US 20060243314A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2006/0243314 A1**

Ota et al. (43) **Pub. Date: Nov. 2, 2006**

(54) THERMOELECTRIC SEMICONDUCTOR MATERIAL, THERMOELECTRIC SEMICONDUCTOR ELEMENT THEREFROM, THERMOELECTRIC MODULE INCLUDING THERMOELECTRIC SEMICONDUCTOR ELEMENT AND PROCESS FOR PRODUCING THESE

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(21) Appl. No.: **10/555,855**

(22) PCT Filed: **May 7, 2004**

(86) PCT No.: **PCT/JP04/06493**

(30) **Foreign Application Priority Data**

May 8, 2003 (JP) 2003-130618

Publication Classification

(51) **Int. Cl.**
H01L 35/00 (2006.01)

(52) **U.S. Cl.** **136/200**

(57) ABSTRACT

A metal mixture is prepared, in which an excess amount of Te is added to a (Bi—Sb)$_2$Te$_3$ based composition. After melting the metal mixture, the molten metal is solidified on a surface of a cooling roll of which the circumferential velocity is no higher than 5 m/sec, so as to have a thickness of no less than 30 μm. Thus, a plate shaped raw thermoelectric semiconductor materials **10** are manufactured, in which Te rich phases are microscopically dispersed in complex compound semiconductor phases, and extending directions of C face of most of crystal grains are uniformly oriented. The raw thermoelectric semiconductor materials **10** are layered in the direction of the plate thickness. And the layered body is solidified and formed to form a compact **12**. After that, the compact **12** is plastically deformed in such a manner that a shear force is applied in a uniaxial direction that is approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials **10**. As a result, a thermoelectric semiconductor **17** having crystal orientation in which extending direction of C face and the don of c-axis of the hexagonal structure are approximately aligned. As a result, the crystalline orientation is improved, and the thermoelectric Figure-of-Merit is increased.

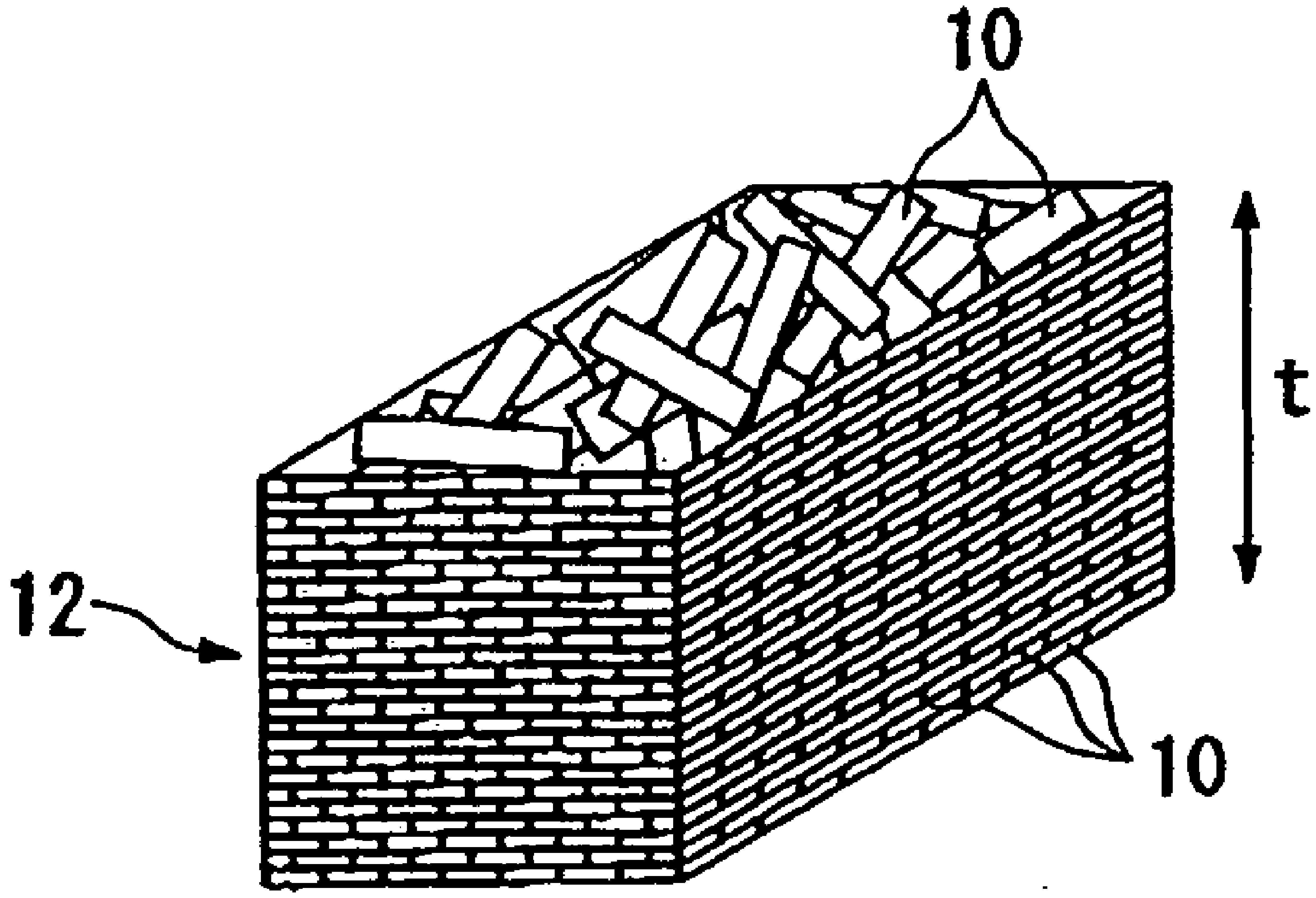


FIG.1

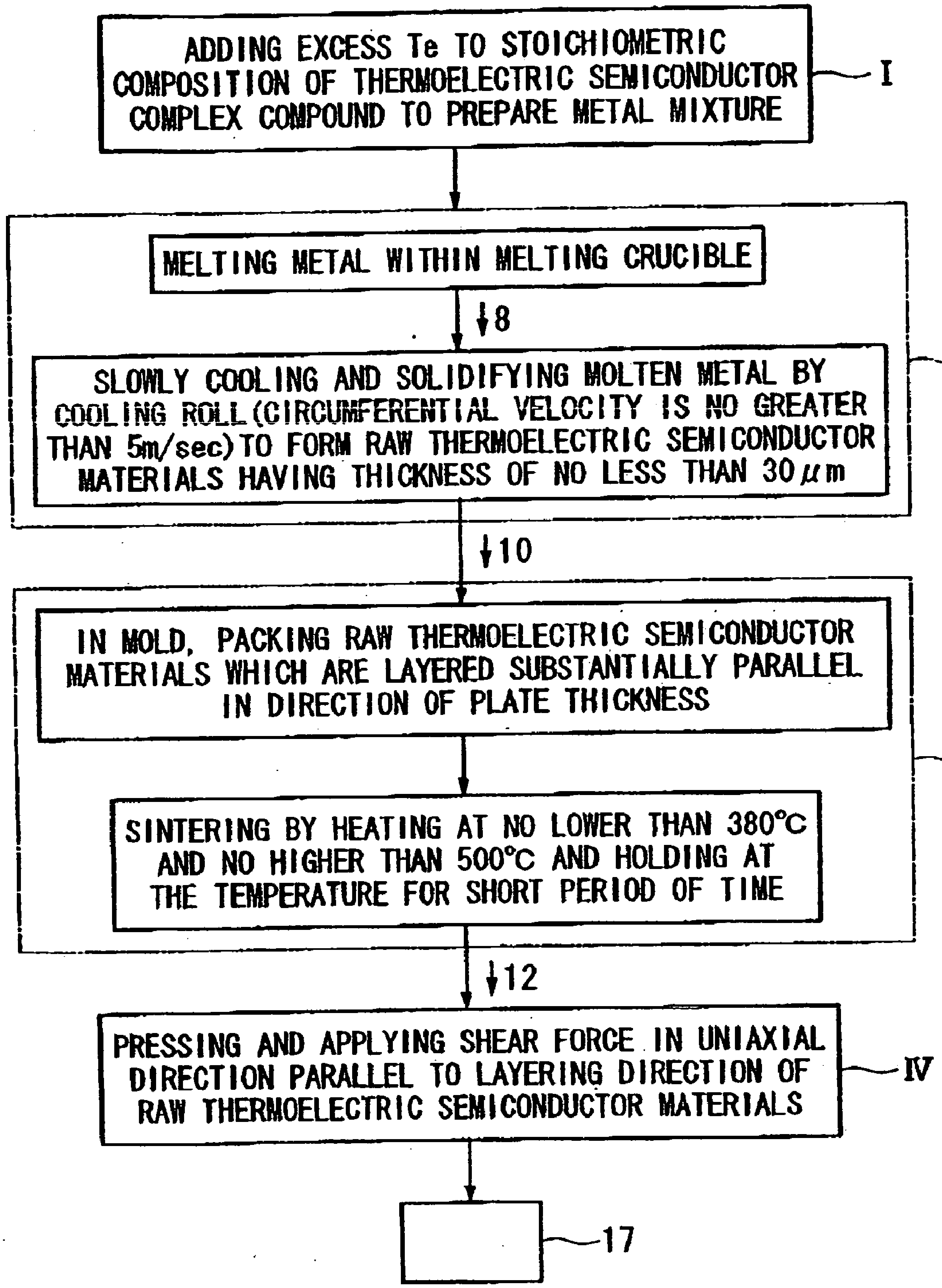

ADDING EXCESS Te TO STOICHIOMETRIC COMPOSITION OF THERMOELECTRIC SEMICONDUCTOR COMPLEX COMPOUND TO PREPARE METAL MIXTURE
I
MELTING METAL WITHIN MELTING CRUCIBLE
8
SLOWLY COOLING AND SOLIDIFYING MOLTEN METAL BY COOLING ROLL (CIRCUMFERENTIAL VELOCITY IS NO GREATER THAN 5m/sec) TO FORM RAW THERMOELECTRIC SEMICONDUCTOR MATERIALS HAVING THICKNESS OF NO LESS THAN 30μm
II
10
IN MOLD, PACKING RAW THERMOELECTRIC SEMICONDUCTOR MATERIALS WHICH ARE LAYERED SUBSTANTIALLY PARALLEL IN DIRECTION OF PLATE THICKNESS
SINTERING BY HEATING AT NO LOWER THAN 380°C AND NO HIGHER THAN 500°C AND HOLDING AT THE TEMPERATURE FOR SHORT PERIOD OF TIME
III
12
PRESSING AND APPLYING SHEAR FORCE IN UNIAXIAL DIRECTION PARALLEL TO LAYERING DIRECTION OF RAW THERMOELECTRIC SEMICONDUCTOR MATERIALS
IV
17

