b) optionally polishing: polishing a fiber outlet face of the tantalum spin-

neret treated in step (a) to remove the Ta<sub>2</sub>O<sub>5</sub> film on a surface of the fiber outlet face; and (c) coating: subjecting the tantalum spinneret treated in step (b) to a coating treatment by a molten salt electrochemical method to form a film layer containing lithium-containing compound.

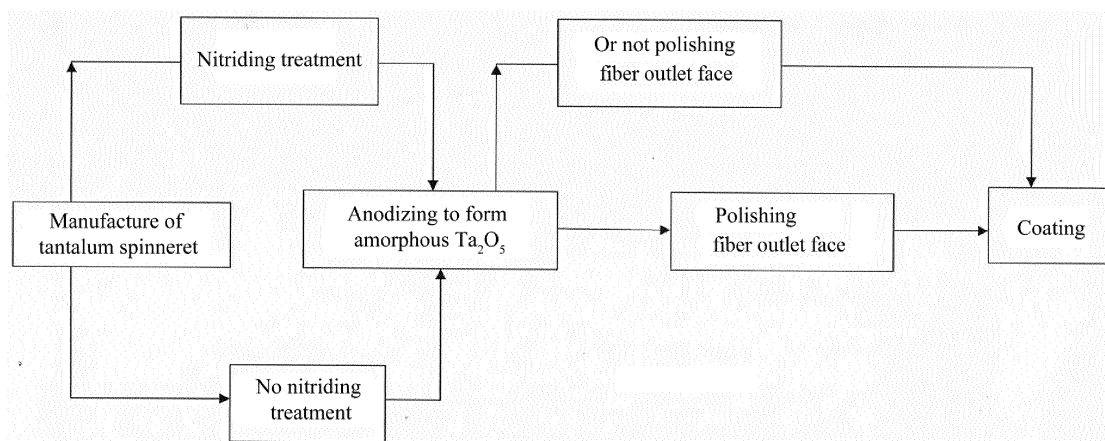


FIG. 2

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**Description****Field of the Invention**

5 **[0001]** The present invention relates to a surface treatment method of tantalum spinneret. More specifically, the present invention relates to a surface treatment method of tantalum spinneret for wet spinning or dry-wet spinning, and more particularly to a surface treatment method of tantalum spinneret.

**Background of the Invention**

10 **[0002]** Chemical fiber production has developed vigorously at the end of the 20th century. With the vigorous development of China's economy, China has become the world's largest producer of chemical fiber. The chemical fiber industry has become an important part of the national economy, and the spinneret (plate) is the most precise and critical component in the production of chemical fiber. The quality of the spinneret (plate) directly affects the quality of the chemical fiber  
15 production and labor productivity, cost and so on. The spinneret has been continuously improved to meet the development needs of chemical fiber production.

**[0003]** The process for producing chemical fiber is different, and the requirements for the spinneret (plate) are also different. In the industry, chemical fiber production usually employs three processes, namely, melt spinning, dry spinning (also called dry-wet spinning), and wet spinning. Among them, in melt spinning, the spinneret used needs to withstand  
20 a pressure of up to several hundred atmospheric pressures. Therefore, the material for manufacturing the spinneret is required to have good physical and mechanical properties, and the thickness of the spinneret reaches 10 mm to 30 mm. In wet spinning, the spinneret used is subjected to much less pressure and its thickness is generally between 0.2 and 0.75 mm. In dry spinning, the pressure that the spinneret needs to withstand and the thickness required for the spinneret are between those for the spinneret used for melt spinning and the spinneret used for the wet spinning. Since wet  
25 spinning is carried out in a strong acid and alkali environment, the spinneret used needs to have strong corrosion resistance. Therefore, in the early stage of chemical fiber production, in most wet spinning processes, for example, in the production process of viscose fiber, acrylic yarn, etc., the spinneret is made of a noble metal such as an alloy of gold, platinum, rhodium or palladium. In the past three decades, the applicant of the present invention has developed a spinneret made of tantalum instead of gold-platinum, and such a spinneret is gradually being widely used, in which a  
30 coated tantalum spinneret made by electrochemical reaction (see Chinese patents ZL85101505, ZL86102269 and ZL02106915.8 for details) has good effect and wide application in place of gold-platinum spinneret in wet spinning because of its good spinnability.

**[0004]** For the quality of the spinneret, the most critical criterion is the spinnability of the spinneret. The spinnability of the spinneret is judged based on various aspects such as the unplanned spinneret change rate of the spinneret, the  
35 spinning cycle of a single spinneret, the quality of the chemical fiber spun using the spinneret, and the broken filament ratio of the filament (broken filament ratio = the number of bobbins in which the filament grade is decreased within one working day / the total amount of bobbins producing filament), the defects, strength and uniformity of the spun yarn. Spinneret with good spinnability will result in low unplanned spinneret change rate, long spinning cycle, good quality of spun chemical fiber, low broken filament ratio, few defects, high strength and good uniformity. In the art, the broken  
40 filament ratio is detected for the filament and the defect ratio is detected for the staple fiber. These directly affect the quality of the chemical fiber produced and the labor productivity and cost in the production of chemical fiber, as well as the labor intensity of the spinning workers.

**[0005]** For a spinneret in wet spinning, its spinnability depends to a large extent on the material used and the finish of the work surface. Therefore, it is desirable to improve the surface finish of the inner walls and surfaces of the micropores  
45 of the spinneret by surface treatment. In addition to affecting the surface hardness, surface treatment is important to affect the surface characteristics of the spinneret. The surface-treated tantalum spinneret can reduce the adsorption of charged waste around the micropores of the spinneret, or affect the deposition speed, and thus affect the plugging of the spinneret, thereby improving the spinnability index (such as broken filament, spinneret change rate, etc.). In addition, the surface treatment also has an effect on the surface roughness, and if the roughness is lowered, the spinnability is  
50 better. For the initially processed spinneret, it is desirable to further reduce the roughness of the micropore wall and the surface of the spinneret after micropore punching. At present, the processed tantalum spinneret has been tried to reduce the roughness of the micropore wall by the surface treatment process, thereby improving the spinnability of the spinneret, but there has been no effective method.

**[0006]** At the same time, the surface treatment after the spinneret processing needs to balance the surface properties, surface finish and surface hardness to obtain a suitable comprehensive and optimal effect, but the most critical aspects  
55 related to the spinnability of the spinneret are the surface properties and finish to meet the different requirements of different chemical fiber varieties. For example, a nitriding only tantalum spinneret can be used for wet spinning of acrylic fibers, but for wet spinning of viscose fibers, the spinnability is poor.

**[0007]** Patents ZL 85101505, ZL 86102269 (hereinafter referred to as the first generation patent) and patent ZL 02106915.8 granted in 2006 (hereinafter referred to as the second generation patent) are widely used in the chemical fiber wet spinning in which spinnerets are prepared by replacing gold with tantalum. The produced tantalum spinneret coated with lithium-containing compound is similar to the noble metal gold-platinum (rhodium) alloy spinneret, and even superior to the noble metal gold-platinum (rhodium) alloy spinneret. When the spinning process is unstable, for example, when the spinning dope of the viscose fiber is not well filtered or the coarse particles of the raw solution are increased, the spinnability of the gold-platinum spinneret and the coated tantalum spinneret decreased, but the coated tantalum spinneret decreased more. The more prominent problem appears when spinning special fibers, such as spinning matt fibers, it is necessary to add a certain amount of titanium dioxide powder particles to the raw solution, when spinning flame retardant fibers, it is necessary to add a certain amount of particulate flame retardant to the raw solution. At this time, the spinnability of the coated tantalum spinneret is significantly inferior to that of the gold-platinum spinneret. For example, in the case of spunbonded staple fiber flame retardant fiber, the spinneret change period of the above-mentioned coated tantalum spinneret is only 8 hours, otherwise the quality of the filament will be affected, but the gold-platinum spinneret can be spun for 16 to 24 hours. This is because the roughness of the micropore wall of the coated tantalum spinneret is larger than that of the gold-platinum spinneret. If the powdery additive is added during the spinning of the above special fiber, or if the particles appear in the raw solution since the spinning process is unstable, it is desirable that the roughness of the micropore wall of the spinneret is lower, otherwise the pores are more likely to be blocked, thereby affecting the spinnability of the spinneret.

**[0008]** Accordingly, there is still a need to provide a spinneret for wet spinning that further reduces the roughness of the micropore wall and surface of the spinneret while maintaining a certain strength of the spinneret.

#### Summary of The Invention

**[0009]** It is an object of the present invention to provide a surface treatment method of tantalum spinneret, and more particularly to a surface treatment method of tantalum spinneret for wet spinning to provide a spinneret having a film having significantly reduced micropore wall roughness and better surface characteristics to ensure that the surface finish of the micropores is improved for the tantalum spinneret while satisfying the required surface characteristics and surface hardness for spinning fiber, so that the obtained spinneret has excellent spinnability, improves fiber quality and economic efficiency, and reduces cost, thereby widely replaces the noble metal spinneret.

**[0010]** The present invention relates to a surface treatment method of tantalum spinneret, in particular to a surface treatment method of tantalum spinneret for wet spinning, wherein the method comprises the following steps:

- (a) forming a layer of  $Ta_2O_5$  film on the tantalum spinneret;
- (b) optionally polishing: polishing a fiber outlet face of the tantalum spinneret treated in step (a) to remove the  $Ta_2O_5$  film on a surface of the fiber outlet face; and
- (c) coating: subjecting the tantalum spinneret treated in step (b) to a coating treatment by a molten salt electrochemical method to form a film layer containing lithium-containing compound.

**[0011]** The method of the present invention further comprises a polishing step (d): subjecting the fiber outlet face of the tantalum spinneret treated in step (c) to a polishing treatment to remove the film layer containing lithium-containing compound on the surface of the fiber outlet face.

**[0012]** In step (a), the  $Ta_2O_5$  film formed on the tantalum spinneret is an amorphous  $Ta_2O_5$  film.

**[0013]** In an embodiment of the present invention, a layer of amorphous  $Ta_2O_5$  film is formed on the tantalum spinneret by anodization in step (a). Specifically, in step (a), the tantalum spinneret is placed in an oxygen-containing electrolyte solution at room temperature to  $380^\circ\text{C}$ , preferably room temperature to  $300^\circ\text{C}$ , and an anode voltage of 3 to 800V is applied constantly for 0.01 to 2 hours, with a voltage-increasing current density of 1 to 200  $\text{mA}/\text{cm}^2$  to form a layer of amorphous  $Ta_2O_5$  film.

**[0014]** In step (a), if the solution temperature is high, the applied voltage should be low, and vice versa. For example, for a 0.01%  $H_3PO_4$  solution at room temperature, a voltage of up to 600V can be applied. Regardless of the solution, the applied voltage should be below the flashover voltage of the solution.

**[0015]** In step (a), the oxygen-containing electrolyte solution may be an aqueous solution, a non-aqueous solution, or a mixture of an aqueous electrolyte and an organic compound.

**[0016]** The aqueous oxygen-containing electrolyte may be, for example, an aqueous solution of an acid, a base, or a salt. The solution temperature is from room temperature (about  $25^\circ\text{C}$ ) to  $95^\circ\text{C}$ , the anode voltage is 5 to 600V, and the constant voltage time is within 60 to 90 minutes. When the temperature is too high, the water volatilizes too quickly. When the solution temperature is high, the anode voltage should be low. A high solution temperature, a high anode voltage, and a long constant voltage time tend to result in crystallization of the amorphous anodic oxide film, which should be prevented because the roughness is increased after crystallization or partial crystallization of the amorphous

Ta<sub>2</sub>O<sub>5</sub> film.

**[0017]** The non-aqueous oxygen-containing electrolyte may be anhydrous concentrated sulfuric acid or a molten salt or a mixture of a molten salt and a base, such as potassium nitrate, sodium nitrate, lithium nitrate, or a mixture thereof with a base such as lithium, sodium or potassium-containing base. The melting temperature should be controlled to the melting point of the molten salt to below 380°C, because tantalum will be significantly oxidized above 400°C. A voltage of 3 to 66V is applied.

**[0018]** Another kind of oxygen-containing electrolyte solution may be a mixture of an aqueous electrolyte and an organic compound such as ethanol, ethylene glycol, n-butanol or the like. The temperature of the aqueous solution should be below 95°C, otherwise the water volatilizes quickly, and it is difficult to control.

**[0019]** When the coating temperature in step (c) is from 250°C to 430°C, preferably from 300°C to 400°C, more preferably from 300°C to 350°C, step (a) of forming a layer of Ta<sub>2</sub>O<sub>5</sub> film before coating on the tantalum spinneret may be omitted.

**[0020]** In an embodiment of the present invention, in step (c), the spinneret is placed in an oxygen-containing inorganic lithium salt (such as LiNO<sub>3</sub>) or a mixed melt of oxygen-containing inorganic lithium salt and lithium hydroxide, or a mixed melt liquid of a salt and lithium hydroxide or a mixed melt liquid of a lithium salt and an oxygen-containing salt at a temperature of 250°C to 650°C, preferably 250°C to 430°C, and an anode voltage of 1 to 66V is applied constantly for 0.01 to 200 hours, with a voltage-increasing current density of 1 to 1000 mA/cm<sup>2</sup> to form a film layer of lithium-containing compound.

**[0021]** Preferably, in step (c), the mixed melt or the mixed melt liquid has a temperature of 300°C to 520°C, the applied anode voltage is 5 to 25V, and the voltage-increasing current density is 5 to 20 mA/cm<sup>2</sup>. In a preferred embodiment, an ultrasonic generator can be placed in the mixed melt or the mixed melt liquid in step (c).

**[0022]** Preferably, the molten salt electrochemical method in step (c) is a molten lithium salt electrochemical method.

**[0023]** In an embodiment of the present invention, the surface treatment method of the present invention comprises subjecting the tantalum spinneret to a nitriding treatment prior to step (a), as in accordance with the method of step (b) of the specification of ZL02106915.8. That is, an ion nitriding furnace is used, with a tantalum spinneret as a cathode, a furnace temperature of 500 to 1000°C, a furnace pressure of 20 to 2000 Pa, a filled gas such as nitrogen and hydrogen with nitrogen : hydrogen = 2:1 to 1:10, and a nitriding time of 0.5 to 6 hours, thus forming a nitriding layer on the surface of the tantalum spinneret, and controlling the hardness of the tantalum spinneret after nitriding to be between HV180 and 480. However, the nitriding treatment may not be performed prior to step (a). Whether or not nitriding treatment is carried out is determined according to different fiber spinning requirements. For example, a fiber type having a low spinning speed and a low-pressure requirement may not be nitrided in advance, which can save costs. However, if the electrochemical coating treatment is carried out in step (c), a relatively low temperature such as 400°C or lower is employed, a nitriding treatment may be employed in order to obtain a high hardness,

**[0024]** The tantalum spinneret suitable for use in the present invention comprises a pure tantalum spinneret and a tantalum alloy spinneret, wherein the tantalum alloy spinneret is preferably a tantalum-niobium alloy spinneret.

Table 1. Comparison of surface hardness and roughness of the first and second generation coated tantalum spinnerets and tantalum spinneret of the present invention

| Type of spinneret                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Surface hardness (transition layer) | Roughness (or finish) |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|-----------------------|
| The first generation coated tantalum spinneret                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | HV 400±                             | 0.134 μm              |
| The second generation coated tantalum spinneret                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | HV 600±                             | 0.059 μm              |
| Coated tantalum spinneret of the present invention                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | HV 350±                             | 0.027 μm              |
| <p>Note: The first generation: coating conditions, 488°C, a constant voltage of 10V for 3 hours</p> <p>The second generation: coating conditions, 498°C, a constant voltage of 10V for 3 hours</p> <p>The present invention: coating conditions, 482°C, a constant voltage of 10V for 1.5 hours, before coating, an anode voltage of 140 volts was applied in a 90°C aqueous solution of phosphoric acid ethylene glycol at a constant voltage for 1 hour to form an amorphous Ta<sub>2</sub>O<sub>5</sub> film.</p> <p><sup>1)</sup> The HV was measured at a constant pressure of 100 grams for 15 seconds;</p> <p><sup>2)</sup> The transition layer refers to the lower modified layer after the film layer of the fiber outlet face of the spinneret is polished, that is, the film layer is removed by polishing, leaving the tantalum metal transition layer, that is, the fiber outlet face of the spinneret (as shown in FIG. 7).</p> |                                     |                       |

**[0025]** Table 1 shows that the film roughness of the coated tantalum spinneret of the present invention is nearly four times lower than those of the coated tantalum spinnerets of the prior art patents ZL 85101505 and ZL86102269, and 1 to 2 times lower than that of the coated tantalum spinneret of the patent ZL02106915.8.

**[0026]** Although the roughness of the micropore wall of the spinneret is not technically detectable at present, due to the automatic balancing effect of the electrochemical coating, it is considered that the film layer of the micropore wall of the spinneret has the same roughness as the film layer on the surface of the spinneret, or has a corresponding relationship.

**[0027]** The roughness of the film layer of lithium-containing compound formed after subjecting the amorphous Ta<sub>2</sub>O<sub>5</sub> film which is obtained by using different anodization voltages in step (a) of the present invention to the treatment of step (c) is shown in Table 2.

Table 2. Effect of different anodization voltages in step (a) on the roughness of film layer of lithium-containing compound

| Anodizing voltage                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 130V  | 240V  | 420V  | 30V (molten salt) |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|-------|-------|-------------------|
| Roughness                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 0.027 | 0.051 | 0.061 | 0.053             |
| <p>Note: 1. For the anodizing solutions, except for that the molten salt was subjected to a constant anode voltage of 30V for 1 hour at 300°C in LiNO<sub>3</sub> salt, the other three were all kept at a constant voltage of 90°C in an aqueous solution of phosphoric acid ethylene glycol for 1 hour. The solution volume ratio was 0.01% H<sub>3</sub>PO<sub>4</sub> solution: ethylene glycol = 1:2.</p> <p>2. The coating of step (c) in Table 2 was applied with an anode voltage of 10V constantly for 1.5 hours.</p> |       |       |       |                   |

**[0028]** It can be seen from Table 2 that the voltage of the oxidation is increased, and the roughness of the film layer of lithium-containing compound after the coating is increased, so that the voltage of the anodization is not too high. Anodizing forms an amorphous Ta<sub>2</sub>O<sub>5</sub> film. As the amorphous Ta<sub>2</sub>O<sub>5</sub> film thickens, its roughness increases or its molecular aggregate volume increases, resulting in an increase in the crystal nuclei of the formed lithium-containing compound, thereby an increase in the roughness of the film layer of lithium-containing compound. The voltage for anodization in step (a) is preferably between 5 and 240V, wherein the treatment of the molten salt is to apply an anode voltage of 30V constantly for 1.5 hours at 300°C. If a higher anodization voltage such as 480V is used, the constant voltage time

is shorter.

**[0029]** After the amorphous  $Ta_2O_5$  film is electrochemically reacted to form a film layer of lithium-containing compound, the roughness of the obtained film layer of lithium-containing compound is affected by the solution temperature, the applied anode voltage, and the constant voltage time of step (c). That is, as the temperature rises, the anode voltage increases, and the time extension increases the roughness of the film layer of lithium-containing compound. Wherein, the change with voltage is shown in Table 3:

Table 3. Changes of roughness of the film layer of lithium-containing compound in step (c) with anode voltage

| Anode voltage                                                                                                                                                                                                                                                                          | 10V   | 25V   | 30V   |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|-------|-------|
| Film layer roughness                                                                                                                                                                                                                                                                   | 0.027 | 0.096 | 0.127 |
| Hardness (HV)                                                                                                                                                                                                                                                                          | 346.8 | 406.7 | 433.3 |
| Note: 1. The anodization of step (a) was carried out in an aqueous solution of phosphoric acid ethylene glycol, and a voltage of 60V was applied thereto constantly for 1.0 hour.<br>2. The solution used in step (c) was pure $LiNO_3$ at 488°C and a constant voltage for 1.5 hours. |       |       |       |

**[0030]** In the polishing step (b) of the present invention, the amorphous  $Ta_2O_5$  film on the fiber outlet face of the spinneret is removed and the amorphous  $Ta_2O_5$  film on the micropore inner wall of the spinneret is retained, that is because if there is an amorphous  $Ta_2O_5$  film on the fiber outlet face of the spinneret and then step (c) electrochemical coating is performed, the hardness of the surface of the obtained coating is much lower than that of the surface of the coating obtained by electrochemical coating after removing the amorphous  $Ta_2O_5$  film by polishing, as shown in Table 4. Through such a polishing operation, it can maintain the low roughness of the micropore wall of the spinneret and ensure high hardness of the surface, thereby increasing the scratch resistance of the spinneret having the film layer of lithium-containing compound. If step (b) is not employed before step (c), i.e., step (c) is directly performed without removing the amorphous  $Ta_2O_5$  film, and the surface hardness of the obtained spinneret is adjusted to be close to the surface hardness of the noble metal spinneret, for example, both around HV220, which can also be adapted to some specific spinning conditions, such as chemical fiber with low spinning speed and low spinning pressure, to simplify the operation process and reduce the cost.

Table 4. Effect of removing the amorphous  $Ta_2O_5$  film on the fiber outlet face of the spinneret by polishing before electrochemical coating on the surface hardness (HV)

| Anode voltage of step (a)                                                                                                                                                                                                                                                                          | 130V  | 240V  | 480V  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|-------|-------|
| Anodizing (a) + coating (c)                                                                                                                                                                                                                                                                        | 238   | 162.7 | 150.9 |
| Anodizing (a) + coating (c) + polishing (d)                                                                                                                                                                                                                                                        | 236.6 | 157   | 132   |
| Anodizing (a) + polishing (b) + coating (c) + polishing (d)                                                                                                                                                                                                                                        | 376   | 377   | 395.2 |
| Note: 1. 012 spinneret, anodized at 90°C for 1.5 hours in aqueous solution of phosphoric acid ethylene glycol.<br>2. The weight for hardness measurement was 100 g.<br>3. The coating step (c) is to apply an anode voltage of 10V at 488°C in a molten salt of $LiNO_3$ constantly for 1.5 hours. |       |       |       |

**[0031]** In the case when the coating temperature in step (c) was lowered to 350°C, an anode voltage of 10V or 39V is applied, and the reaction time is 20 hours, 30 hours, or 40 hours, the roughness of the film layer of lithium-containing compound is lower, and the spinnability is better. The measured roughness and hardness are shown in Table 5.