FIG. 2

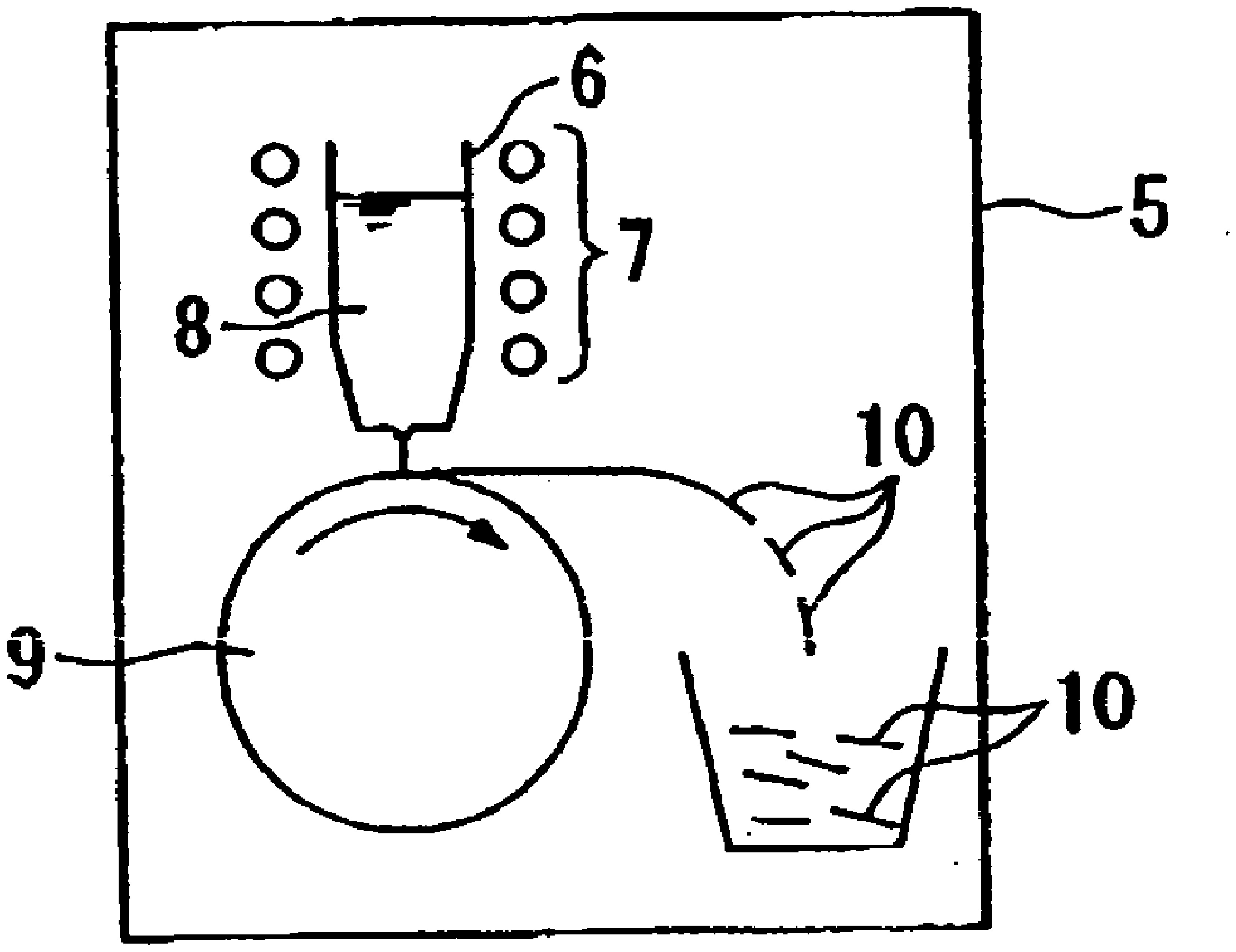


FIG. 3

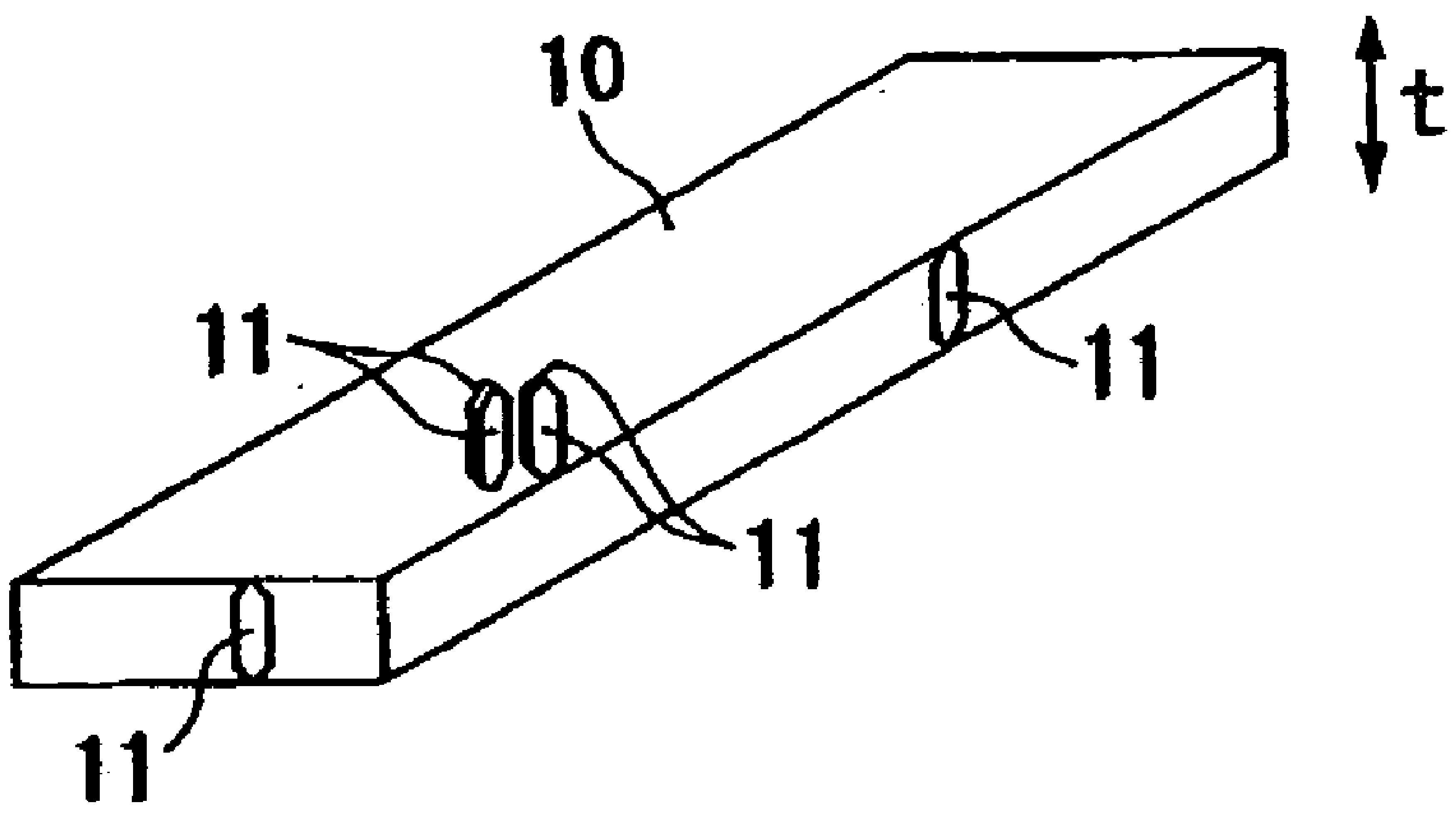


FIG. 4

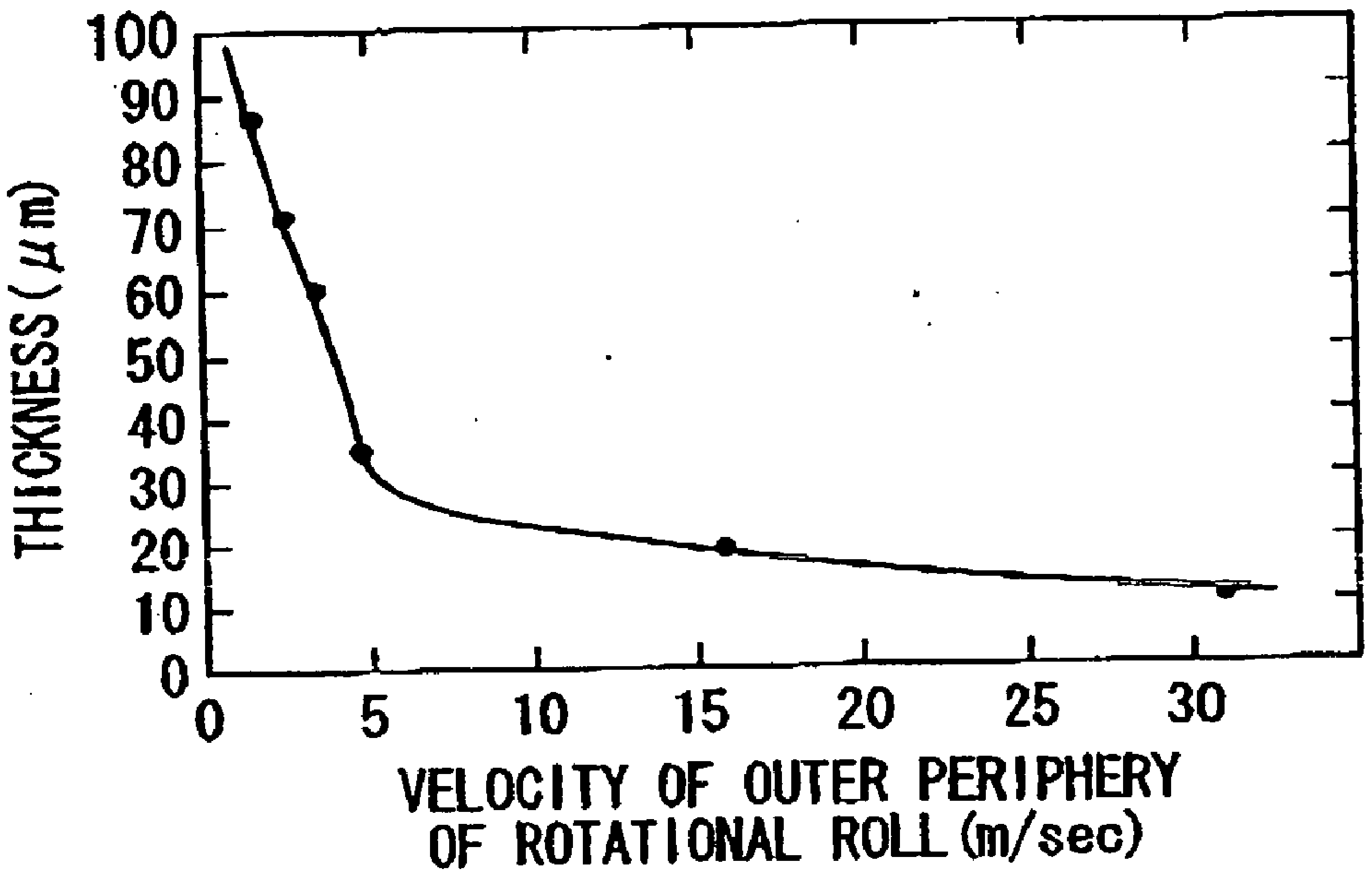

100
90
80
70
60
50
40
30
20
10
0
THICKNESS (μm)
0
5
10
15
20
25
30
VELOCITY OF OUTER PERIPHERY OF ROTATIONAL ROLL (m/sec)

FIG. 5

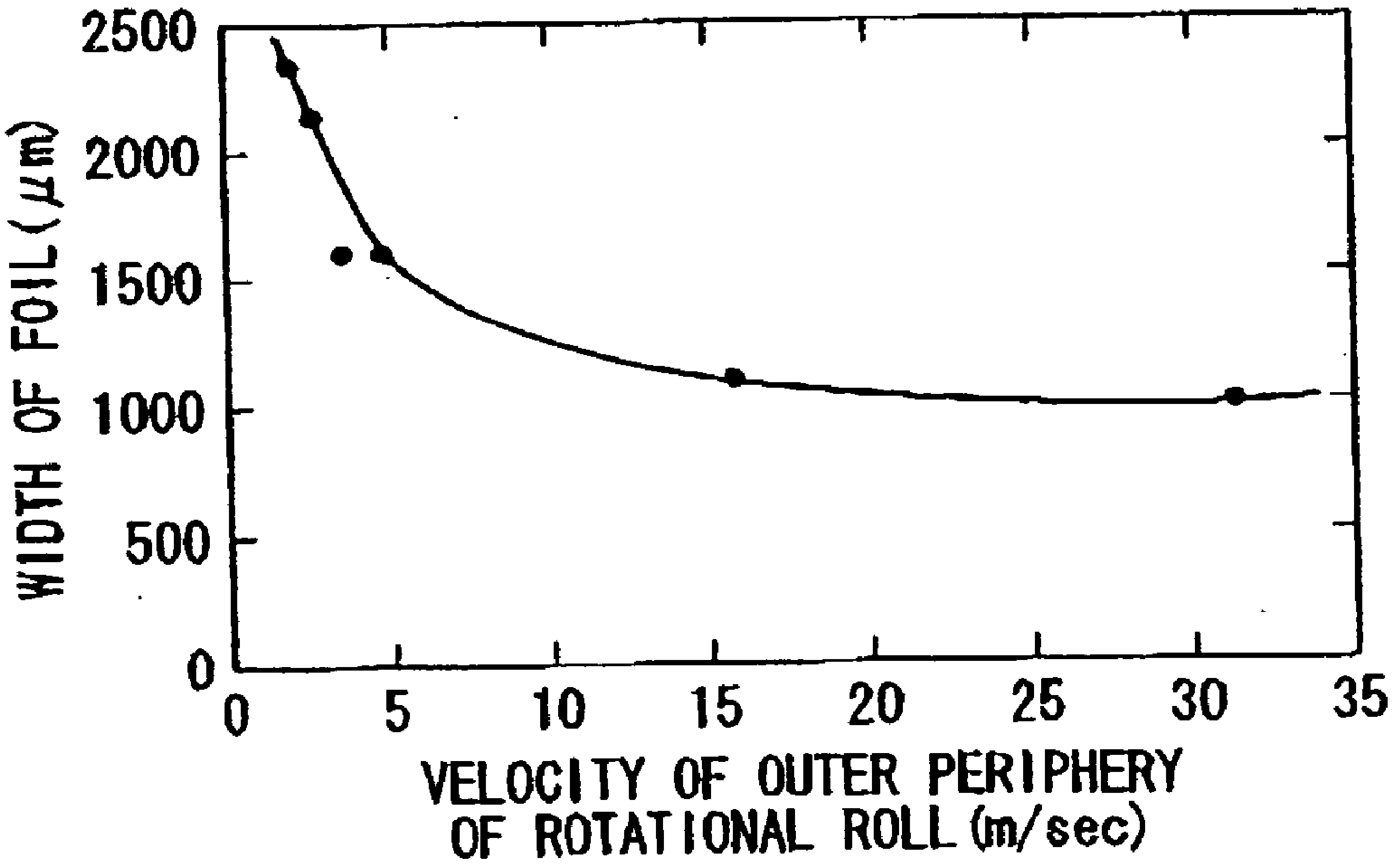

2500
2000
1500
1000
500
0
WIDTH OF FOIL (μm)
0
5
10
15
20
25
30
35
VELOCITY OF OUTER PERIPHERY OF ROTATIONAL ROLL (m/sec)