Table 5. Relationship between roughness, surface hardness and process parameters such as coating (350°C/10V)

| Coating time<br>Process characteristics |                                                  | Coating for 20 hours |               |                       |               | Coating for 30 hours |               |                       |               | Coating for 40 hours |               |                       |               |
|-----------------------------------------|--------------------------------------------------|----------------------|---------------|-----------------------|---------------|----------------------|---------------|-----------------------|---------------|----------------------|---------------|-----------------------|---------------|
|                                         |                                                  | Roughness (μm)       |               | Surface hardness (HV) |               | Roughness (μm)       |               | Surface hardness (HV) |               | Roughness (μm)       |               | Surface hardness (HV) |               |
| Whether nitriding before anodizing      | Voltage for forming anodized film before coating | Before coating       | After coating | Before coating        | After coating | Before coating       | After coating | Before coating        | After coating | Before coating       | After coating | Before coating        | After coating |
| Non-nitriding (first generation)        | 0V, oxidation                                    | 0.030                | 0.034         | 93.38                 | 176.0         | 0.035                | 0.138         | 112.8                 | 237           | 0.025                | 0.140         | 117.4                 | 229.0         |
|                                         | 60V oxidation                                    | 0.041                | 0.044         | 91.83                 | 143.5         | 0.025                | 0.056         | 114.9                 | 218.0         | 0.021                | 0.060         | 126.4                 | 243.0         |
|                                         | 150V oxidation                                   | 0.031                | 0.033         | 96.33                 | 125.6         | 0.032                | 0.062         | 120.4                 | 246.0         | 0.030                | 0.083         | 118.5                 | 231.0         |
| Nitriding                               | 0V, oxidation                                    | 0.034                | 0.050         | 333.1                 | 496.1         | 0.056                | 0.067         | 311                   | 520.5         | 0.030                | 0.063         | 267.7                 | 428.1         |
| (second generation)                     | 60V oxidation                                    | 0.034                | 0.052         | 334.0                 | 567.2         | 0.028                | 0.055         | 291.3                 | 494.0         | 0.028                | 0.066         | 283.0                 | 452.2         |
|                                         | 150V oxidation                                   | 0.036                | 0.051         | 307.4                 | 526.9         | 0.029                | 0.100         | 288.0                 | 455.6         | 0.031                | 0.130         | 272.0                 | 416.0         |

Note: The samples with parameters listed in this table are all tantalum spinneret blanks in pure lithium nitrate (LiNO<sub>3</sub>) at 350°C with an anode voltage of 10V applied constantly for 20, 30, 40 hours as described in the table.

Table 6. Relationship between roughness, surface hardness and process parameters such as coating (350°C/39V)

| Coating time<br>Process characteristics |                                                  | Coating for 20 hours |               |                       |               |
|-----------------------------------------|--------------------------------------------------|----------------------|---------------|-----------------------|---------------|
|                                         |                                                  | Roughness (μm)       |               | Surface hardness (HV) |               |
| Whether nitriding before anodizing      | Voltage for forming anodized film before coating | Before coating       | After coating | Before coating        | After coating |
| Non-nitriding (first generation)        | 0V, oxidation                                    | 0.030                | 0.223         | 90.57                 | 287.2         |
|                                         | 60V oxidation                                    | 0.033                | 0.103         | 95.79                 | 229.7         |
|                                         | 150V oxidation                                   | 0.038                | 0.064         | 98.57                 | 287.7         |
| Nitriding (second generation)           | 0V, oxidation                                    | 0.033                | 0.036         | 385.4                 | 518.8         |
|                                         | 60V oxidation                                    | 0.028                | 0.074         | 364.3                 | 513.0         |
|                                         | 150V oxidation                                   | 0.029                | 0.110         | 374.6                 | 521.0         |

[0032] As can be seen from Table 5:

1. For the non-nitriding tantalum spinneret (first generation), the anodizing is applied before the coating, and within the electrochemical reaction for 20 to 40 hours, the roughness of the tantalum spinneret is 2 to 3 times lower than the roughness of the tantalum spinneret to which no anodization is applied.
2. For the nitriding tantalum spinneret (second generation), the anodizing applied before the coating has no obvious influence on the roughness of the tantalum spinneret after coating, and even the roughness is increased.

#### Brief Description of the Drawings

[0033]

- FIG. 1 is a schematic view showing overall appearance of a tantalum spinneret of the present invention.
- FIG. 2 is a flow chart showing a surface treatment method of tantalum spinneret for wet spinning of the present invention.
- FIG. 3 is a partially enlarged cross-sectional view showing micropores of a tantalum spinneret of the present invention after forming an amorphous Ta<sub>2</sub>O<sub>5</sub> film.
- FIG. 4 is a partially enlarged cross-sectional view showing micropores of a tantalum spinneret of the present invention after polishing the fiber outlet face.

FIG. 5 is a cross-sectional view showing a tantalum spinneret coated with a film layer of lithium-containing compound.  
 FIG. 6 is a cross-sectional view showing a tantalum spinneret coated with a film layer of lithium-containing compound after polishing the fiber outlet face.  
 FIG. 7 is a schematic view of an entire tantalum spinneret.  
 FIGs. 8-14 show the results of XRD comparison of samples before and after annealing under different surface treatment conditions.

[0034] In the figure: 1 indicates a fiber outlet face of a tantalum spinneret; 2 indicates a spinneret body; 3 indicates a Ta<sub>2</sub>O<sub>5</sub> film; 6 indicates a film layer of lithium-containing compound; 7 indicates a modified layer; and the modified layer is the film layer of lithium-containing compound plus a transition layer; 8 indicates a transition layer.

### Detailed Description of The Invention

Example 1.

[0035] Referring to FIG. 2, the surface treatment method for wet spinning of the present invention is illustrated. The steps of Example 1 are as follows:

Step 1. A tantalum metal plate was processed into 45 tantalum spinnerets. Each tantalum spinneret is shown in FIG. 1. The tantalum spinneret comprised a body 2, the outer diameter of the spinneret fiber outlet face 1 was 16 mm, the number of micropores 12 was 2600, and the inner diameter of the micropores was  $0.052 \pm 0.001$  mm.

Step 2. At room temperature of 25°C, using 0.01% H<sub>3</sub>PO<sub>4</sub>, with an anode voltage of 150V applied constantly for 1 hour and then washed, a layer of amorphous Ta<sub>2</sub>O<sub>5</sub> film 3 was formed on the surface of the tantalum spinneret, as shown in FIG. 4.

Step 3. The amorphous Ta<sub>2</sub>O<sub>5</sub> film 3 of the fiber outlet face 1 was removed by polishing.

Step 4. Coating: A film layer of lithium-containing compound 6 was obtained by applying an anode voltage of 10V constantly for 1.5 hours in a molten lithium nitrate solution at 482°C. The inner diameter of the micropores after coating was  $0.050 \pm 0.001$  mm.

Step 5. Polishing the fiber outlet face 1 of the tantalum spinneret, the film layer of lithium-containing compound 6 on the fiber outlet face 1 of the tantalum spinneret was ground away, leaving the transition layer 8, as shown in FIG. 6. The hardness of the transition layer was HV229.

[0036] The above-mentioned 45 coated tantalum spinneret having a film layer of lithium-containing compound after anodization were mounted on a base plate of a viscose short-staple stainless-steel combined spinneret, and were subjected to a viscose short-staple spinning test in comparison with a coated tantalum spinneret of the prior art (which was not anodized before coating), and the results are shown in Table 7.

[0037] The results showed that the broken filament and fiber strand of the tantalum spinneret obtained by the method of the present invention were significantly lower than those of the prior art and the results are shown in Table 7 below:

Table 7. Comparison results of spinning with coated tantalum spinnerets after anodization according to the present invention and the prior art

|                                                          | Broken filament |                    | Fiber strand  |                    |
|----------------------------------------------------------|-----------------|--------------------|---------------|--------------------|
|                                                          | Average value   | Standard deviation | Average value | Standard deviation |
| First generation coated tantalum spinneret in prior art  | 1.89            | 2.4                | 0.56          | 0.58               |
| Second generation coated tantalum spinneret in prior art | 0.77            | 1.84               | 0.34          | 0.36               |
| coated tantalum spinneret of the present invention       | 0.17            | 0.14               | 0.12          | 0.07               |

[0038] From Table 7, it can be seen that the coated tantalum spinneret having a film layer of lithium-containing compound which is subjected to anodization and then coating treatment of the present invention can significantly reduce the fiber strand and the broken filament. Table 7 shows the results of a combined spinneret formed by a combination of 45 of single spinnerets of Ø16\*2600 holes\*0.05. The conditions for forming the three coated tantalum spinnerets listed in

Table 7 are shown in the notes of Table 1.

#### Example 2

5 **[0039]** Referring to FIG. 2, the surface treatment method of spinneret for wet spinning of the present invention is illustrated. The steps of Example 2 are as follows:

Step 1. A tantalum metal plate was processed into 27 tantalum spinnerets, each of which is shown in FIG. 1. The tantalum spinneret comprised a body 2, the outer diameter of the spinneret fiber outlet face 1 was 16 mm, the number of micropores 12 was 1400, and the inner diameter of the micropores was  $0.083 \pm 0.001$  mm.  
 Step 2. At room temperature of 25°C, using 0.01%  $H_3PO_4$ , with an anode voltage of 150V applied constantly for 1 hour and then washed, a layer of amorphous  $Ta_2O_5$  film 3 was formed on the surface of the tantalum spinneret.  
 Step 3. The amorphous  $Ta_2O_5$  film 3 of the fiber outlet face 1 was removed by polishing.  
 Step 4. Coating: A film layer of lithium-containing compound 6 was obtained by applying an anode voltage of 10V constantly for 2 hours in a molten lithium nitrate solution at 488°C. The inner diameter of the micropores after coating was  $0.08 \pm 0.001$  mm, as shown in FIG. 5.  
 Step 5. Polishing the fiber outlet face 1 of the tantalum spinneret, the film layer of lithium-containing compound 6 on the fiber outlet face 1 of the tantalum spinneret was ground away, leaving the transition layer 8, as shown in FIG. 6. The hardness of the transition layer was HV426.

20 **[0040]** The above-mentioned 27 anodized and coated tantalum spinneret were mounted on a base plate of a viscose short-staple stainless-steel combined spinneret, and were subjected to a viscose short-staple flame-retardant fiber spinning test in comparison with a coated tantalum spinneret which was not anodized before coating of the prior art. The results showed that the spinneret change period of the coated tantalum spinneret of the present invention was 16  
 25 hours, and the best second-generation coated tantalum spinneret (i.e., patent ZL2101015.8) in the prior art had a spinneret change period of 8 hours, therefore, the time had been doubled.

**[0041]** The method is also applicable to the tantalum-niobium spinneret made of tantalum-niobium alloy which is cheaper, but the corrosion resistance and processing performance of tantalum-niobium are inferior to those of pure tantalum. However, the tantalum-niobium alloy spinneret is superior to the pure niobium spinneret, thus can be considered  
 30 for some wet spinning without strong acid and alkali requirements.

#### Example 3

35 **[0042]** Referring to FIG. 2, the surface treatment method for wet spinning of the present invention is illustrated. The steps of Example 3 are as follows:

Step 1. A tantalum metal plate was processed into one tantalum spinneret, as shown in FIG. 1. The tantalum spinneret comprised a body 2, the outer diameter of the spinneret fiber outlet face 1 was 22 mm, the number of micropores was 330, and the inner diameter of the micropores was  $0.082 \pm 0.001$  mm.  
 40 Step 2. The tantalum spinneret obtained in step (1) was subjected to nitriding treatment, and the obtained spinneret had a hardness of HV385.  
 Step 3. Using a solution having a volume ratio of ethylene glycol: 0.01%  $H_3PO_4$  = 2:1 at a solution temperature of 90°C, with an anode voltage of 60V applied constantly for 1.5 hours and then washed, a layer of amorphous  $Ta_2O_5$  film 3 was formed on the surface of the spinneret.  
 45 Step 4. The amorphous  $Ta_2O_5$  film 3 of the fiber outlet face was removed by polishing.  
 Step 5. Coating: A film layer of lithium-containing compound 6 was obtained by applying an anode voltage of 10V constantly for 20 hours in a molten lithium nitrate solution at 350°C. The inner diameter of the micropores after coating was  $0.08 \pm 0.001$  mm, as shown in FIG. 5.  
 Step 6. Polishing the fiber outlet face 1 of the tantalum spinneret: the insulating coating layer 6 of the fiber outlet face 1 of the tantalum spinneret was ground away, leaving the transition layer 8, as shown in FIG. 6. The hardness of the transition layer was HV455.

#### Example 4

55 **[0043]** Referring to FIG. 2, the surface treatment method for wet spinning of the present invention is illustrated. The steps of Example 4 are as follows:

Step 1. A tantalum metal plate was processed into one tantalum spinneret, as shown in FIG. 1. The tantalum

spinneret comprised a body 2, the outer diameter of the spinneret fiber outlet face 1 was 22 mm, the number of micropores was 330, and the inner diameter of the micropores was  $0.082 \pm 0.001$  mm. The tantalum spinneret was not subjected to nitriding treatment, and the obtained spinneret had a hardness of HV98.

Step 2. Using a solution having a volume ratio of ethylene glycol:  $0.01\% \text{H}_3\text{PO}_4 = 2:1$  at a solution temperature of  $90^\circ\text{C}$ , with an anode voltage of 140V applied constantly for 1.5 hours and then washed, a layer of amorphous  $\text{Ta}_2\text{O}_5$  film 3 was formed on the surface of the spinneret.

Step 3. The amorphous  $\text{Ta}_2\text{O}_5$  film 3 of the fiber outlet face was removed by polishing.

Step 4. Coating: A film layer containing lithium-containing compound 6 was obtained by applying an anode voltage of 39V constantly for 20 hours in a molten lithium nitrate solution at  $350^\circ\text{C}$ . The inner diameter of the micropores after coating was  $0.08 \pm 0.001$  mm, as shown in FIG. 5.

Step 5. Polishing the fiber outlet face 1 of the tantalum spinneret: the insulating coating layer 6 of the fiber outlet face 1 of the tantalum spinneret was ground away, leaving the transition layer 8, as shown in FIG. 6. The hardness of the transition layer was HV287.

#### Example 5

**[0044]** Referring to FIG. 2, the surface treatment method for wet spinning of the present invention is illustrated. The steps of Example 5 are as follows:

Step 1. A tantalum metal plate was processed into one tantalum spinneret, as shown in FIG. 1. The tantalum spinneret comprised a body 2, the outer diameter of the spinneret fiber outlet face 1 was 22 mm, the number of micropores was 330, and the inner diameter of the micropores was  $0.082 \pm 0.001$  mm.

Step 2. The tantalum spinneret obtained in step (1) was subjected to nitriding treatment, and the obtained spinneret had a hardness of HV283.

Step 3. Using a solution having a volume ratio of ethylene glycol:  $0.01\% \text{H}_3\text{PO}_4 = 2:1$  at a solution temperature of  $90^\circ\text{C}$ , with an anode voltage of 140V applied constantly for 1.5 hours and then washed, a layer of amorphous  $\text{Ta}_2\text{O}_5$  film 3 was formed on the surface of the spinneret.

Step 4. The amorphous  $\text{Ta}_2\text{O}_5$  film 3 of the fiber outlet face was removed by polishing.

Step 5. Coating: A film layer containing lithium-containing compound 6 was obtained by applying an anode voltage of 10V constantly for 12 hours in a molten lithium nitrate solution at  $400^\circ\text{C}$ . The inner diameter of the micropores after coating was  $0.08 \pm 0.001$  mm, as shown in FIG. 5.

Step 6. Polishing the fiber outlet face 1 of the tantalum spinneret: the insulating coating layer 6 of the fiber outlet face 1 of the tantalum spinneret was ground away, leaving the transition layer 8, as shown in FIG. 6. The hardness of the transition layer was HV536.

#### Example 6

**[0045]** Referring to FIG. 2, the surface treatment method for wet spinning of the present invention is illustrated. The steps of Example 6 are as follows:

Step 1. A tantalum metal plate was processed into one tantalum spinneret, as shown in FIG. 1. The tantalum spinneret comprised a body 2, the outer diameter of the spinneret fiber outlet face 1 was 22 mm, the number of micropores was 330, and the inner diameter of the micropores was  $0.081 \pm 0.001$  mm. The tantalum spinneret was not subjected to nitriding treatment, and the obtained spinneret had a hardness of HV387.

Step 2. Using a solution having a volume ratio of ethylene glycol:  $0.01\% \text{H}_3\text{PO}_4 = 2:1$  at a solution temperature of  $90^\circ\text{C}$ , with an anode voltage of 140V applied constantly for 1.5 hours and then washed, a layer of amorphous  $\text{Ta}_2\text{O}_5$  film 3 was formed on the surface of the spinneret.

Step 3. The amorphous  $\text{Ta}_2\text{O}_5$  film 3 of the fiber outlet face was removed by polishing.

Step 4. Coating: A film layer containing lithium-containing compound 6 was obtained by applying an anode voltage of 39V constantly for 6 hours in a molten lithium nitrate solution at  $350^\circ\text{C}$ . The inner diameter of the micropores after coating was  $0.08 \pm 0.001$  mm, as shown in FIG. 5.

Step 5. Polishing the fiber outlet face 1 of the tantalum spinneret: the insulating coating layer 6 of the fiber outlet face 1 of the tantalum spinneret was ground away, leaving the transition layer 8, as shown in FIG. 6. The hardness of the transition layer was HV374.

Table 8. Process conditions and parameters for treating the tantalum spinneret in Examples 3-6

| Formation condition/<br>corresponding parameter                                                                                                          | Oxidation solution temperature (°C) | Anodizing voltage (V) | Coating solution temperature (°C) | Coating voltage (V) | Coating constant voltage time (V) | Roughness of the finished product (μm) | Hardness of the finished product (HV) |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|-----------------------|-----------------------------------|---------------------|-----------------------------------|----------------------------------------|---------------------------------------|
| Example 3                                                                                                                                                | 90                                  | 60                    | 350                               | 10                  | 20                                | (0.030)<br>0.036                       | (118) 229                             |
| Example 4                                                                                                                                                | 90                                  | 140                   | 350                               | 39                  | 20                                | (0.038)<br>0.064                       | (99) 287                              |
| Example 5                                                                                                                                                | 90                                  | 140                   | 400                               | 10                  | 12                                | (0.034)<br>0.052                       | (283) 536                             |
| Example 6                                                                                                                                                | 90                                  | 60                    | 350                               | 39                  | 20                                | (0.028)<br>0.074                       | (387) 632                             |
| Note: The values of roughness and hardness in parentheses were the values before anodization and were detected using an unperforated tantalum spinneret. |                                     |                       |                                   |                     |                                   |                                        |                                       |

**[0046]** The four coated tantalum spinnerets prepared in Examples 3 to 6 were subjected to aramid III spinning test in comparison with the coated tantalum spinneret manufactured by the prior art patent ZL02106915.8. The spinning cycle of the coated tantalum spinneret of the prior patent ZL02106915.8 was about 5-7 days on average, and the spinning cycle of the coated tantalum spinneret of the present invention was more than 20 days on average. The experimental results are shown in Table 9, and thus an unexpected technical effect was obtained.

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Table 9. Effect of surface treatment conditions of tantalum spinneret on aramid III spinning

| Coating process                                               | Anodizing voltage before coating (V) | Fiber mechanical properties |                  |                  |       | Fineness      |       | Spinning cycle    |
|---------------------------------------------------------------|--------------------------------------|-----------------------------|------------------|------------------|-------|---------------|-------|-------------------|
|                                                               |                                      | Average strength            | Maximum strength | Minimum strength | CV%   | average value | CV%   |                   |
| 350°C/10V/20h (first generation)                              | 0                                    | 30.59                       | 31.73            | 29.85            | 1.539 | 149.04        | 0.57  | More than 20 days |
| 350°C/10V/20h Example 3 (first generation)                    | 60                                   | 31.91                       | 33.13            | 30.19            | 2.379 | 146.4         | 0.513 |                   |
| 350°C/39V/20h Example 4 (first generation)                    | 140                                  | 30.66                       | 31.35            | 29.46            | 1.631 | 147.05        | 0.52  |                   |
| 350°C/39V/20h (second generation)                             | 0                                    | 30.39                       | 31.54            | 29.36            | 1.66  |               |       |                   |
| 350°C/39V/20h Example 6                                       | 60                                   | 32.44                       | 33.7             | 31.26            | 1.518 | 149.19        | 0.414 |                   |
| 482°C/10V/3h (second generation)                              | 0                                    | 31.74                       | 32.81            | 30.45            | 1.88  | 147.02        | 0.7   |                   |
| 482°C/10V/3h (second generation)                              | 60                                   | 30.46                       | 31.95            | 29.58            | 1.94  |               |       |                   |
| 482°C/10V/3h (second generation)                              | 140                                  |                             |                  |                  |       |               |       | 5-7 days          |
| Comparison group Second generation, i.e., nitriding + coating |                                      | 31.89                       | 32.95            | 30.56            | 2.04  | 146.83        | 0.704 |                   |
|                                                               |                                      | 32.31                       | 33.81            | 29.37            | 3.241 | 148.19        | 1.303 |                   |

[0047] The spinning results of viscose filaments are shown in Table 10.

Table 10. Comparison results of anodization and non-anodization before coating at low temperature on the spinning of viscose filaments

| Coating oxidation process         |                                      | Spinning data of two months |                    |                                 |                           |                      |
|-----------------------------------|--------------------------------------|-----------------------------|--------------------|---------------------------------|---------------------------|----------------------|
| Coating process                   | Anodizing voltage before coating (V) | Fineness CV value%          | Blocking head rate | Unplanned spinneret change rate | Monofilament insufficient | Broken filament rate |
| 350°C/10V/30h (first generation)  | 0                                    | 0.68                        | 0                  | 0                               | 0                         | 0                    |
| 350°C/10V/30h (first generation)  | 140                                  | 0.97                        | 0                  | 0                               | 0                         | 1.72                 |
| 350°C/10V/30h (second generation) | 0                                    | 0.73                        | 0.27               | 0.26                            | 0                         | 2.59                 |
| 350°C/10V/30h (second generation) | 60                                   | 0.8                         | 1.08               | 0                               | 0                         | 3.45                 |

(continued)

| Coating oxidation process                                                                                                  |                                      | Spinning data of two months |                    |                                 |                           |                      |
|----------------------------------------------------------------------------------------------------------------------------|--------------------------------------|-----------------------------|--------------------|---------------------------------|---------------------------|----------------------|
| Coating process                                                                                                            | Anodizing voltage before coating (V) | Fineness CV value%          | Blocking head rate | Unplanned spinneret change rate | Monofilament insufficient | Broken filament rate |
| 350°C/39V20h (second generation)                                                                                           | 0                                    | 0.26                        | 0                  | 0                               | 0                         | 0.86                 |
| Prior art Comparison group                                                                                                 |                                      | 1.07                        | 1.23               | 0.89                            | 0.02                      | 1.87                 |
| Note: The coating process and anodization in the table were obtained by reference to the methods of the previous examples. |                                      |                             |                    |                                 |                           |                      |

**[0048]** The results in Table 10 show that unexpected results were obtained when no anodization was applied before coating, however, XRD analysis of the sample at a low temperature of 350°C showed no obvious LiTaO<sub>3</sub> diffraction peak, but XRD (X-ray phase analysis) carried out after vacuum treatment at 660°C for 2 hours showed LiTaO<sub>3</sub> diffraction peak (see FIGs. 8-14), indicating that the film layer of LiTaO<sub>3</sub> obtained by coating at a low temperature such as 350°C was an amorphous LiTaO<sub>3</sub> film, and good results were related thereto.

\* The definitions of CV values and standard deviations in the examples are as follows:

The meaning of the CV value: The CV value of a set of data, i.e., the "variation coefficient" or "discrete coefficient", is an indicator used to measure the "consistency" or "discreteness" of the set of data.