FIG. 6A

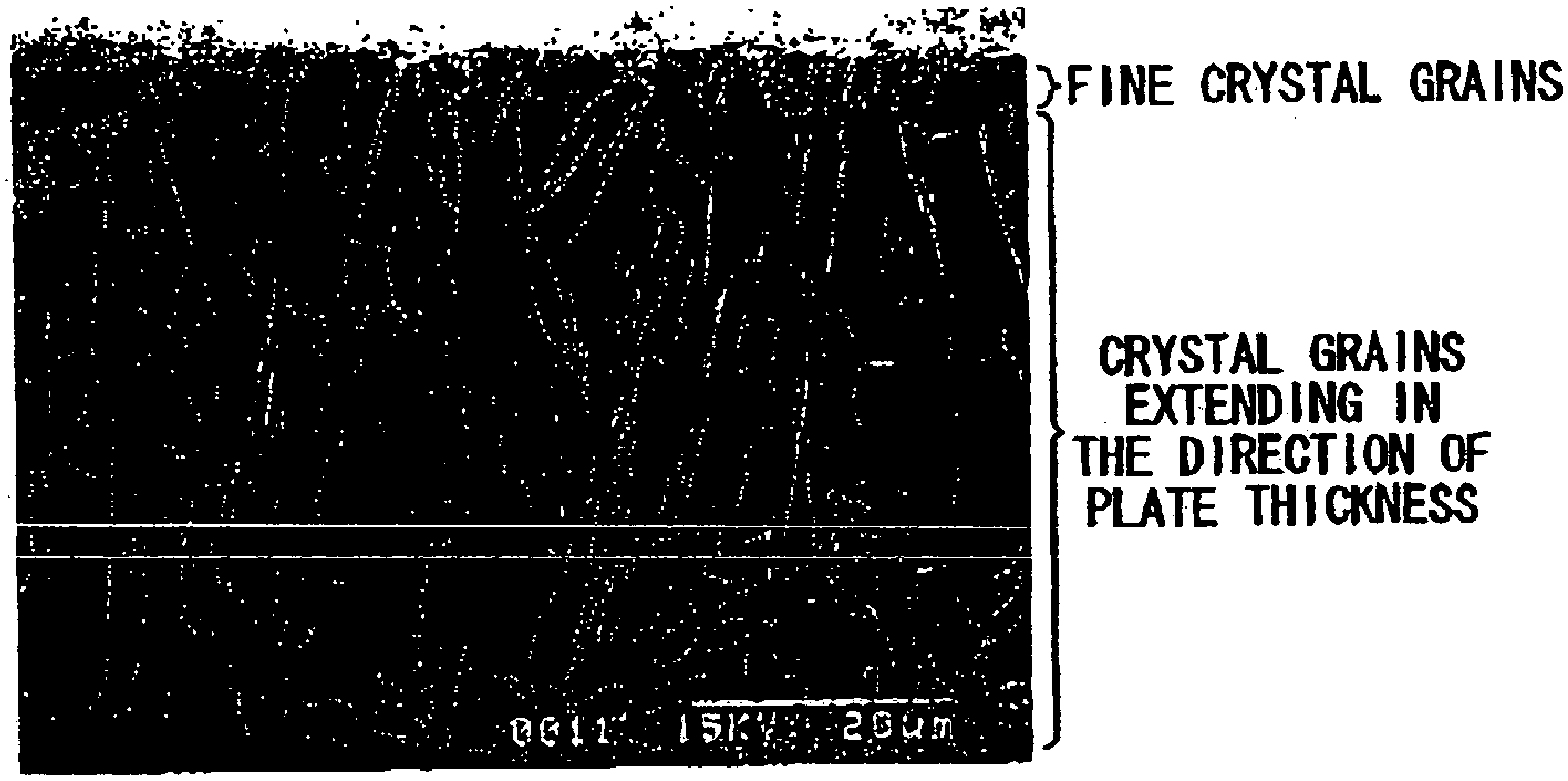

FINE CRYSTAL GRAINS
CRYSTAL GRAINS EXTENDING IN THE DIRECTION OF PLATE THICKNESS
0011 15KV 20um

FIG. 6B

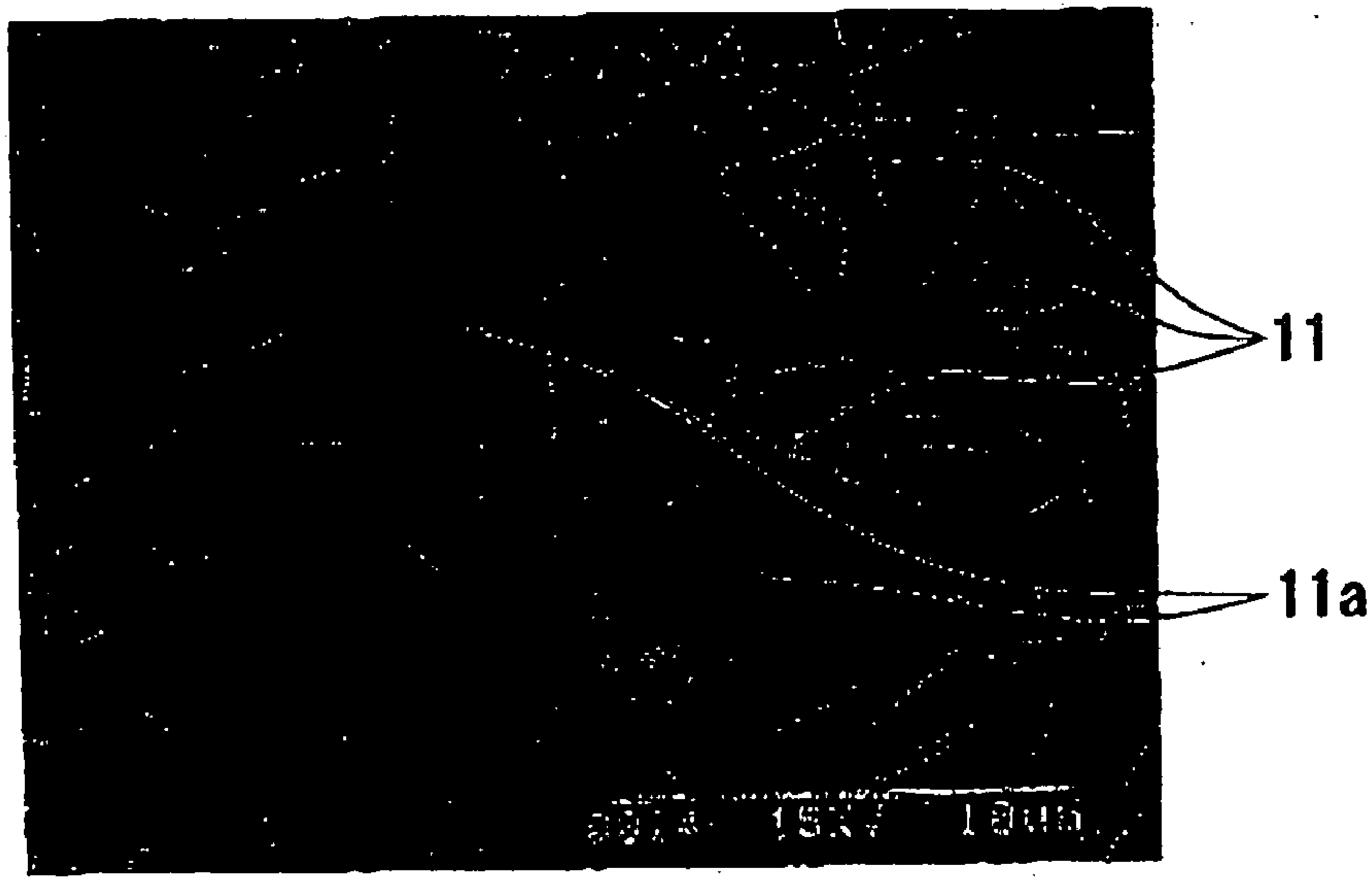

11
11a

FIG. 7A

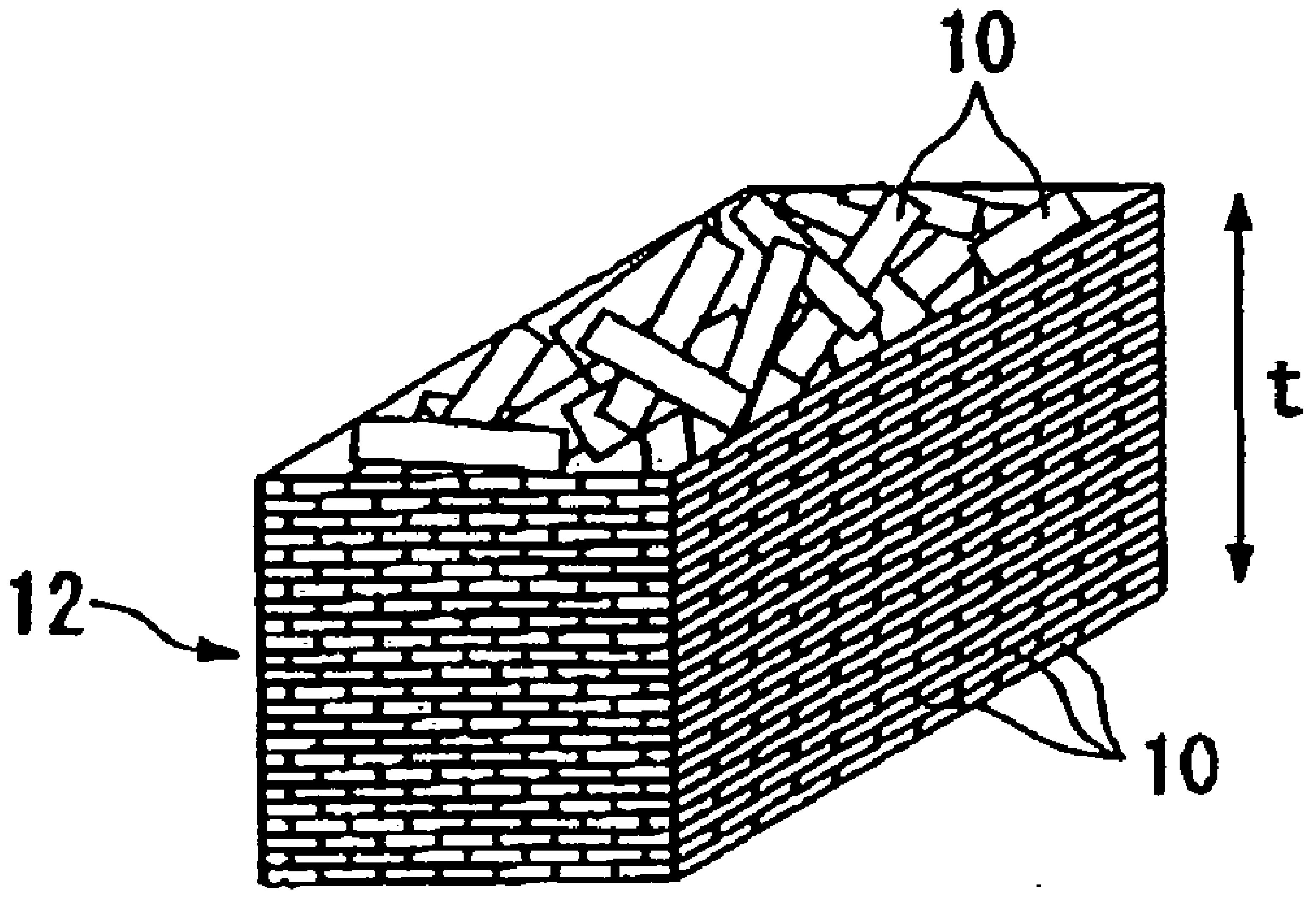


FIG. 7B

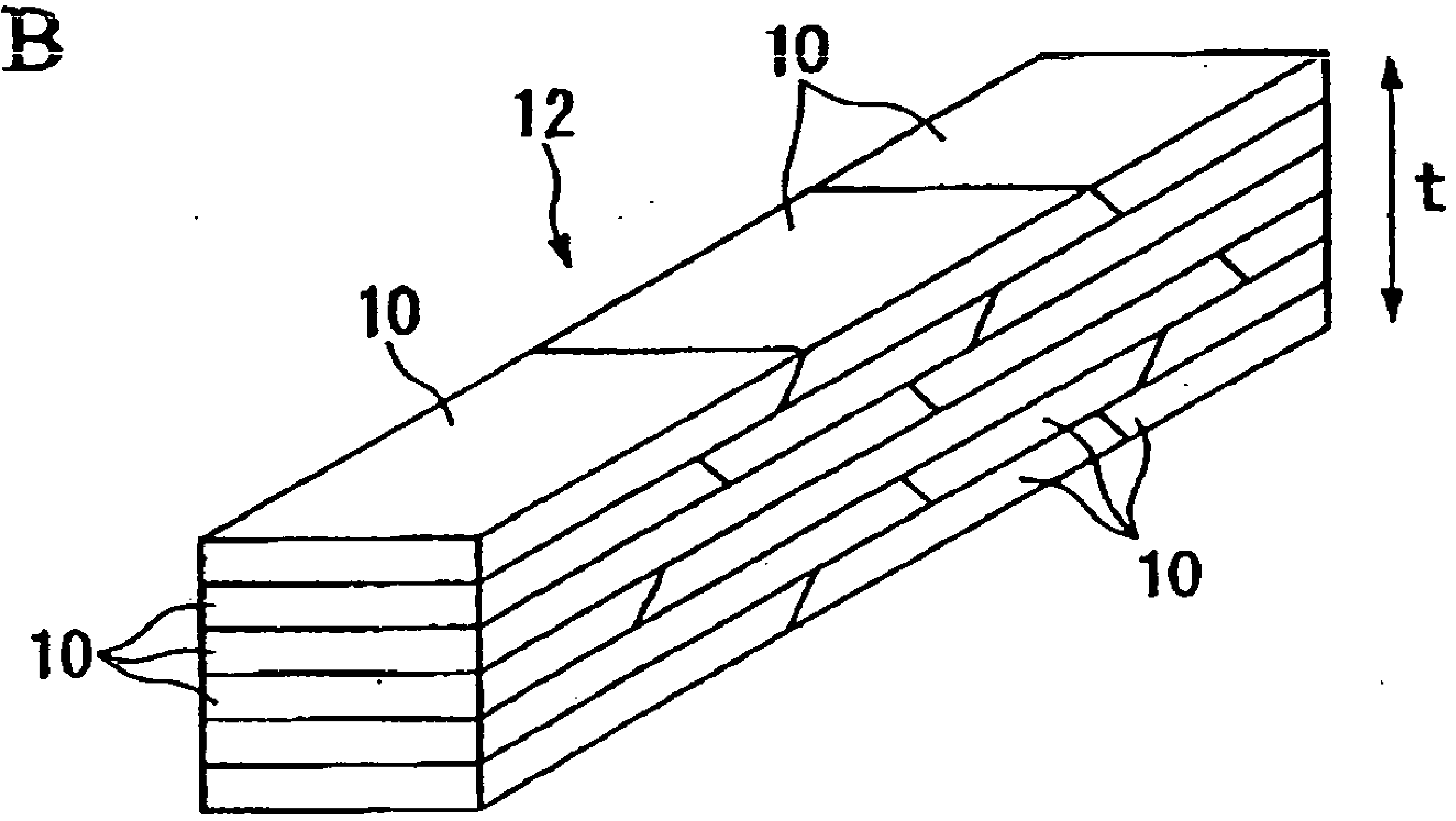


FIG. 7C

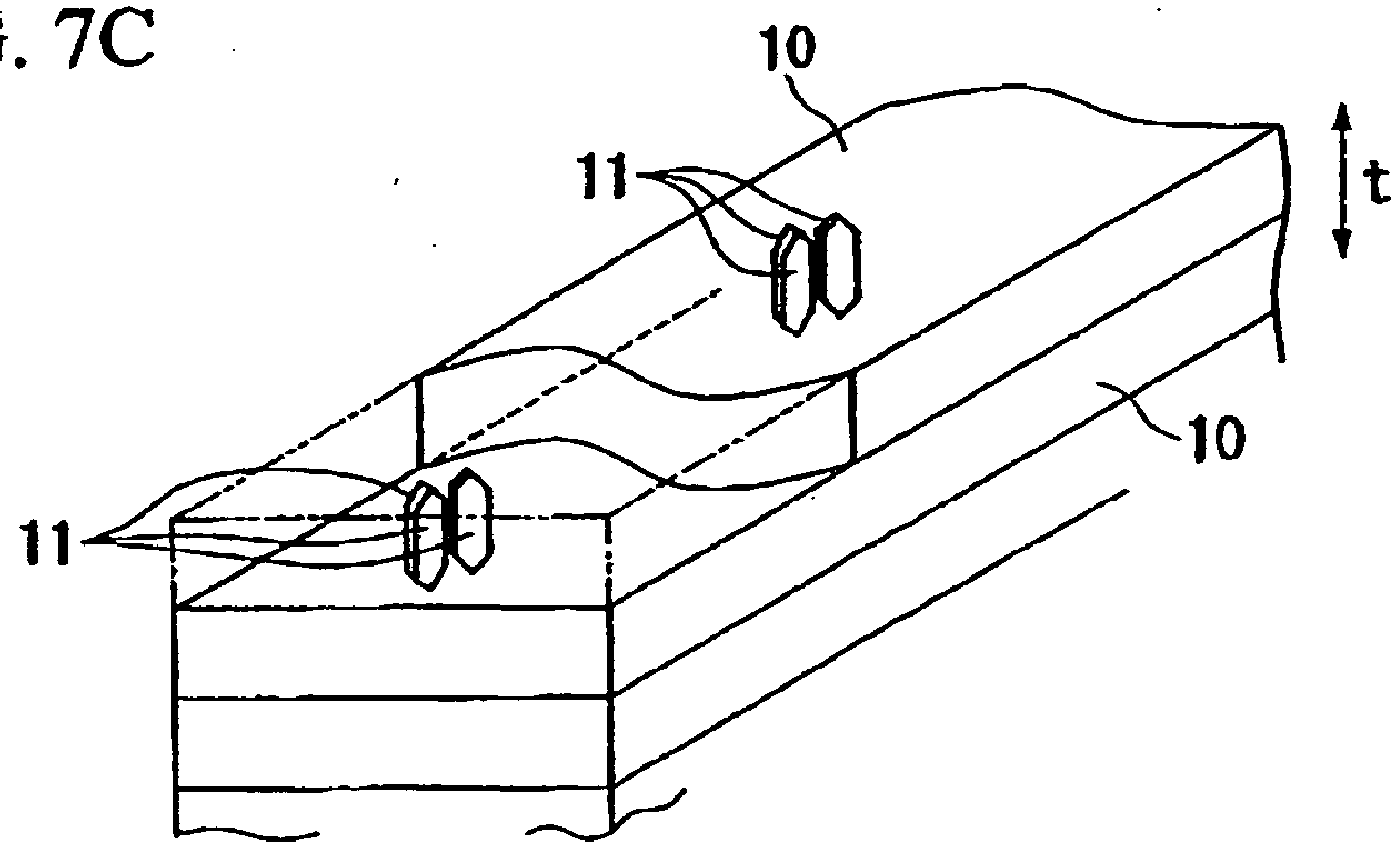


FIG. 8A

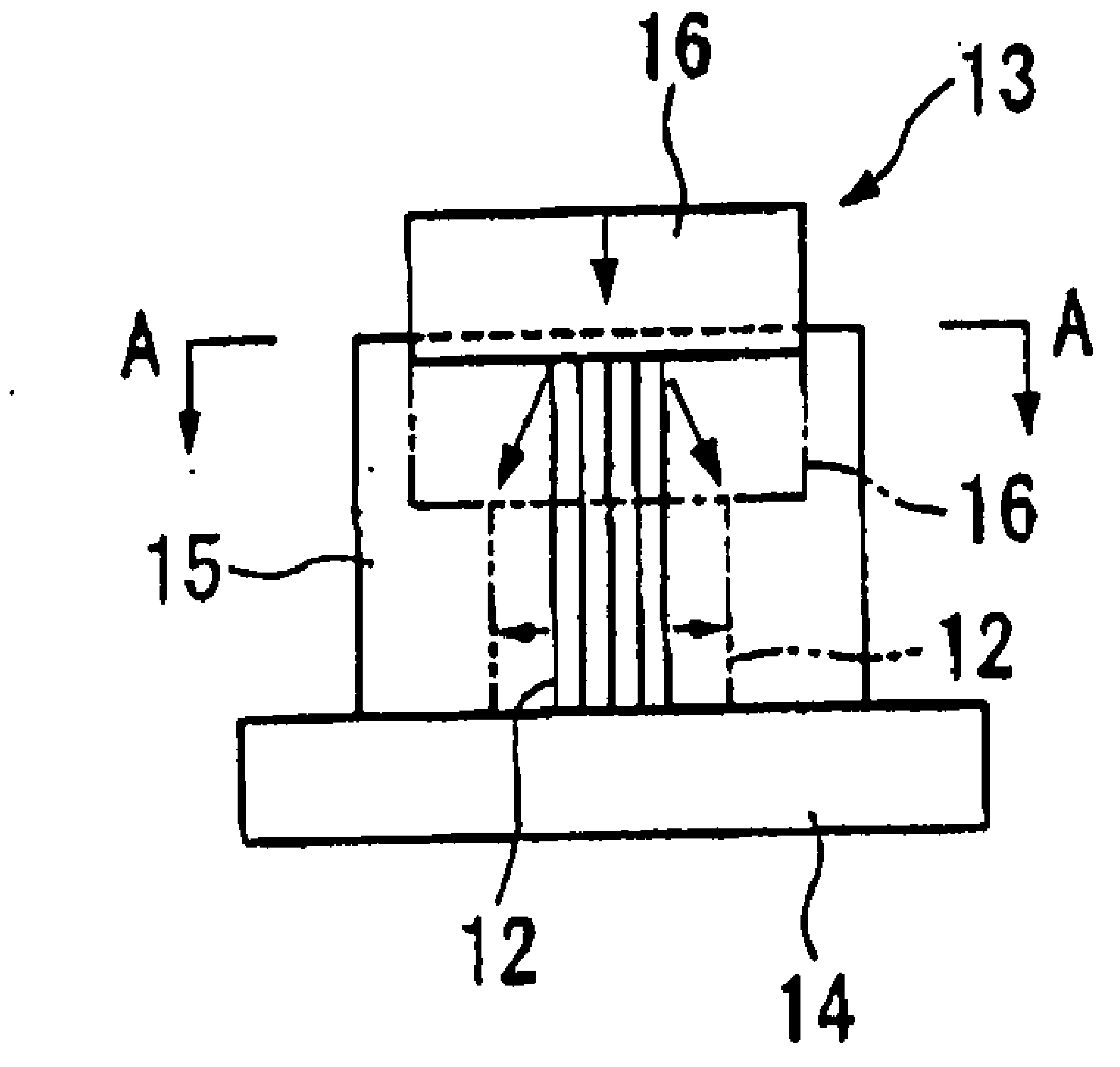


FIG. 8B

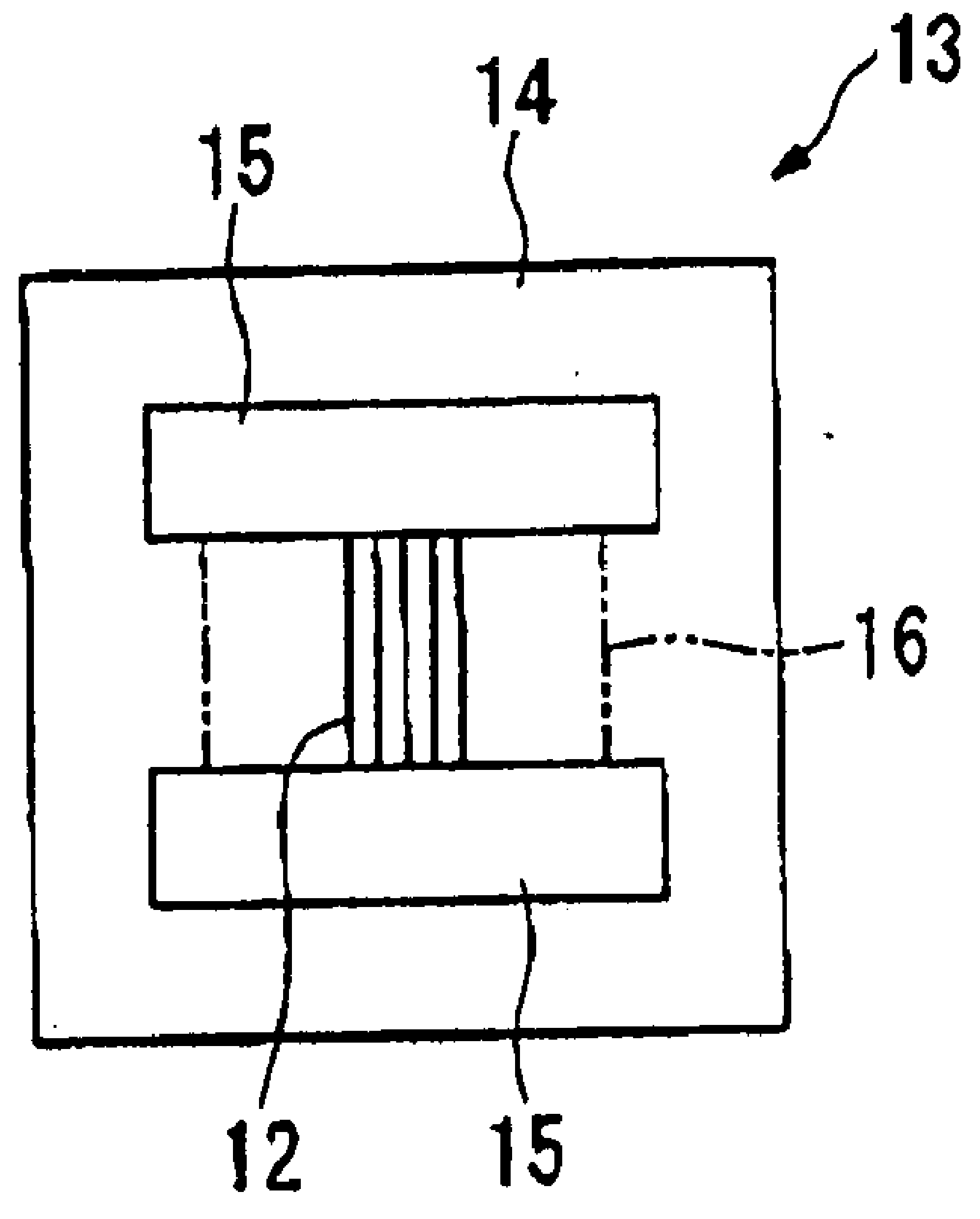


FIG. 8C

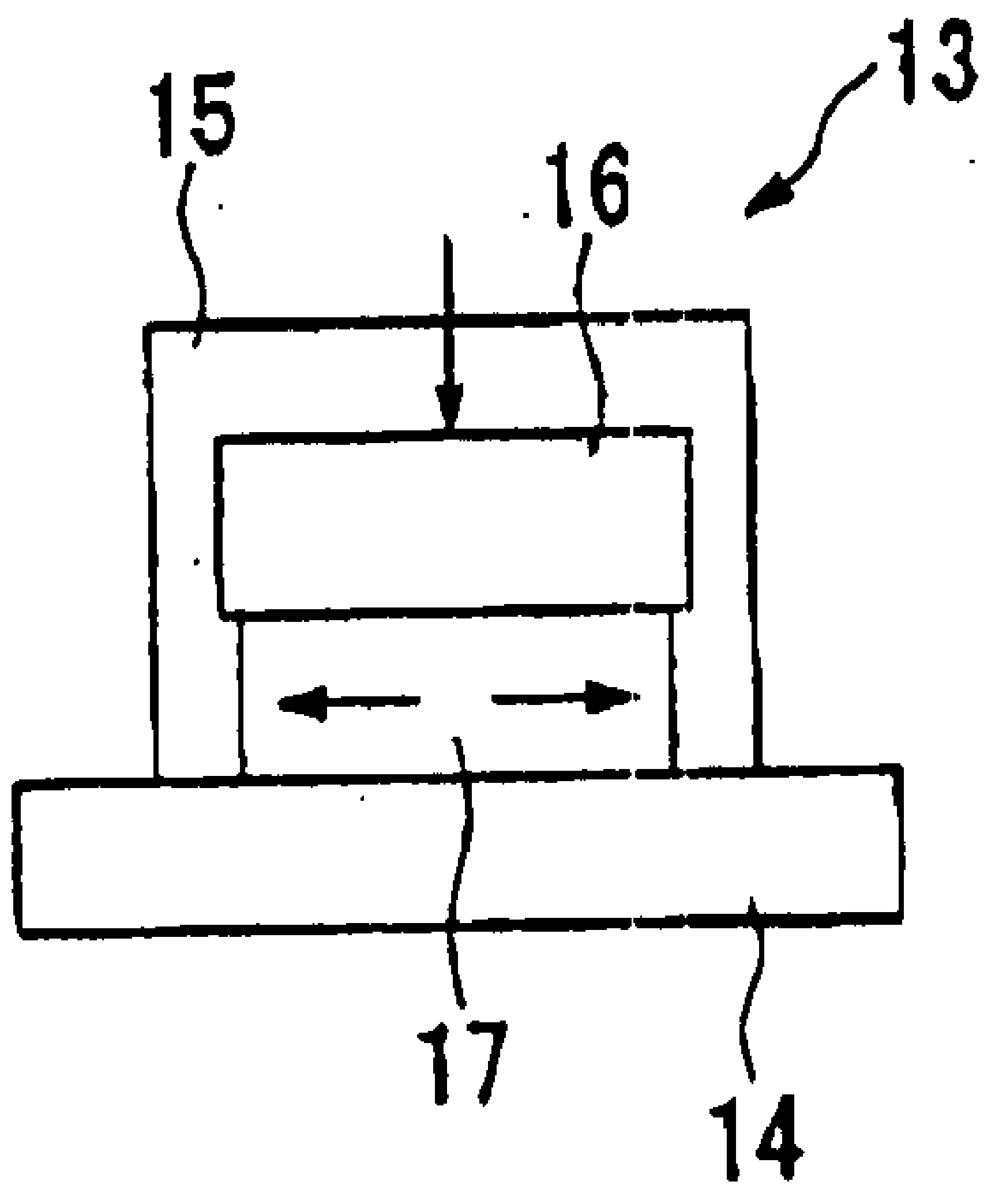


FIG. 8D

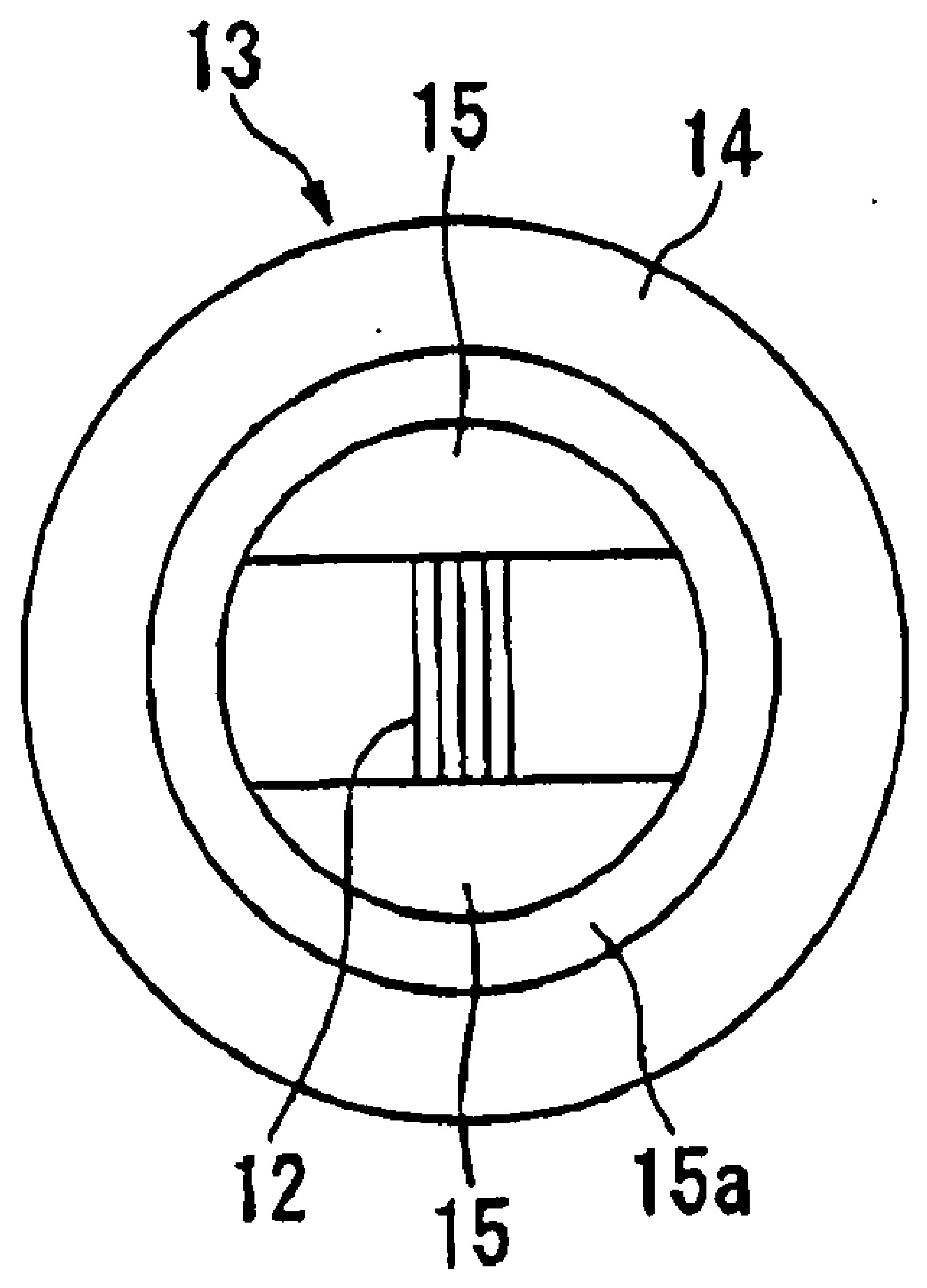


FIG. 9A

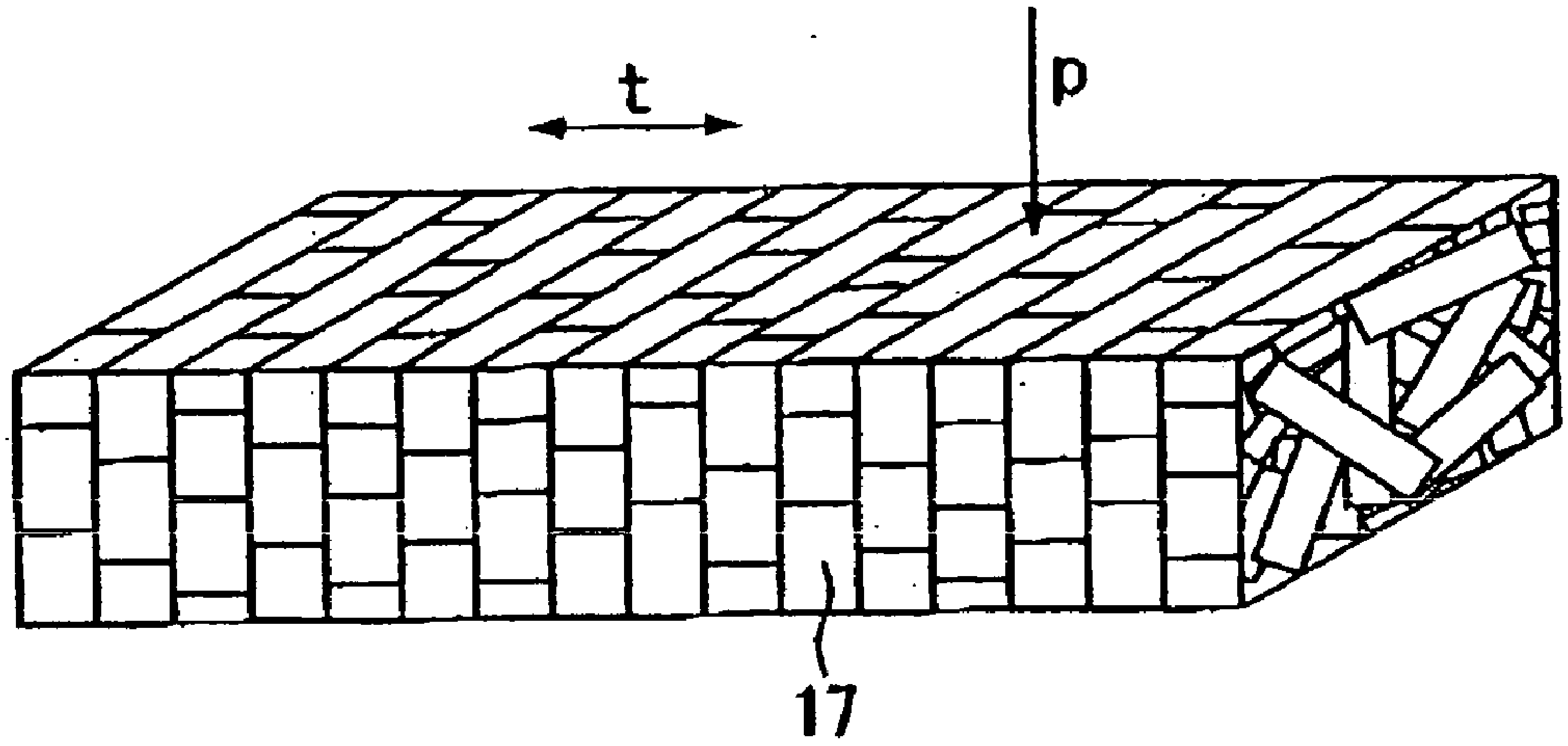


FIG. 9B

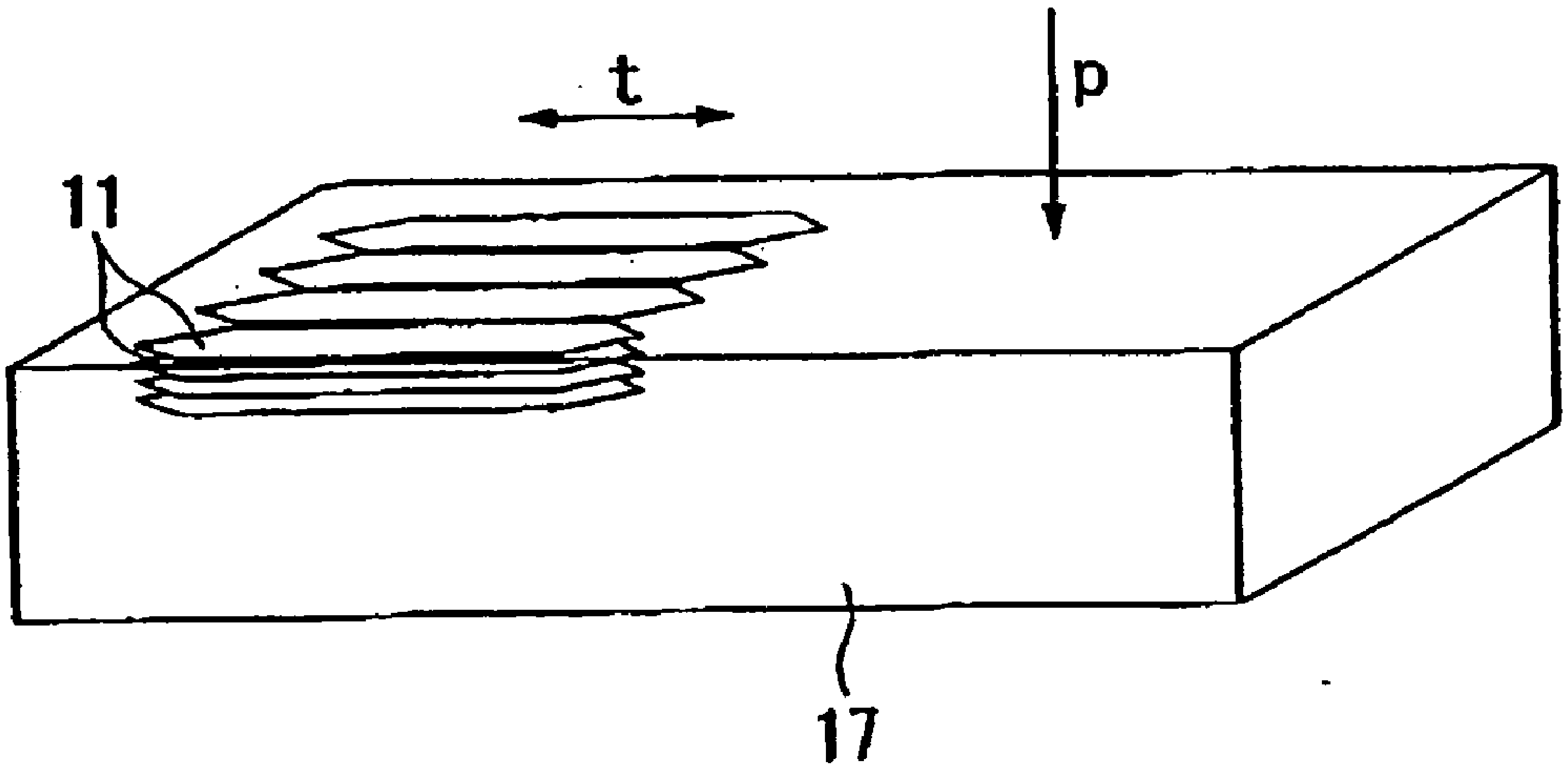


FIG. 10

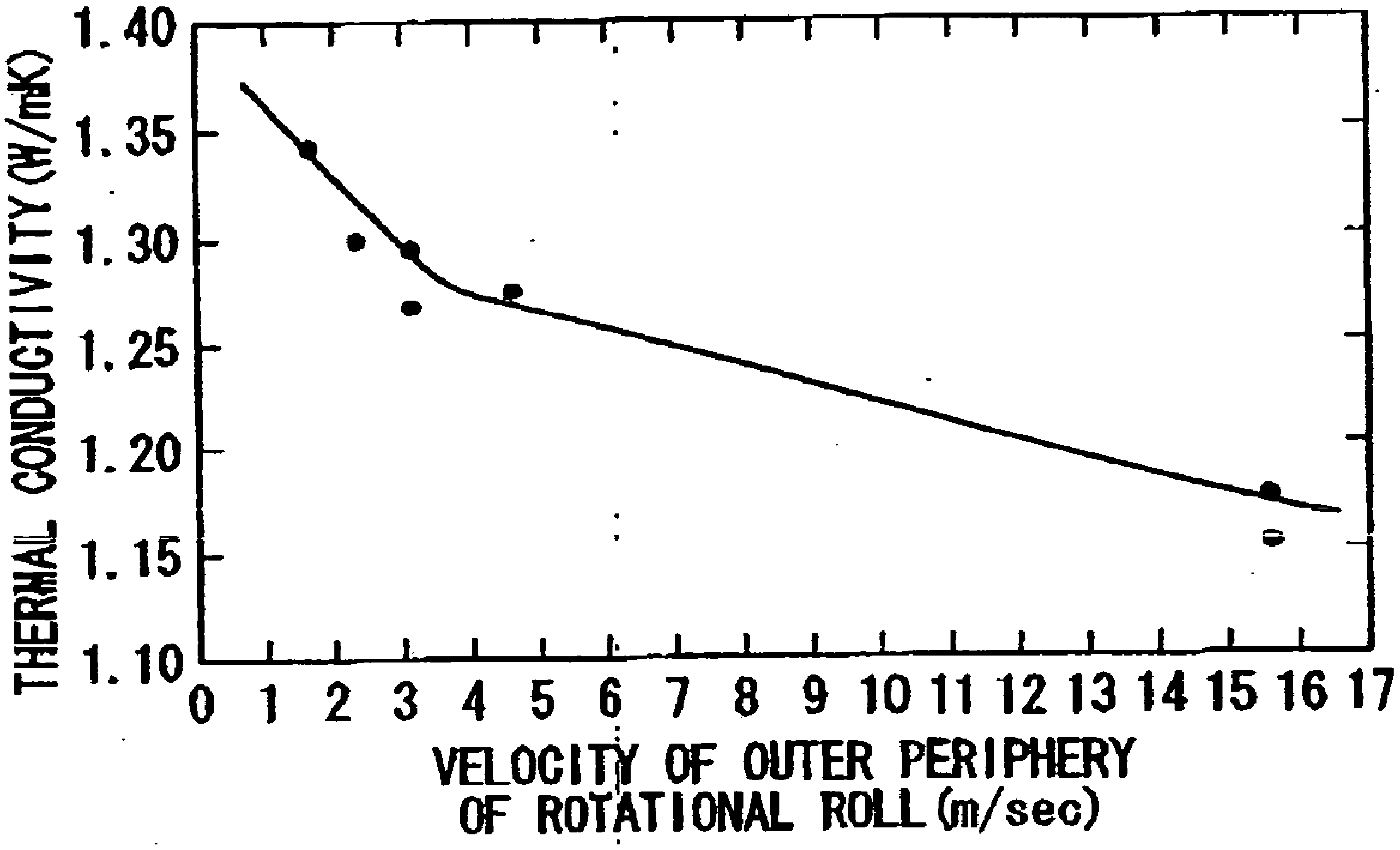

THERMAL CONDUCTIVITY (W/mK)
1.40
1.35
1.30
1.25
1.20
1.15
1.10
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
VELOCITY OF OUTER PERIPHERY OF ROTATIONAL ROLL (m/sec)

FIG. 11