Definition and calculation of CV value:

$$CV = \frac{\sigma}{\mu} \times 100\%,$$

wherein:

$\mu$ : The average of the set of data. That is: assuming a set of data is  $\{x_1, x_2, \dots, x_i, \dots, x_n\}$ , then the average of the set of data is:

$$\mu = \frac{\sum_{i=1}^n x_i}{n} = \frac{x_1 + x_2 + \dots + x_n}{n}$$

$\sigma$ : The standard deviation or standard deviation of the set of data. That is: assuming a set of data is  $\{x_1, x_2, \dots, x_i, \dots, x_n\}$ , then the standard deviation of the set of data is:

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \mu)^2}{n}}$$

$$= \sqrt{\frac{(x_1 - \mu)^2 + (x_2 - \mu)^2 + \dots + (x_n - \mu)^2}{n}}$$

## Claims

1. A surface treatment method of tantalum spinneret, **characterized in that** the method comprises the following steps:

(a) forming a layer of  $Ta_2O_5$  film on the tantalum spinneret;  
 (b) optionally polishing: polishing a fiber outlet face of the tantalum spinneret treated in step (a) to remove the  $Ta_2O_5$  film on a surface of the fiber outlet face; and  
 (c) coating: subjecting the tantalum spinneret treated in step (b) to a coating treatment by a molten salt electrochemical method to form a film layer containing lithium-containing compound.

2. The method according to claim 1, further comprises a polishing step (d): subjecting the fiber outlet face of the tantalum spinneret treated in step (c) to a polishing treatment to remove the film layer containing lithium-containing compound on the surface of the fiber outlet face.
3. The method according to claim 1, wherein in step (a), the  $Ta_2O_5$  film formed on the tantalum spinneret is an amorphous  $Ta_2O_5$  film.
4. The method according to claim 3, wherein a layer of amorphous  $Ta_2O_5$  film is formed on the tantalum spinneret by anodization in step (a).
5. The method according to claim 1, wherein in step (a), the tantalum spinneret is placed in an oxygen-containing electrolyte solution at room temperature to  $380^\circ\text{C}$ , preferably room temperature to  $300^\circ\text{C}$ , and an anode voltage of 3 to 800V is applied constantly for 0.01 to 2 hours, with a voltage-increasing current density of 1 to  $200\text{ mA/cm}^2$  to form a layer of amorphous  $Ta_2O_5$  film.
6. The method according to claim 5, wherein the oxygen-containing electrolyte solution is an aqueous solution, a non-aqueous solution, or a mixture of an aqueous electrolyte and an organic compound.
7. The method according to claim 1, wherein in step (c), the molten salt electrochemical method is a molten lithium salt electrochemical method.
8. The method according to claim 1, wherein in step (c), the spinneret is placed in an oxygen-containing inorganic lithium salt or a mixed melt of oxygen-containing inorganic lithium salt and lithium hydroxide, or a mixed melt liquid of a salt and lithium hydroxide or a mixed melt liquid of a lithium salt and an oxygen-containing salt at a temperature of  $250^\circ\text{C}$  to  $650^\circ\text{C}$ , and an anode voltage of 1 to 66V is applied constantly for 0.01 to 200 hours, with a voltage-increasing current density of 1 to  $1000\text{ mA/cm}^2$  to form a film layer containing lithium-containing compound.
9. The method according to claim 8, wherein the mixed melt or the mixed melt liquid has a temperature of  $300^\circ\text{C}$  to  $520^\circ\text{C}$ , the applied anode voltage is 5 to 25V, and the voltage-increasing current density is 5 to  $20\text{ mA/cm}^2$ .
10. The method according to claim 8, wherein the oxygen-containing inorganic lithium salt is  $LiNO_3$ .
11. The method according to claim 8, wherein an ultrasonic generator is disposed in the mixed melt or the mixed melt liquid in step (c).
12. The method according to claim 1, wherein the tantalum spinneret is nitrided or not nitrided prior to step (a).
13. The method according to claim 1, wherein the tantalum spinneret comprises a pure tantalum spinneret and a tantalum alloy spinneret, preferably a tantalum-niobium alloy spinneret.
14. The method according to claim 1, wherein the method is a surface treatment method of tantalum spinneret for wet spinning.
15. A surface treatment method of tantalum spinneret, wherein the method comprises the steps of: subjecting the tantalum spinneret to a coating treatment by a molten salt electrochemical method to form a film layer containing lithium-containing compound, wherein the coating temperature is from  $250^\circ\text{C}$  to  $430^\circ\text{C}$ .
16. The method according to claim 15, wherein the coating temperature is from  $300^\circ\text{C}$  to  $400^\circ\text{C}$ , preferably from  $300^\circ\text{C}$  to  $350^\circ\text{C}$ .
17. The method according to claim 15, wherein the molten salt electrochemical method is a molten lithium salt electrochemical method.

18. The method according to claim 15, wherein in step (c), the spinneret is placed in an oxygen-containing inorganic lithium salt or a mixed melt of oxygen-containing inorganic lithium salt and lithium hydroxide, or a mixed melt liquid of a salt and lithium hydroxide or a mixed melt liquid of a lithium salt and an oxygen-containing salt at a temperature of 250°C to 430°C, and an anode voltage of 1 to 66V is applied constantly for 0.01 to 200 hours, with a voltage-increasing current density of 1 to 1000 mA/cm<sup>2</sup> to form a film layer containing lithium-containing compound.
19. The method according to claim 18, wherein the mixed melt or the mixed melt liquid has a temperature of 300°C to 350°C, the applied anode voltage is 5 to 25V, and the voltage-increasing current density is 5 to 20 mA/cm<sup>2</sup>.
20. The method according to claim 18, wherein the oxygen-containing inorganic lithium salt is LiNO<sub>3</sub>.
21. The method according to claim 18, wherein an ultrasonic generator is disposed in the mixed melt or the mixed melt liquid.
22. The method according to claim 15, wherein the tantalum spinneret is nitrided or not nitrided before coating.
23. The method according to claim 15, wherein the tantalum spinneret comprises a pure tantalum spinneret and a tantalum alloy spinneret, preferably a tantalum-niobium alloy spinneret.
24. The method according to claim 15, wherein the method is a surface treatment method of tantalum spinneret for wet spinning.
25. A tantalum spinneret obtained by the surface treatment of the method of any one of claims 1 to 24.