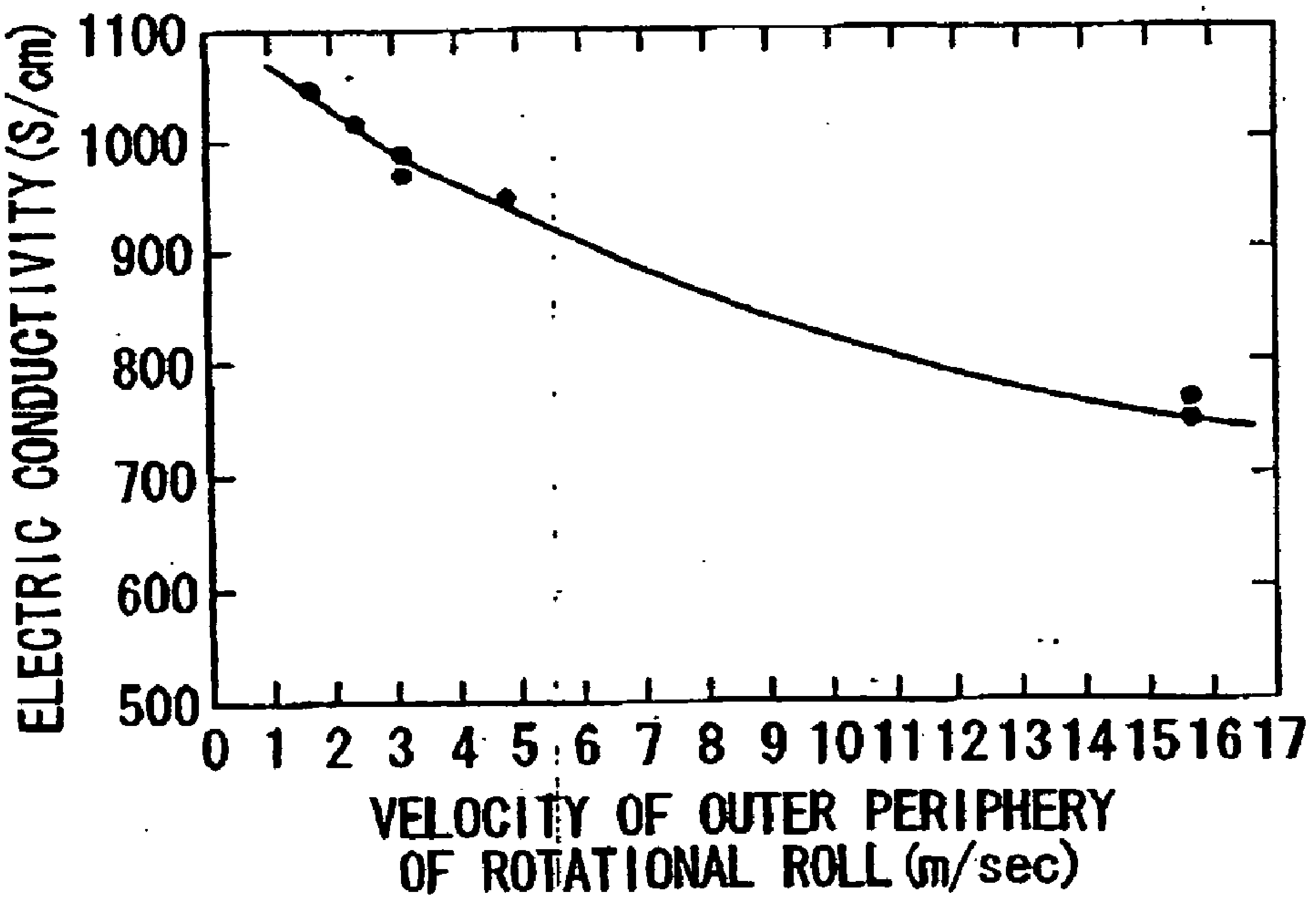

ELECTRIC CONDUCTIVITY (S/cm)
1100
1000
900
800
700
600
500
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
VELOCITY OF OUTER PERIPHERY OF ROTATIONAL ROLL (m/sec)

FIG. 12

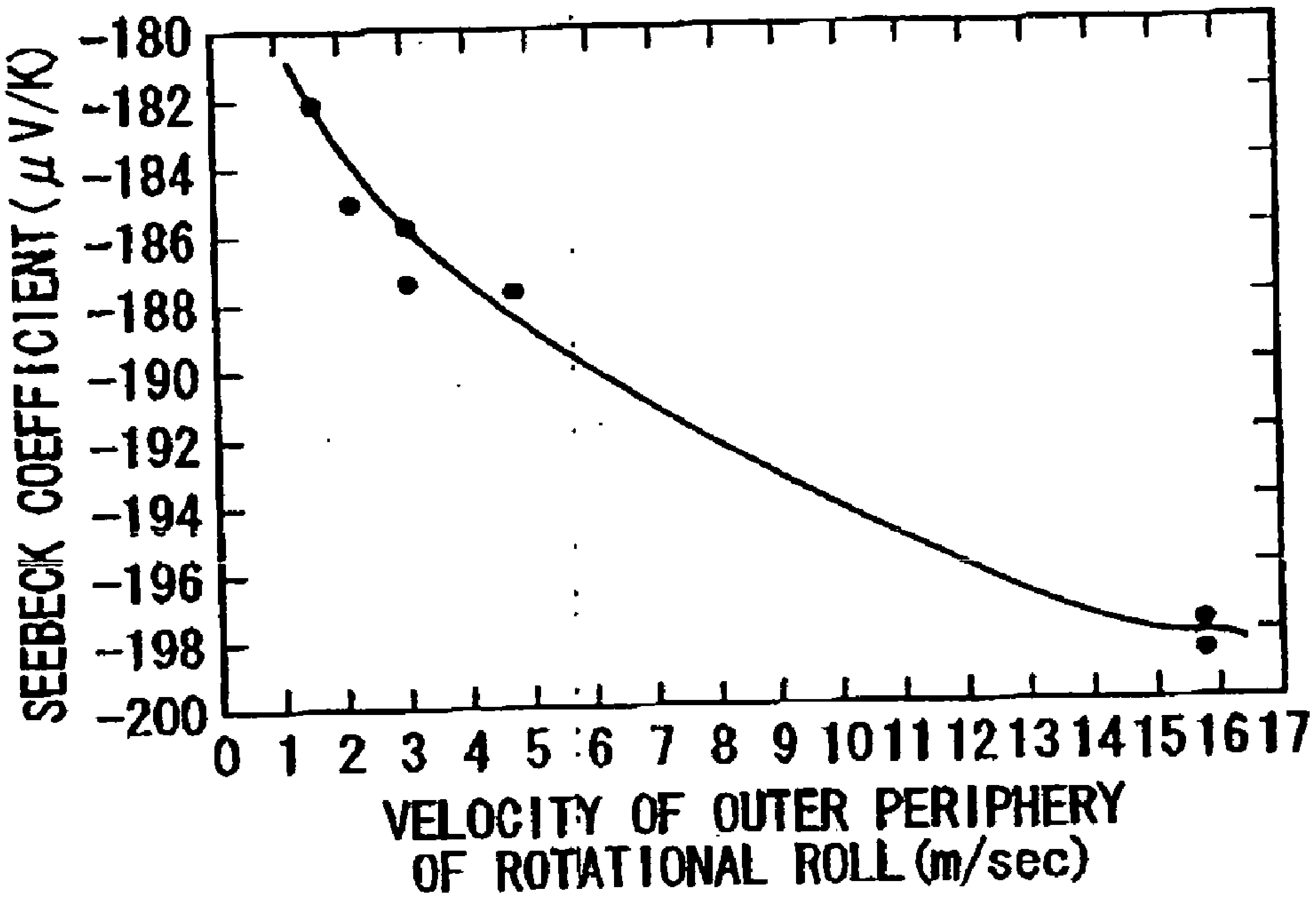

SEEBECK COEFFICIENT (μV/K)
-180
-182
-184
-186
-188
-190
-192
-194
-196
-198
-200
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
VELOCITY OF OUTER PERIPHERY OF ROTATIONAL ROLL (m/sec)

FIG. 13

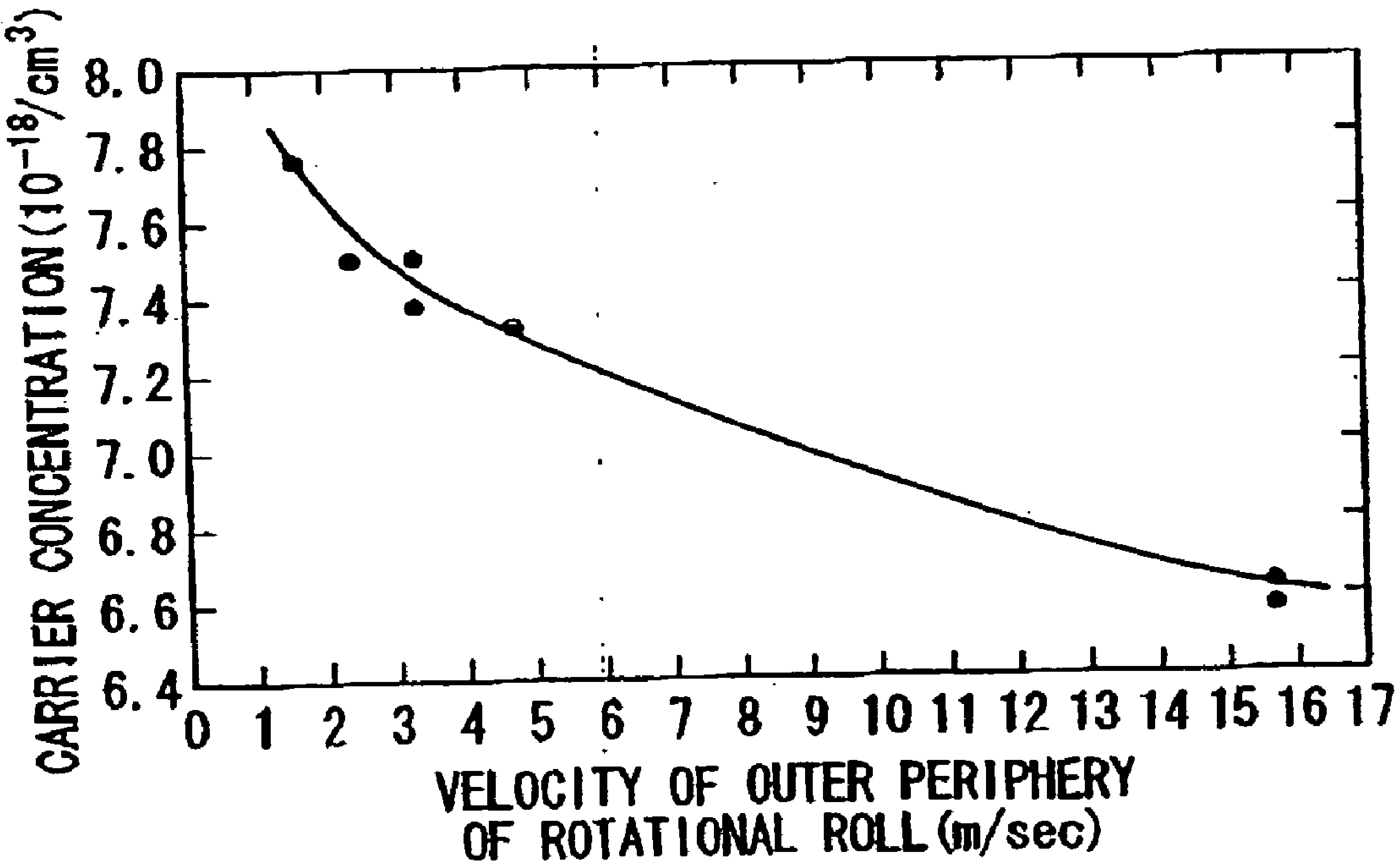

CARRIER CONCENTRATION (10^-18/cm^3)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
VELOCITY OF OUTER PERIPHERY OF ROTATIONAL ROLL (m/sec)

FIG. 14

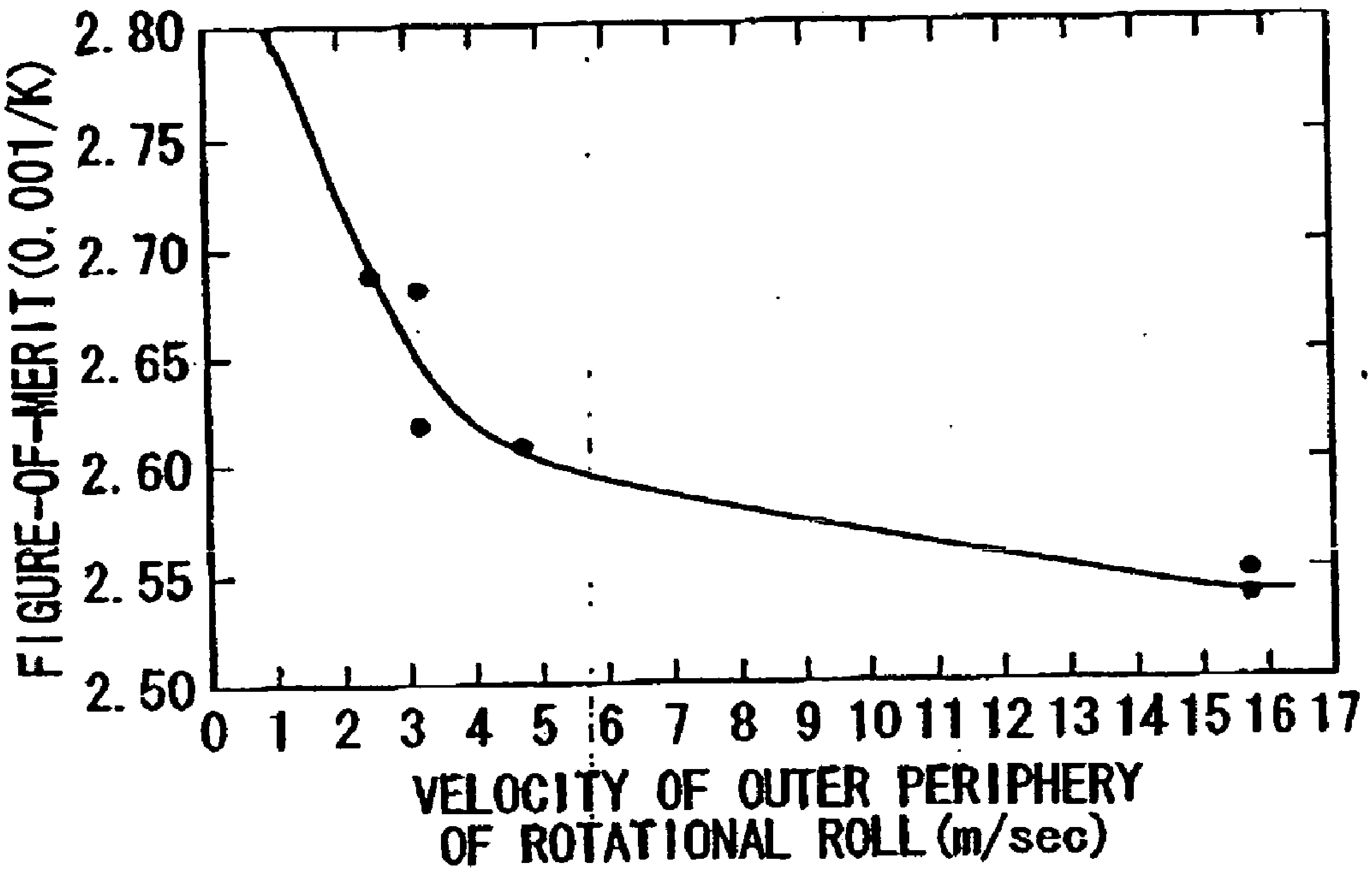


FIGURE-OF-MERIT(0.001/K)
2.80
2.75
2.70
2.65
2.60
2.55
2.50
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
VELOCITY OF OUTER PERIPHERY
OF ROTATIONAL ROLL(m/sec)

FIG. 15

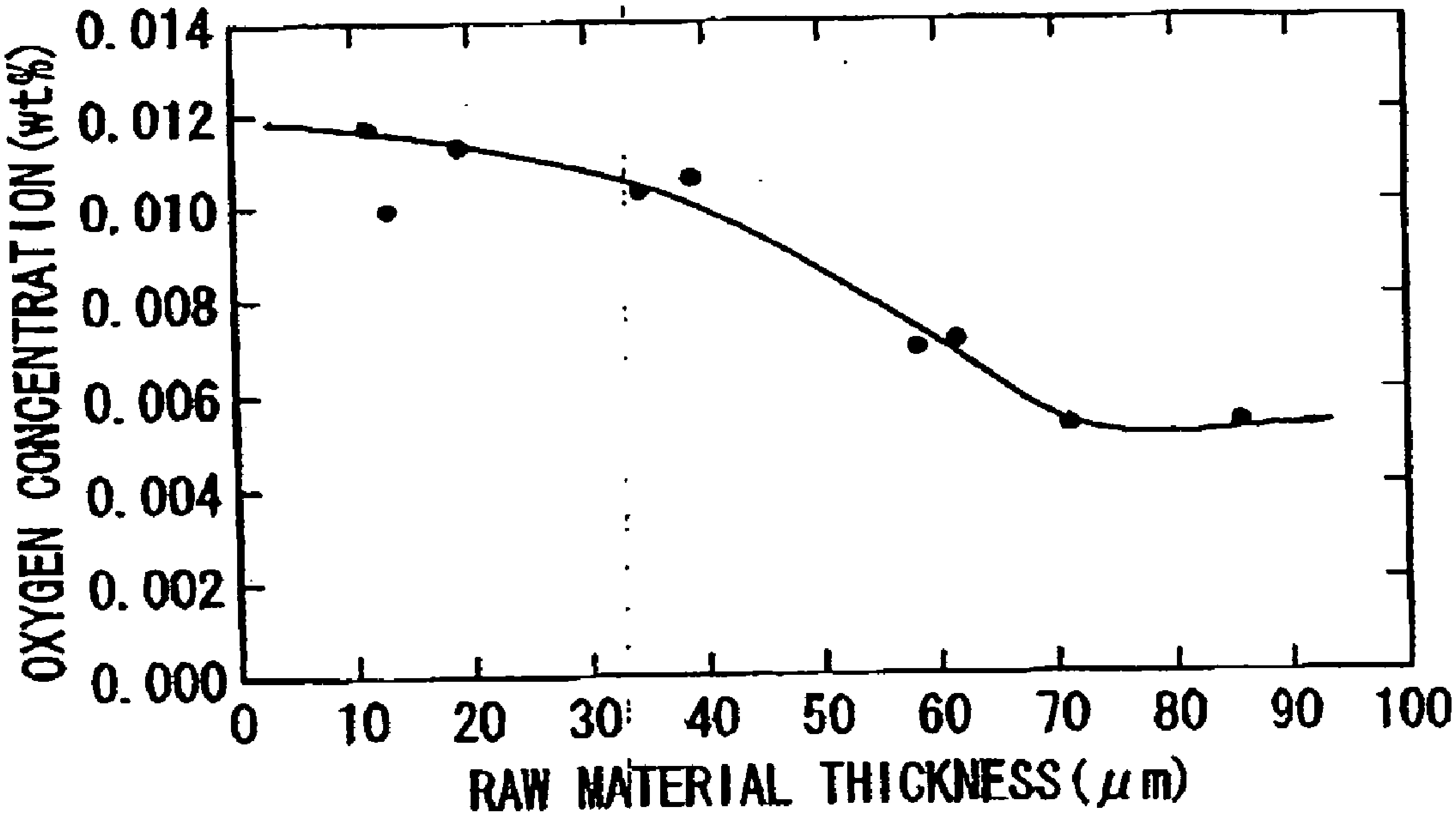

OXYGEN CONCENTRATION(wt%)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0 10 20 30 40 50 60 70 80 90 100
RAW MATERIAL THICKNESS(μm)

FIG. 16

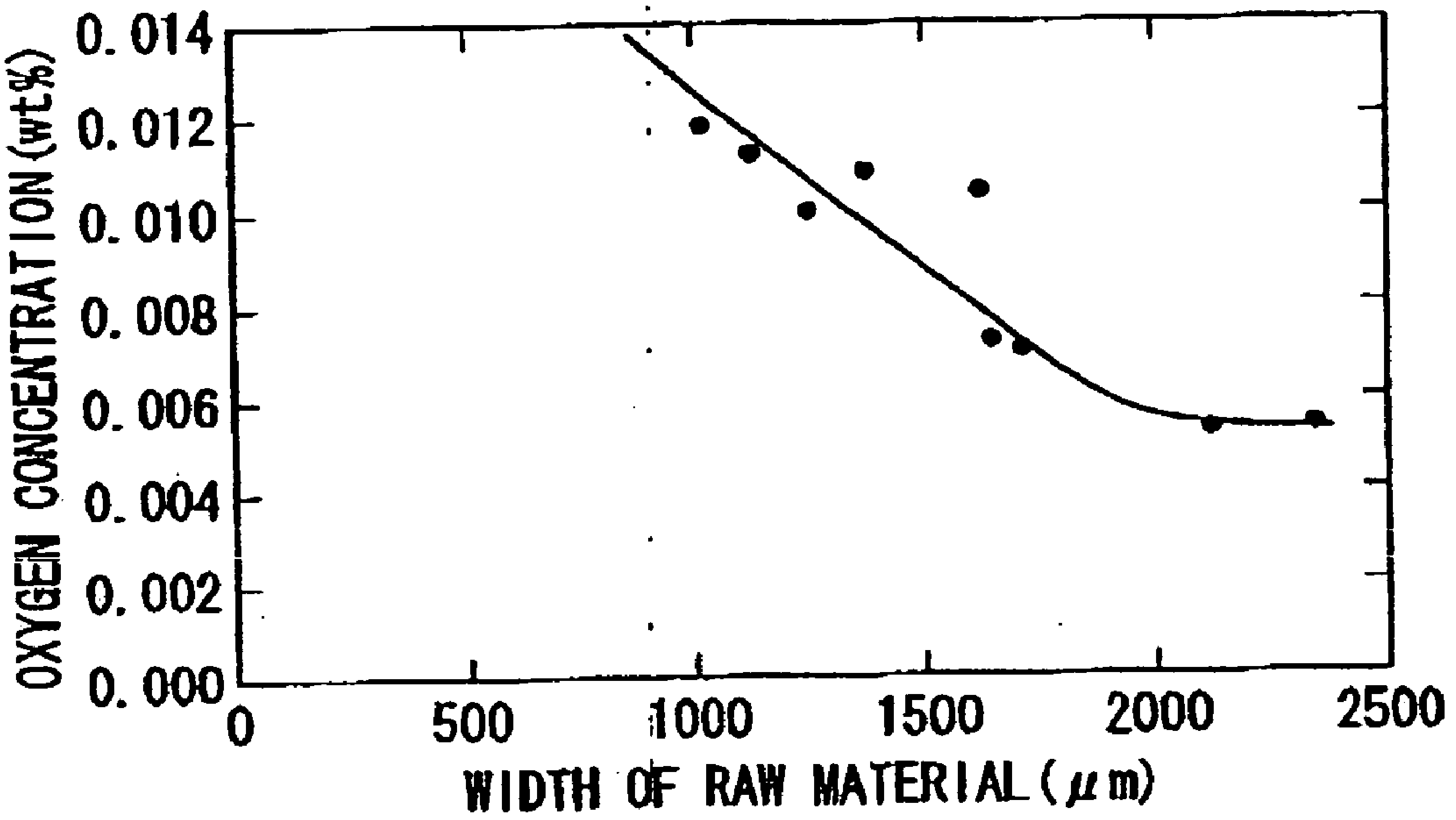

OXYGEN CONCENTRATION (wt%)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
500
1000
1500
2000
2500
WIDTH OF RAW MATERIAL (μm)