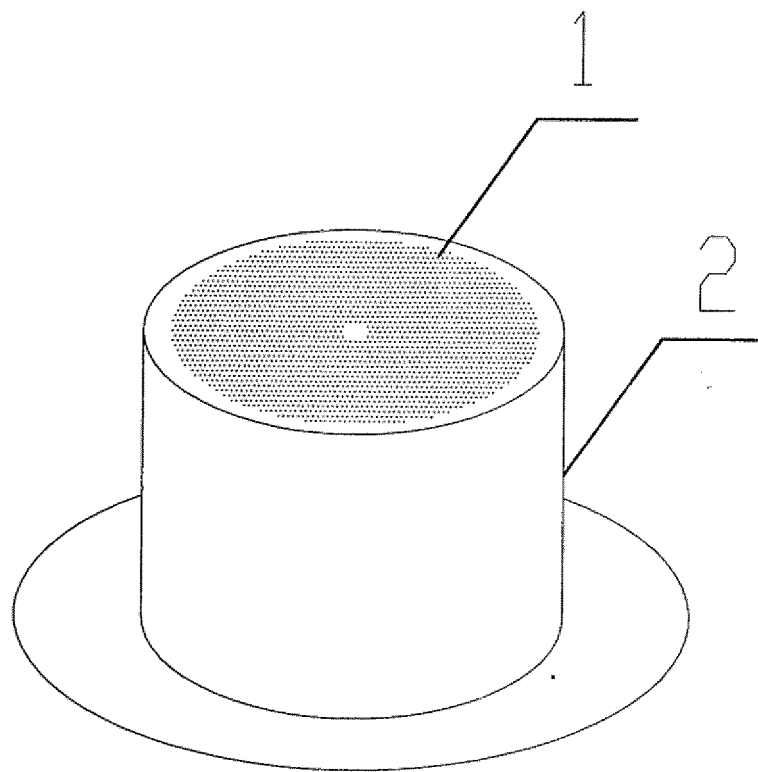


FIG. 1

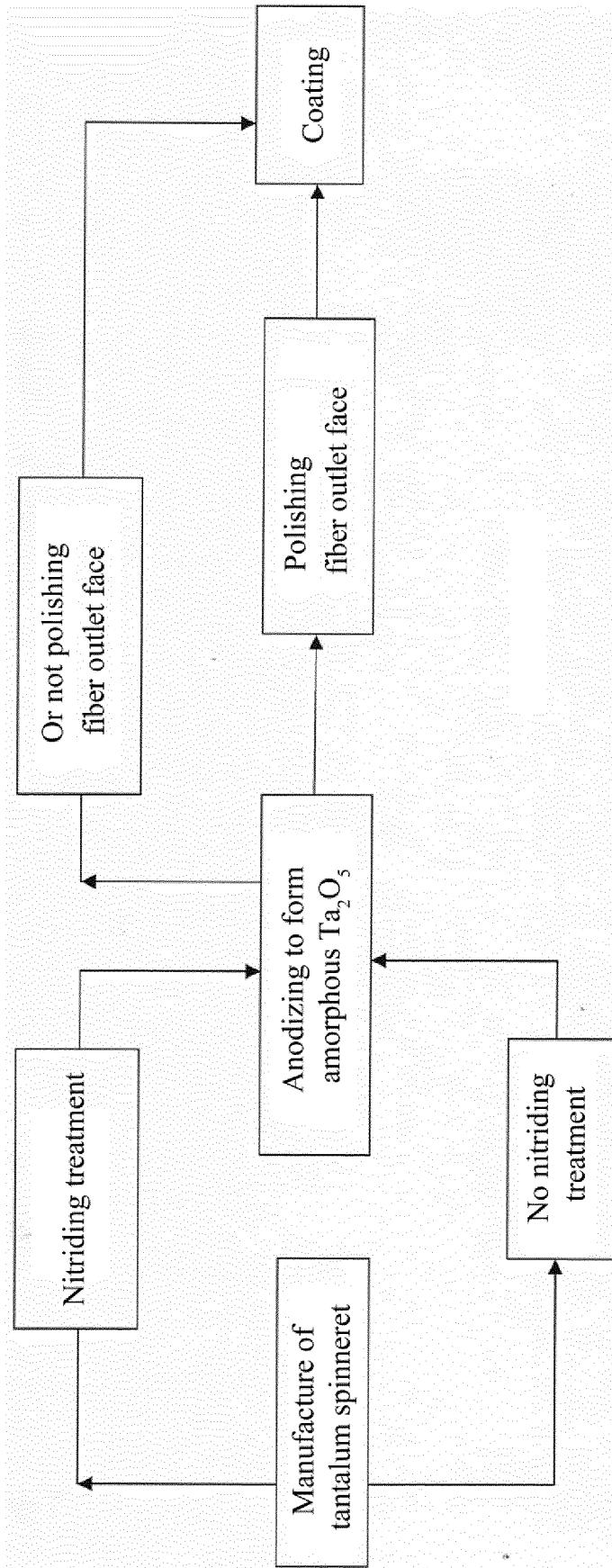


FIG. 2

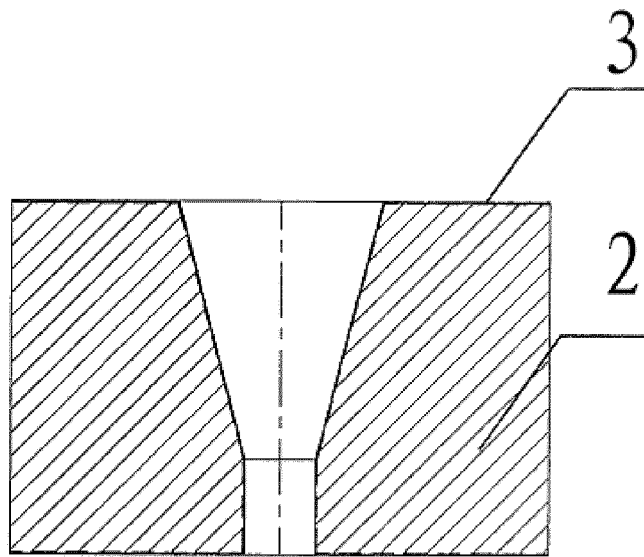


FIG. 3

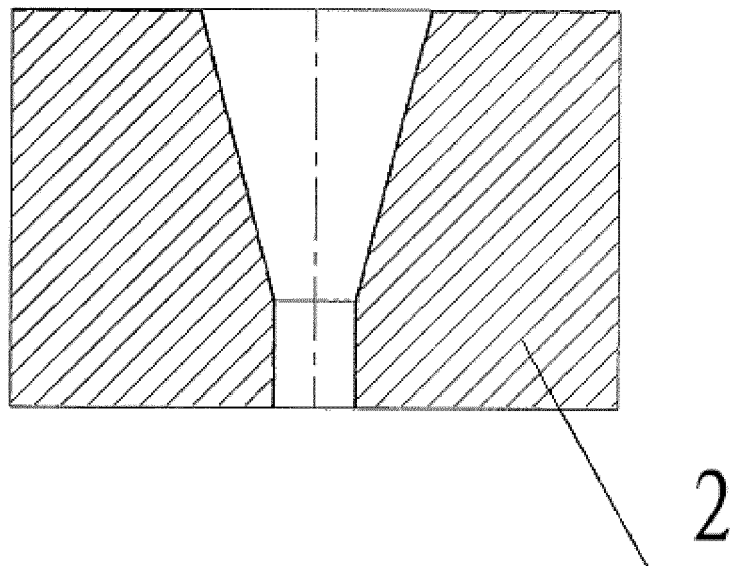


FIG. 4

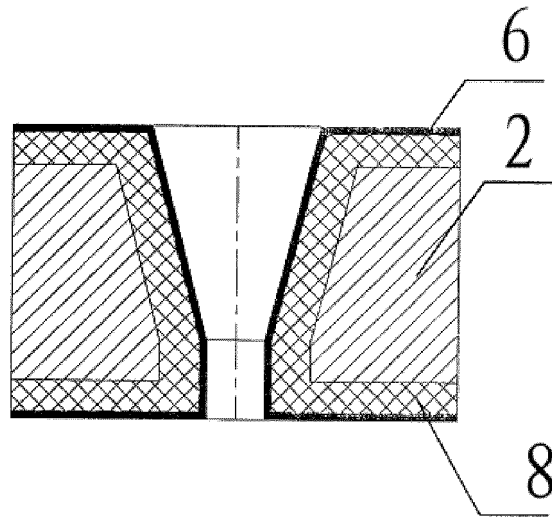


FIG. 5

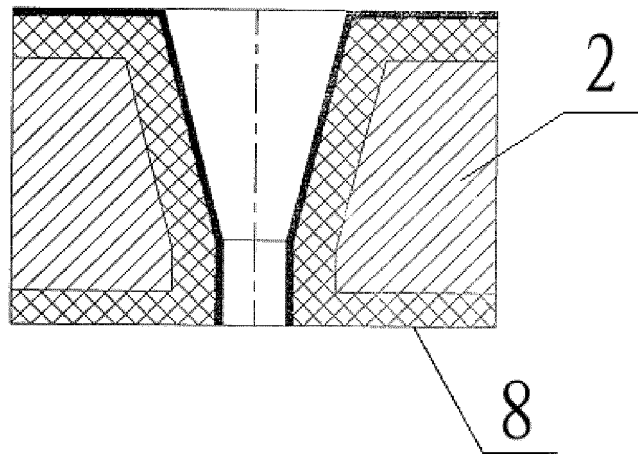


FIG. 6

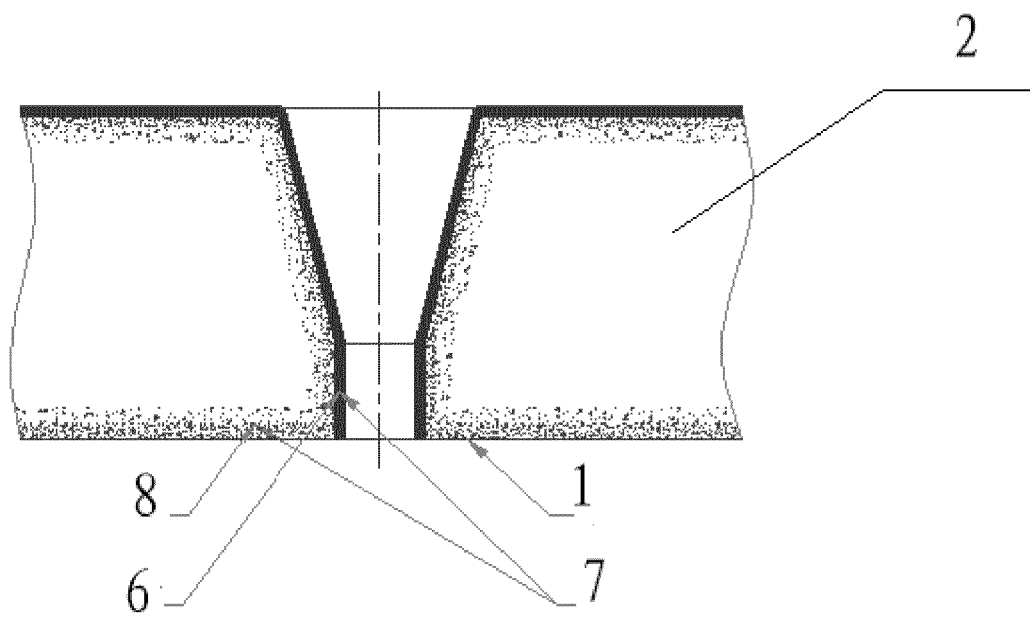


FIG. 7

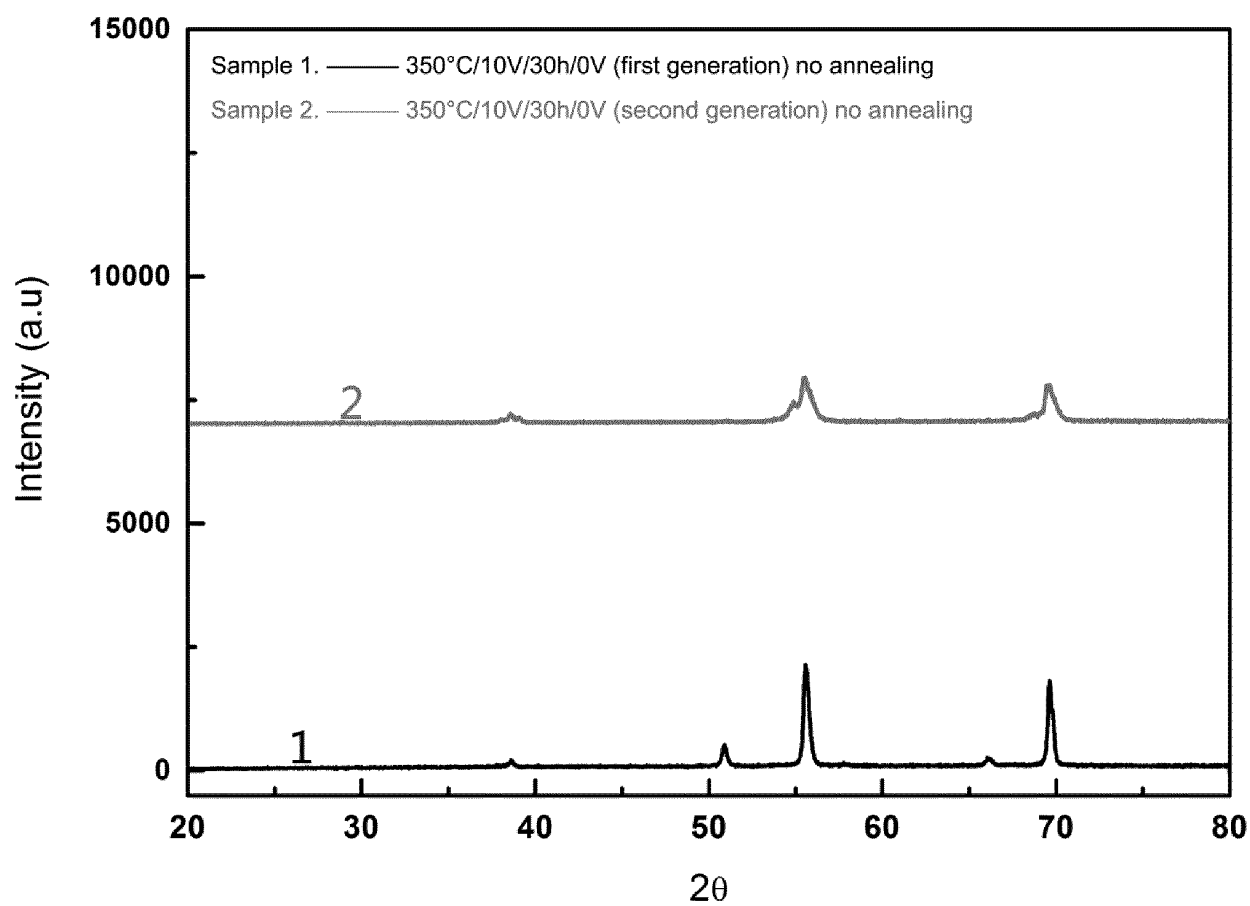


FIG. 8

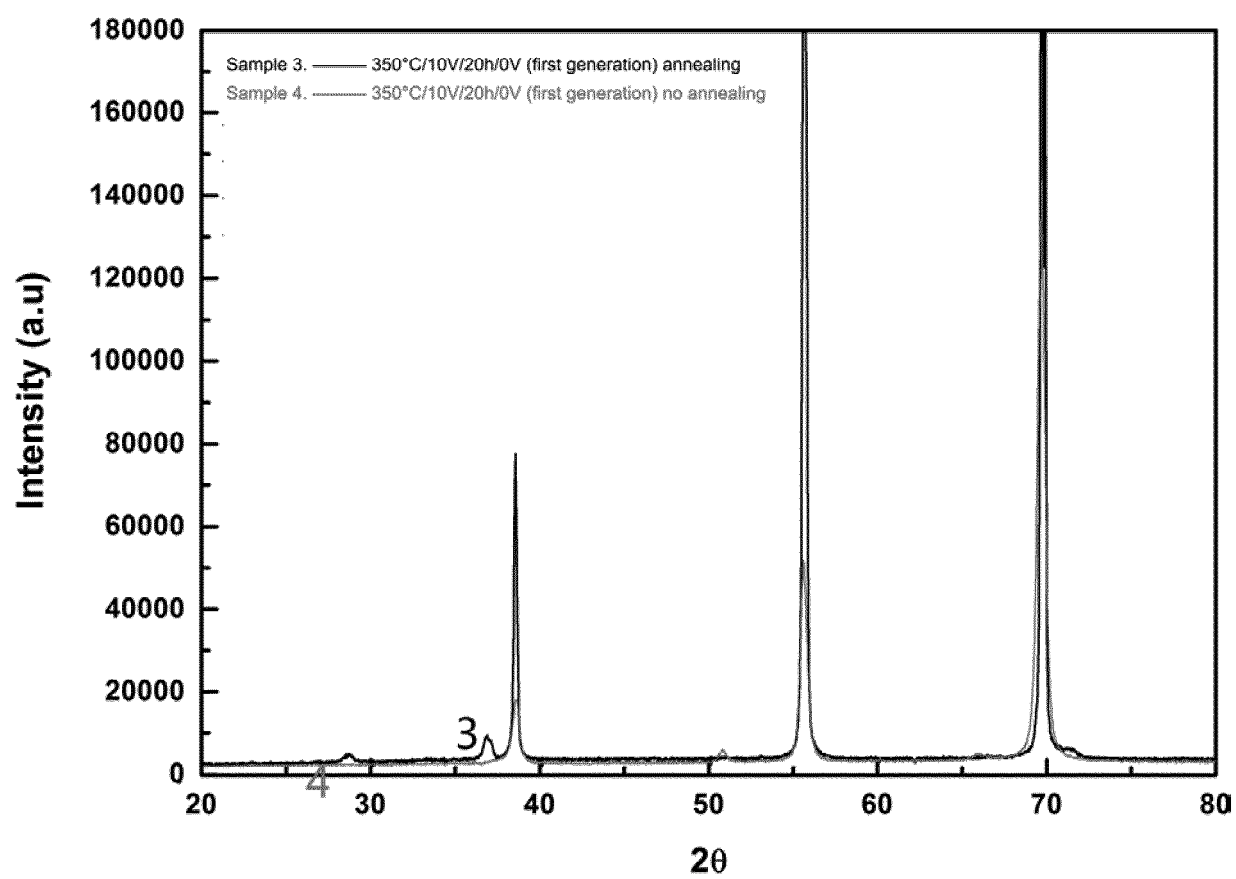


FIG. 9

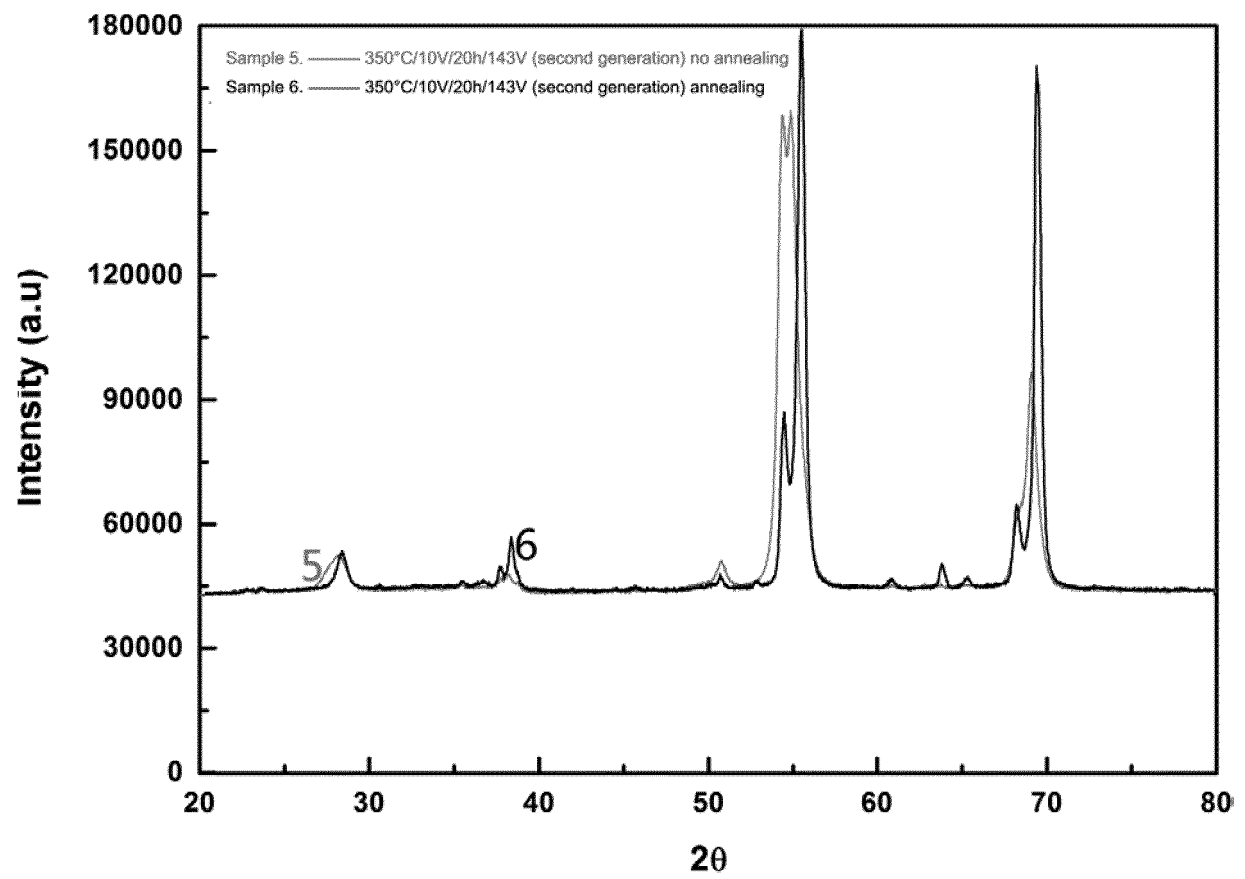


FIG. 10

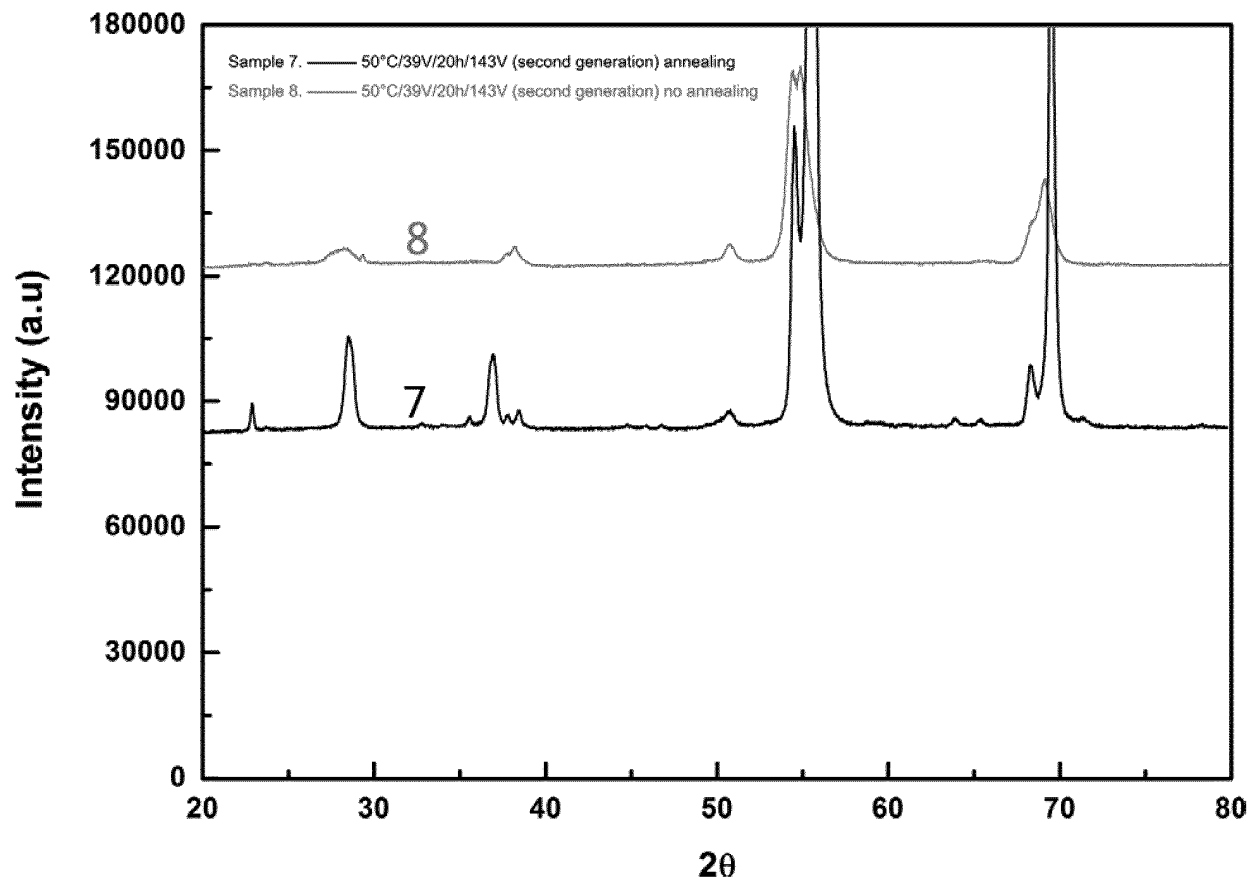


FIG. 11

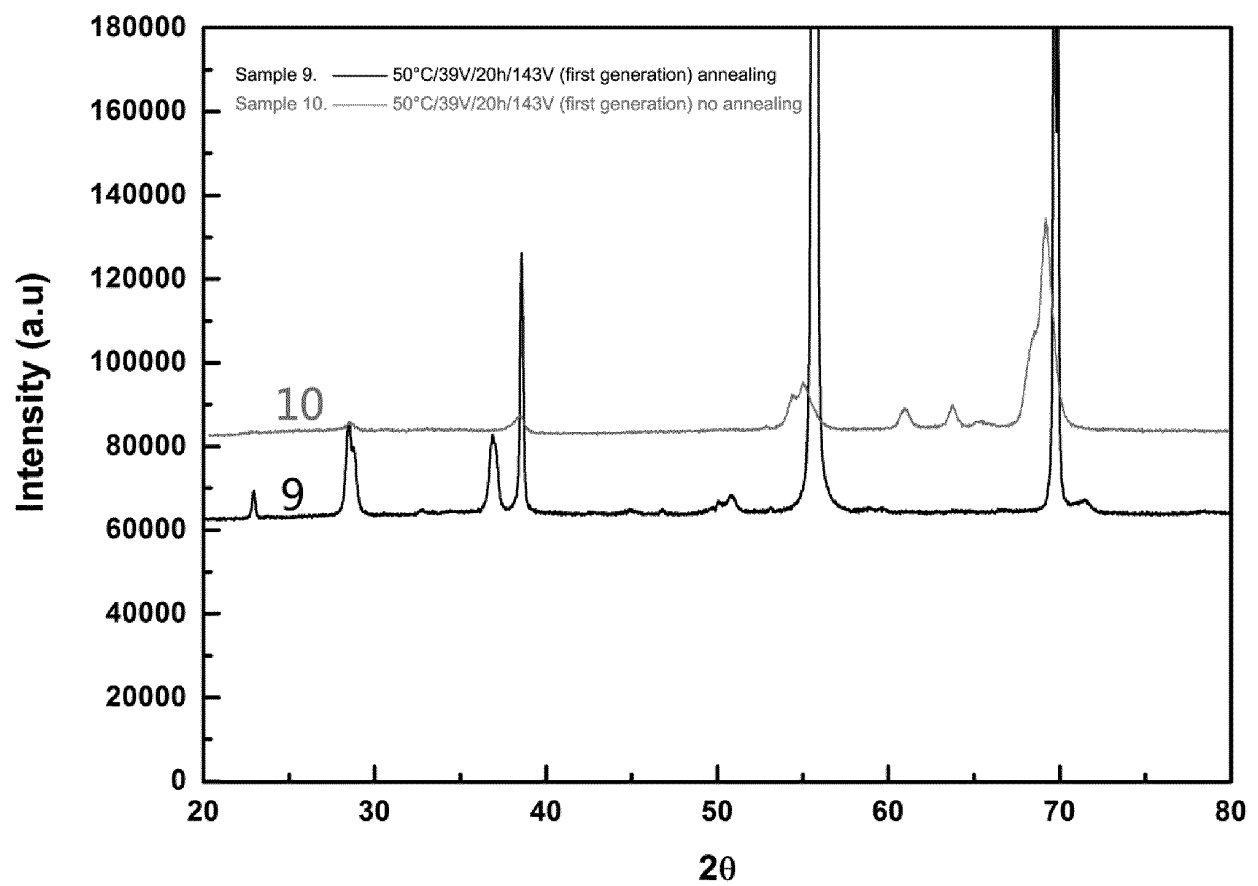


FIG. 12

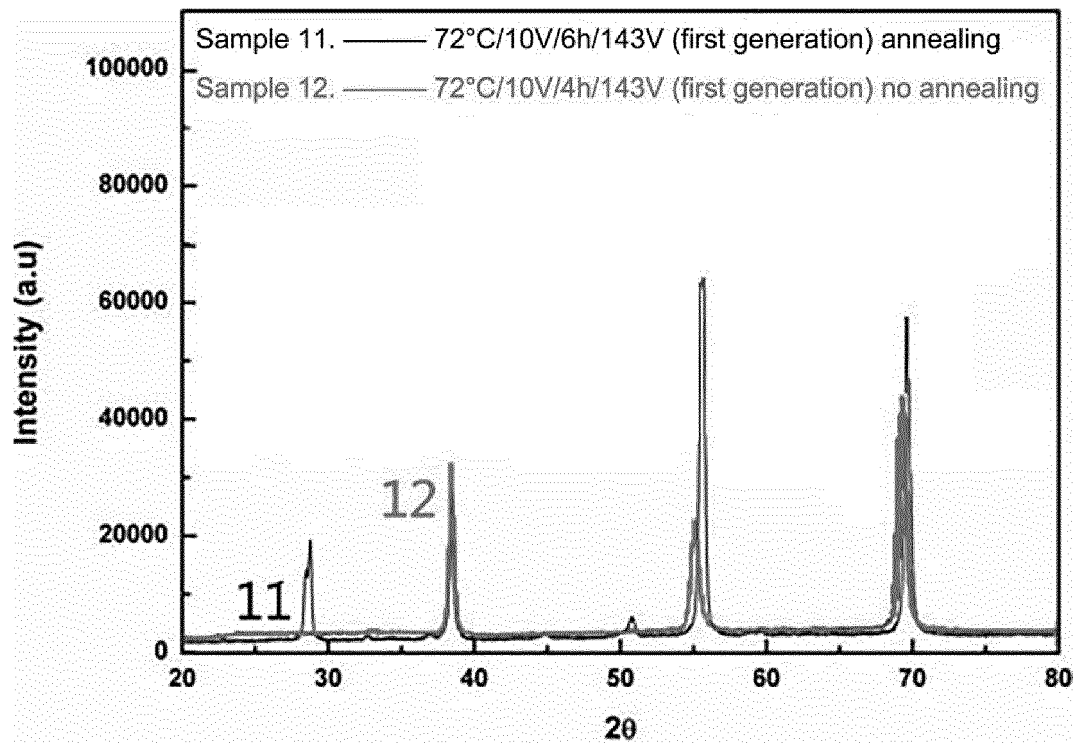


FIG. 13

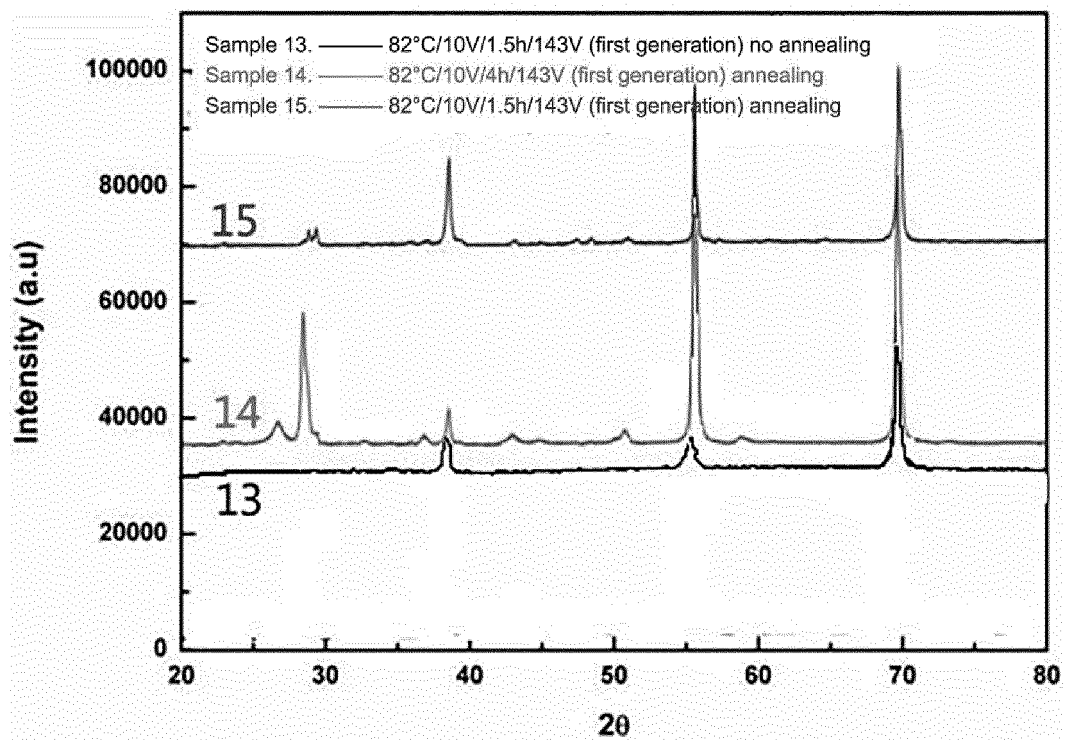


FIG. 14

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/CN2018/077938

## A. CLASSIFICATION OF SUBJECT MATTER

C25D 11/26 (2006.01) i; D01D 4/02 (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)

C25D D01D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
CNTXT, CNABS, VEN, WOTXT, JPTXT, USTXT, EPTXT, Web of Science: 刘寓中, 喷丝头, 纺丝头, 喷丝帽, 纺丝帽, 喷丝板, 纺丝板, 喷丝孔, 纺丝孔, 喷丝, 纺丝, LI, 锂, TA, 钽, 钽酸锂, 电压, 电解, 电流, 电化学, 阳极氧化, 抛光, spinneret+, spinning, nozzle?, lithium tantalate, lithium, tantalum, LiTaO<sub>3</sub>, electro+, anodic oxidation, anodis+, anodiz+

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                       | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | CN 86102269 A (NORTH CHINA RESEARCH INSTITUTE OF ELECTRO-OPTICS), 28 October 1987 (28.10.1987), page 7, lines 7-19, page 8, paragraph 3, page 9, paragraph 2 and page 11, paragraphs 2-3 | 15-25                 |
| X         | US 4678546 A (NORTH CHINA RESEARCH INSTITUTE OF ELECTRO-POTICS), 07 July 1987 (07.07.1987), claim 11                                                                                     | 15-25                 |
| X         | CN 1428465 A (BEIJING HUAYU CHUANGXIN SCIENCE & TRADE CO., LTD.), 09 July 2003 (09.07.2003), claims 1-6, and description, page 11, paragraph 1 and page 14, paragraph 1                  | 15-25                 |
| X         | CN 1380450 A (BEIJING HUAYU CHUANGXIN SCIENCE & TRADE CO., LTD.), 20 November 2002 (20.11.2002), claims 1-6, and description, page 11, paragraph 1 and page 14, paragraph 1              | 15-25                 |
| X         | CN 85101505 A (NORTH CHINA RESEARCH INSTITUTE OF ELECTRO-OPTICS), 27 August 1986 (27.08.1986), claim 14, and page 7, paragraph 4                                                         | 15-25                 |
| A         | CN 1896303 A (SHANGHAI JIAO TONG UNIVERSITY), 17 January 2007 (17.01.2007), entire document                                                                                              | 1-25                  |

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

|                                                                                                                                                                         |                                                                                                                                                                                                                                                  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| * Special categories of cited documents:                                                                                                                                | "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                                              |
| "A" document defining the general state of the art which is not considered to be of particular relevance                                                                |                                                                                                                                                                                                                                                  |
| "E" earlier application or patent but published on or after the international filing date                                                                               | "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                                                                     |
| "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) | "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 |
| "O" document referring to an oral disclosure, use, exhibition or other means                                                                                            | "&" document member of the same patent family                                                                                                                                                                                                    |
| "P" document published prior to the international filing date but later than the priority date claimed                                                                  |                                                                                                                                                                                                                                                  |

|                                                                                                                                                                                                               |                                                                   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|
| Date of the actual completion of the international search<br>18 April 2018                                                                                                                                    | Date of mailing of the international search report<br>09 May 2018 |
| Name and mailing address of the ISA<br>State Intellectual Property Office of the P. R. China<br>No. 6, Xitucheng Road, Jimenqiao<br>Haidian District, Beijing 100088, China<br>Facsimile No. (86-10) 62019451 | Authorized officer<br>WEI, Can<br>Telephone No. (86-20) 28950770  |

Form PCT/ISA/210 (second sheet) (January 2015)

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/077938

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

[1] D1: CN 86102269 A, date of publication: 28 October 1987 (28.10.1987)

[2] D1 discloses a tantalum spinneret for wet spinning: treating a tantalum or tantalum niobium alloy spinneret in oxygen-containing inorganic lithium salt at 400°C to 750°C, with a boost current density being 0.005 A/cm<sup>2</sup> to 10 A/cm<sup>2</sup> and an anode voltage range being 0.5 volts to 40 volts (see page 7, lines 7-19), so as to respectively produce a film containing lithium tantalite or lithium tantalate and niobate of lithium (see page 9, paragraph 2).

[3] The first group involves part of claims 1-14 and 25.

[4] The second group involves part of claims 15-24 and 25.

[5] The same or corresponding technical feature between the first group of inventions and the second group of inventions is "a method for treating the surface of a tantalum spinneret, comprising using a molten salt electrochemical method to carry out film coating on a tantalum spinneret, so as to form a film layer containing a lithium-containing compound". However, the above-mentioned feature has been disclosed in D1. Accordingly, the first group of inventions and the second group of inventions do not have the same or corresponding special technical feature which underlies the contribution of the invention over the prior art, do not have a technical relationship therebetween, and do not fall within a single general inventive concept, and therefore, do not comply with the requirement of unity of invention and do not comply with PCT Rule 13.1.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on protest**

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/CN2018/077938

| Patent Documents referred<br>in the Report | Publication Date | Patent Family  | Publication Date |
|--------------------------------------------|------------------|----------------|------------------|
| CN 86102269 A                              | 28 October 1987  | CN 86102269 B  | 23 November 1988 |
| US 4678546 A                               | 07 July 1987     | BR 8601360 A   | 02 December 1986 |
|                                            |                  | EP 0196093 B1  | 14 March 1990    |
|                                            |                  | EP 0196093 A1  | 01 October 1986  |
|                                            |                  | DE 3669548 D1  | 19 April 1990    |
|                                            |                  | US 4810584 A   | 07 March 1989    |
| CN 1428465 A                               | 09 July 2003     | None           |                  |
| CN 1380450 A                               | 20 November 2002 | CN 1279224 C   | 11 October 2006  |
| CN 85101505 A                              | 27 August 1986   | CN 85101505 B  | 30 March 1988    |
| CN 1896303 A                               | 17 January 2007  | CN 100443629 C | 17 December 2008 |

Form PCT/ISA/210 (patent family annex) (January 2015)

**REFERENCES CITED IN THE DESCRIPTION**

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

**Patent documents cited in the description**

- CN ZL85101505 [0003]
- CN ZL86102269 [0003]
- CN ZL02106915 [0003]
- WO ZL85101505 A [0007] [0025]
- WO ZL86102269 A [0007] [0025]
- WO ZL02106915 A [0007] [0023] [0025] [0046]
- WO ZL2101015 A [0040]