FIG. 17

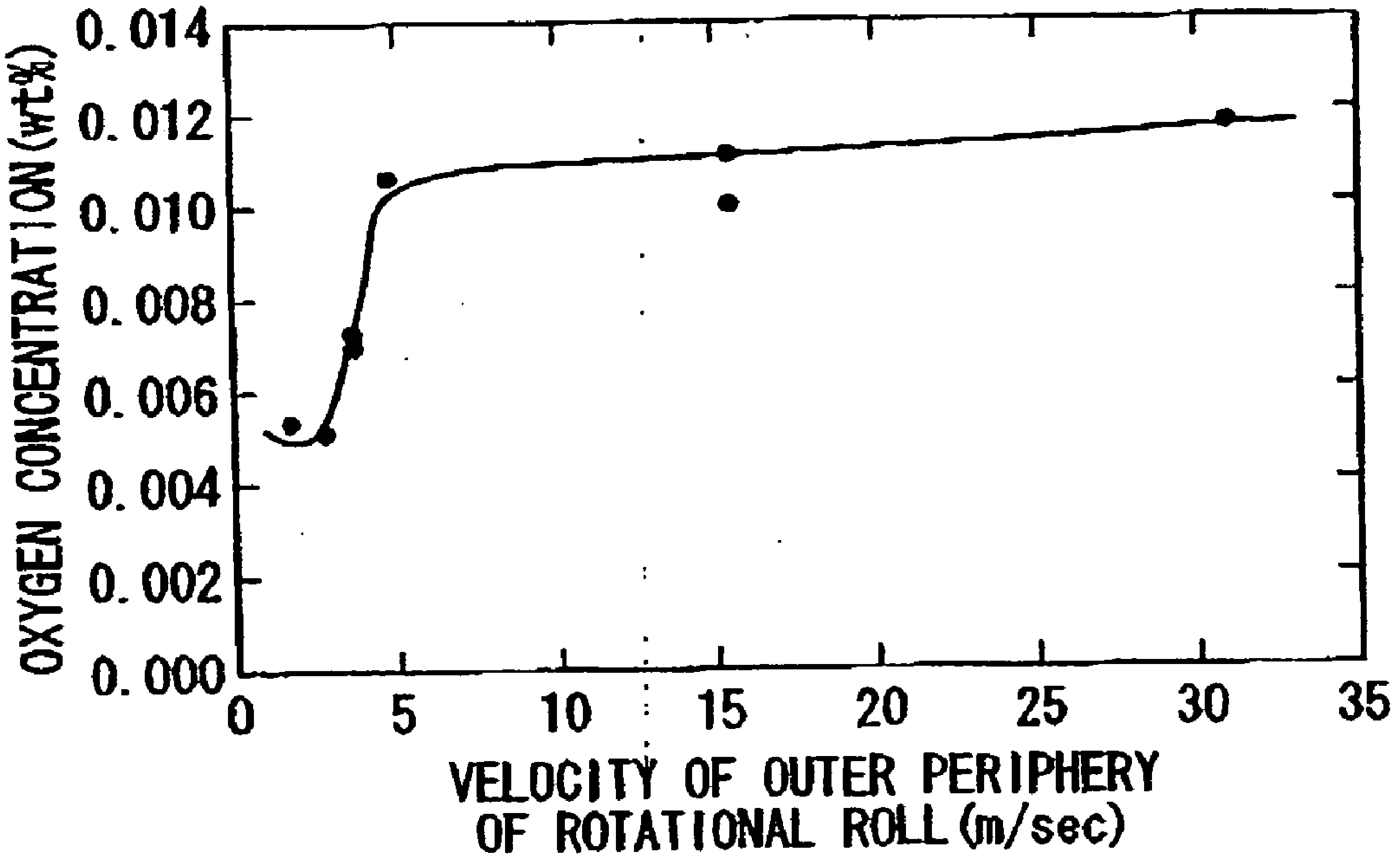

OXYGEN CONCENTRATION (wt%)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
5
10
15
20
25
30
35
VELOCITY OF OUTER PERIPHERY
OF ROTATIONAL ROLL (m/sec)

FIG. 18

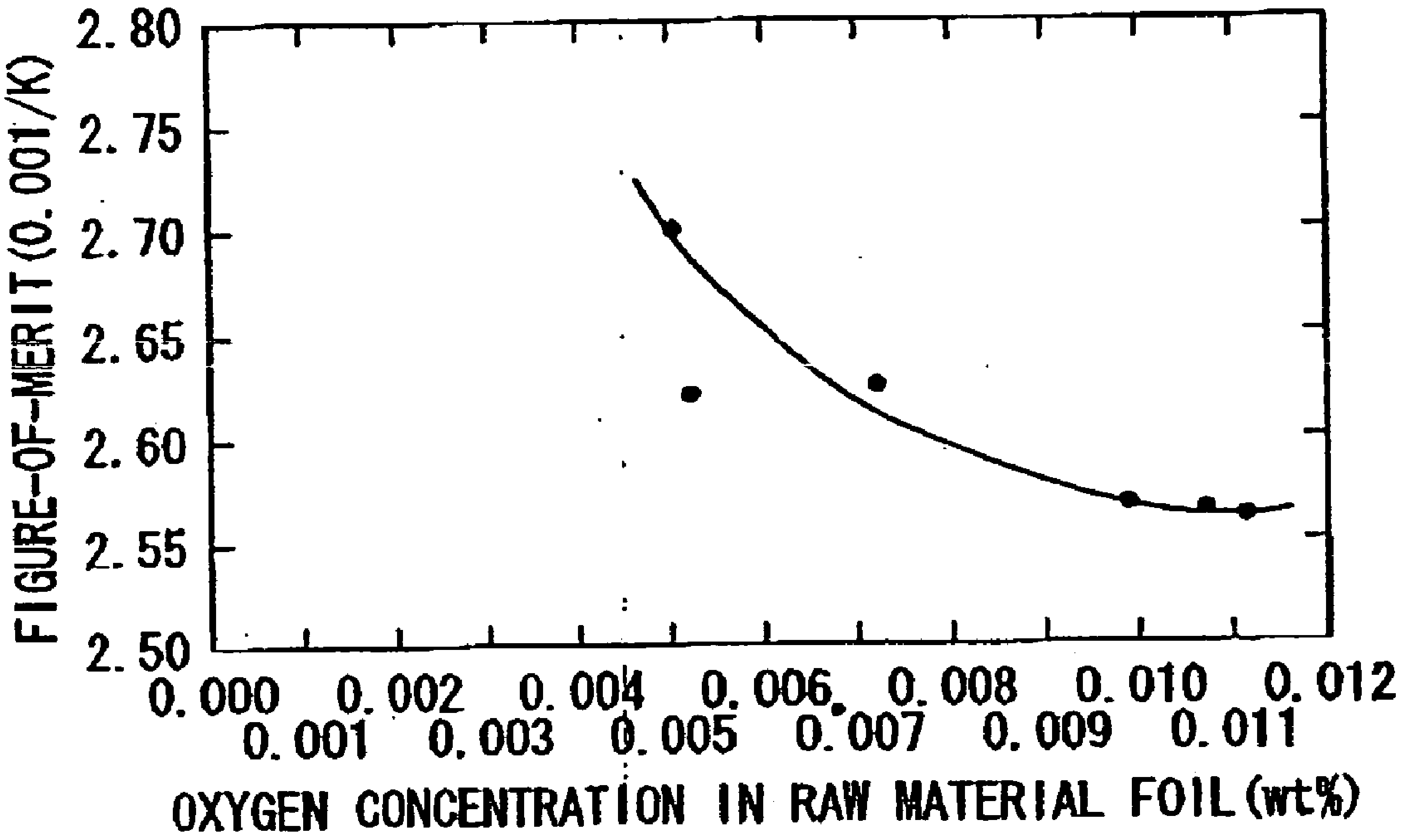
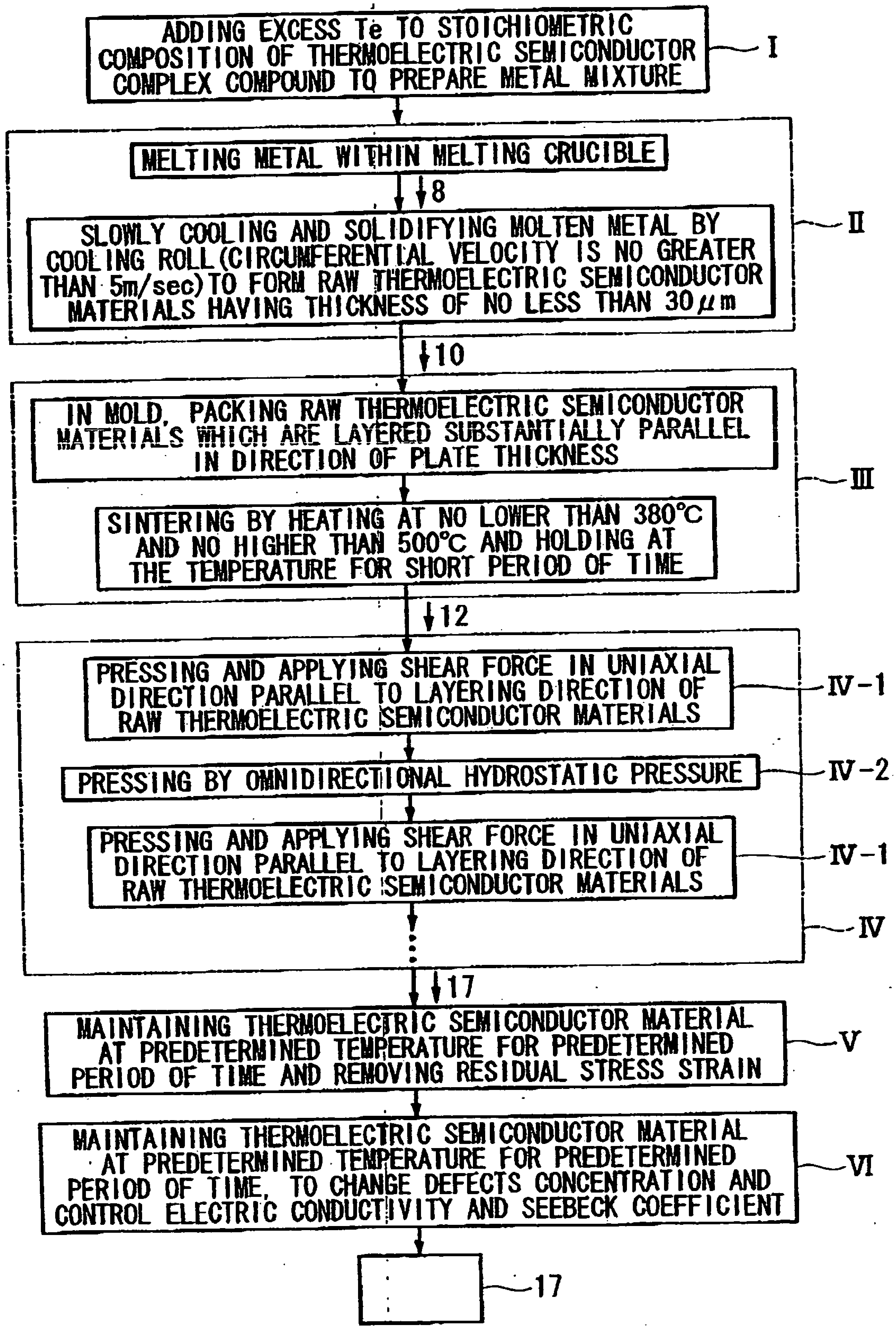


FIGURE-OF-MERIT (0.001/K)
2.80
2.75
2.70
2.65
2.60
2.55
2.50
0.000
0.001
0.002
0.003
0.004
0.005
0.006
0.007
0.008
0.009
0.010
0.011
0.012
OXYGEN CONCENTRATION IN RAW MATERIAL FOIL(wt%)

FIG.19


ADDING EXCESS Te TO STOICHIOMETRIC COMPOSITION OF THERMOELECTRIC SEMICONDUCTOR COMPLEX COMPOUND TO PREPARE METAL MIXTURE
I
MELTING METAL WITHIN MELTING CRUCIBLE
8
SLOWLY COOLING AND SOLIDIFYING MOLTEN METAL BY COOLING ROLL (CIRCUMFERENTIAL VELOCITY IS NO GREATER THAN 5m/sec) TO FORM RAW THERMOELECTRIC SEMICONDUCTOR MATERIALS HAVING THICKNESS OF NO LESS THAN 30μm
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10
IN MOLD, PACKING RAW THERMOELECTRIC SEMICONDUCTOR MATERIALS WHICH ARE LAYERED SUBSTANTIALLY PARALLEL IN DIRECTION OF PLATE THICKNESS
SINTERING BY HEATING AT NO LOWER THAN 380°C AND NO HIGHER THAN 500°C AND HOLDING AT THE TEMPERATURE FOR SHORT PERIOD OF TIME
III
12
PRESSING AND APPLYING SHEAR FORCE IN UNIAXIAL DIRECTION PARALLEL TO LAYERING DIRECTION OF RAW THERMOELECTRIC SEMICONDUCTOR MATERIALS
IV-1
PRESSING BY OMNIDIRECTIONAL HYDROSTATIC PRESSURE
IV-2
PRESSING AND APPLYING SHEAR FORCE IN UNIAXIAL DIRECTION PARALLEL TO LAYERING DIRECTION OF RAW THERMOELECTRIC SEMICONDUCTOR MATERIALS
IV-1
IV
17
MAINTAINING THERMOELECTRIC SEMICONDUCTOR MATERIAL AT PREDETERMINED TEMPERATURE FOR PREDETERMINED PERIOD OF TIME AND REMOVING RESIDUAL STRESS STRAIN
V
MAINTAINING THERMOELECTRIC SEMICONDUCTOR MATERIAL AT PREDETERMINED TEMPERATURE FOR PREDETERMINED PERIOD OF TIME, TO CHANGE DEFECTS CONCENTRATION AND CONTROL ELECTRIC CONDUCTIVITY AND SEEBECK COEFFICIENT
VI
17

FIG. 20A

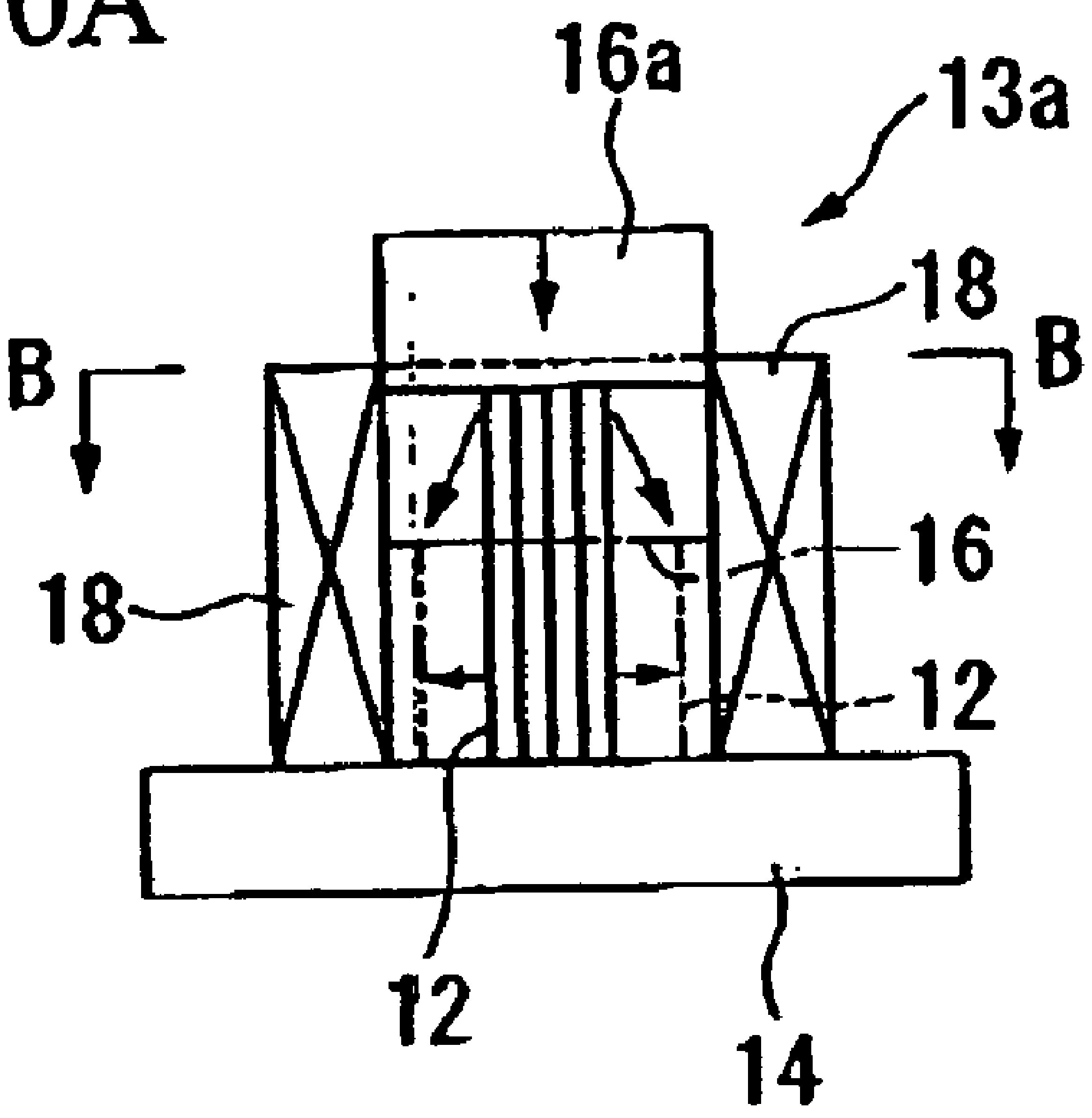


FIG. 20B

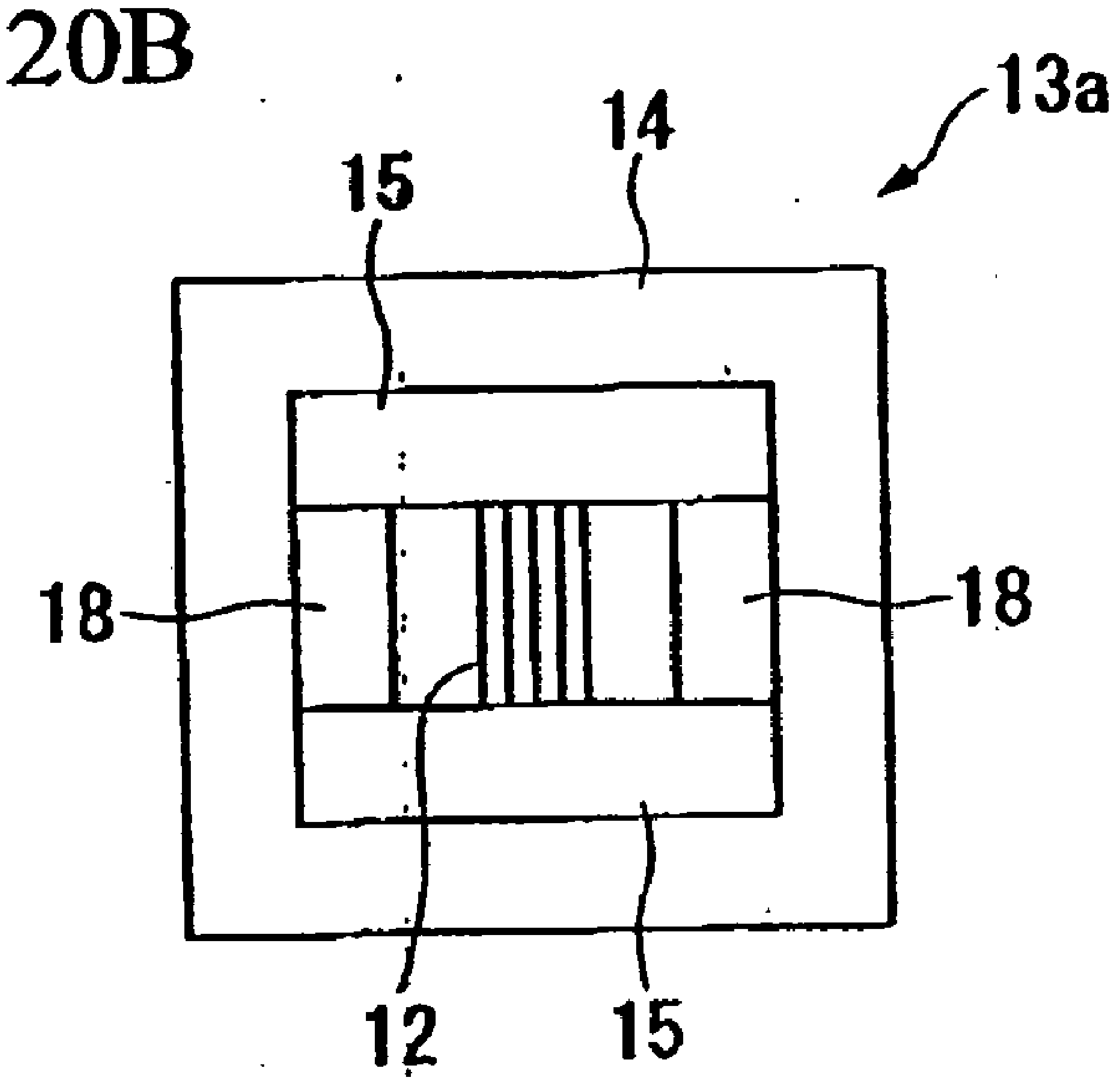


FIG. 20C

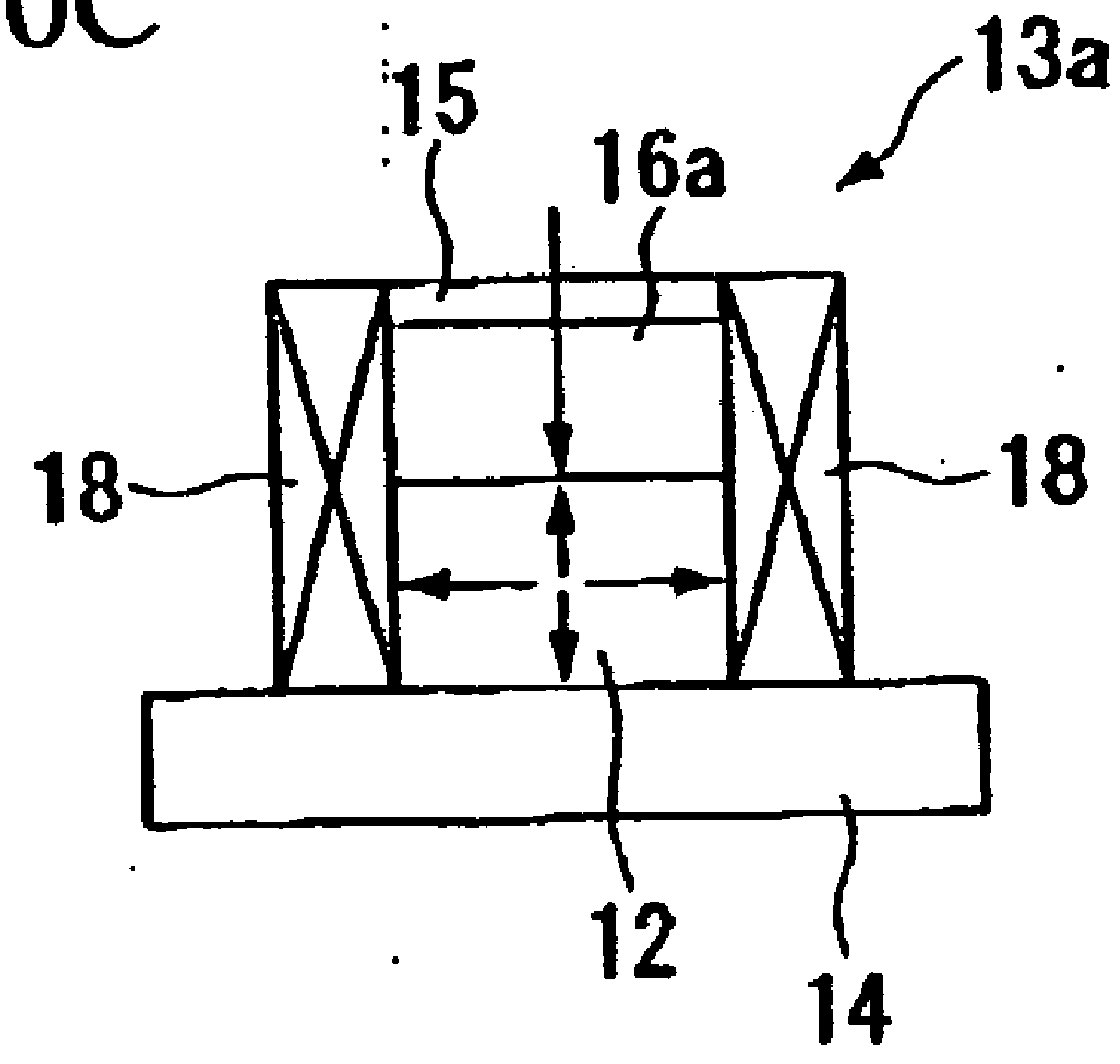


FIG. 21

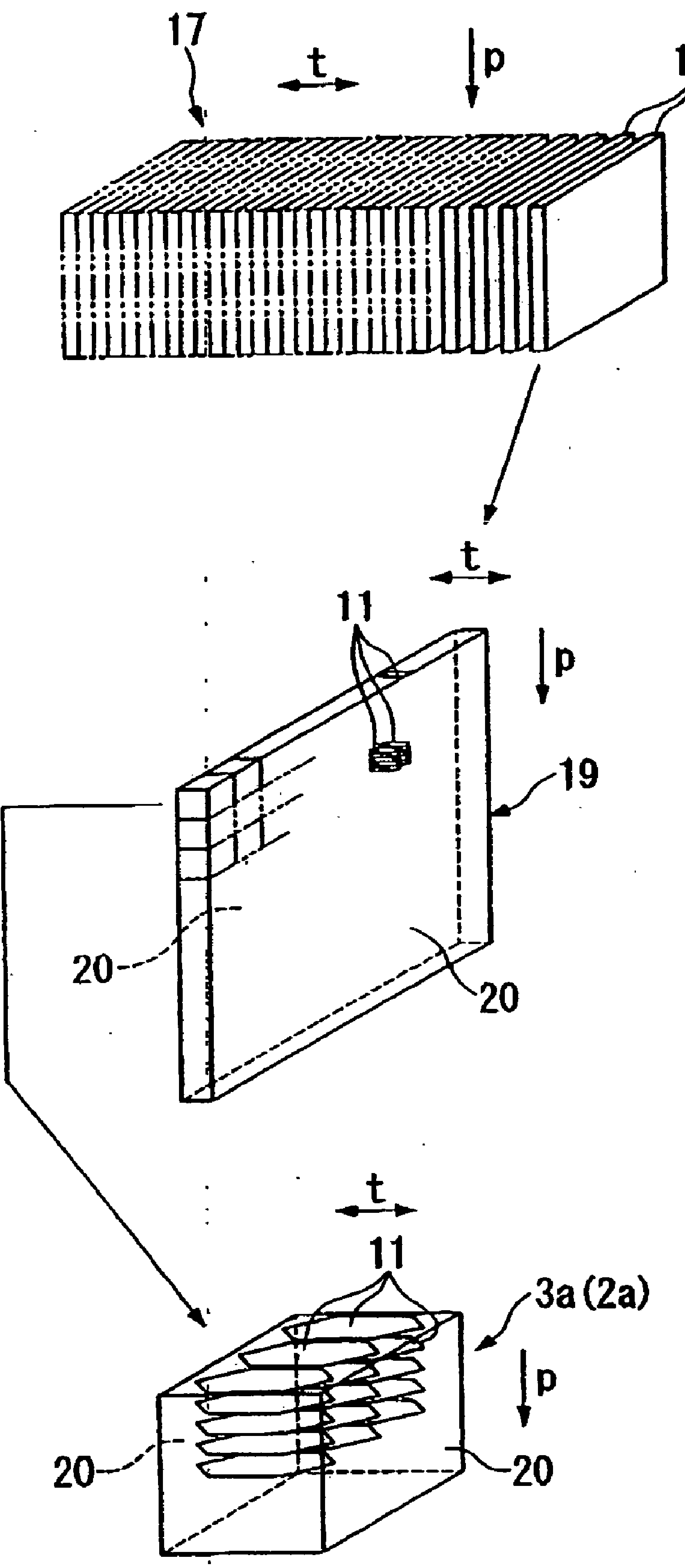


FIG. 22

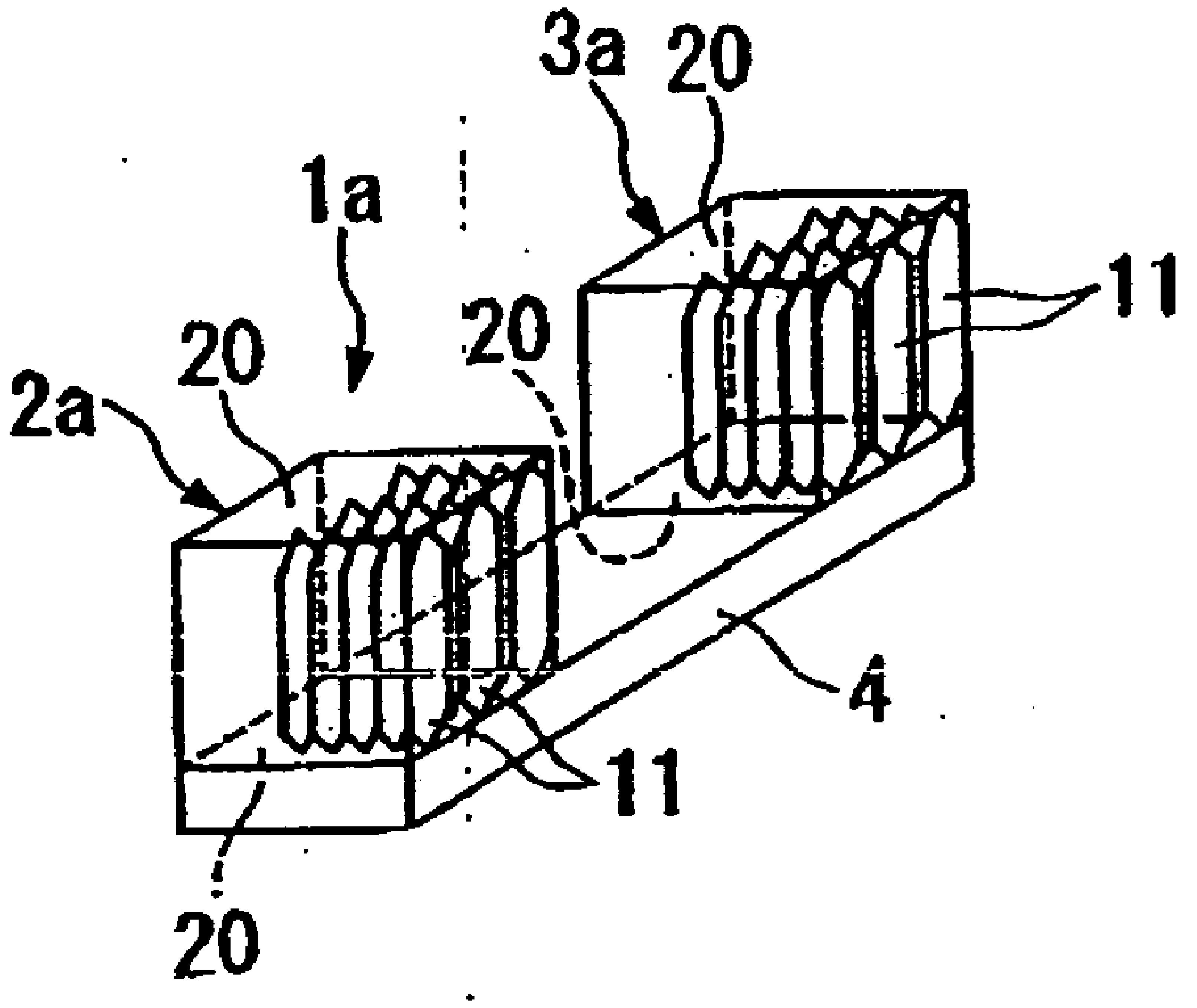


FIG. 23

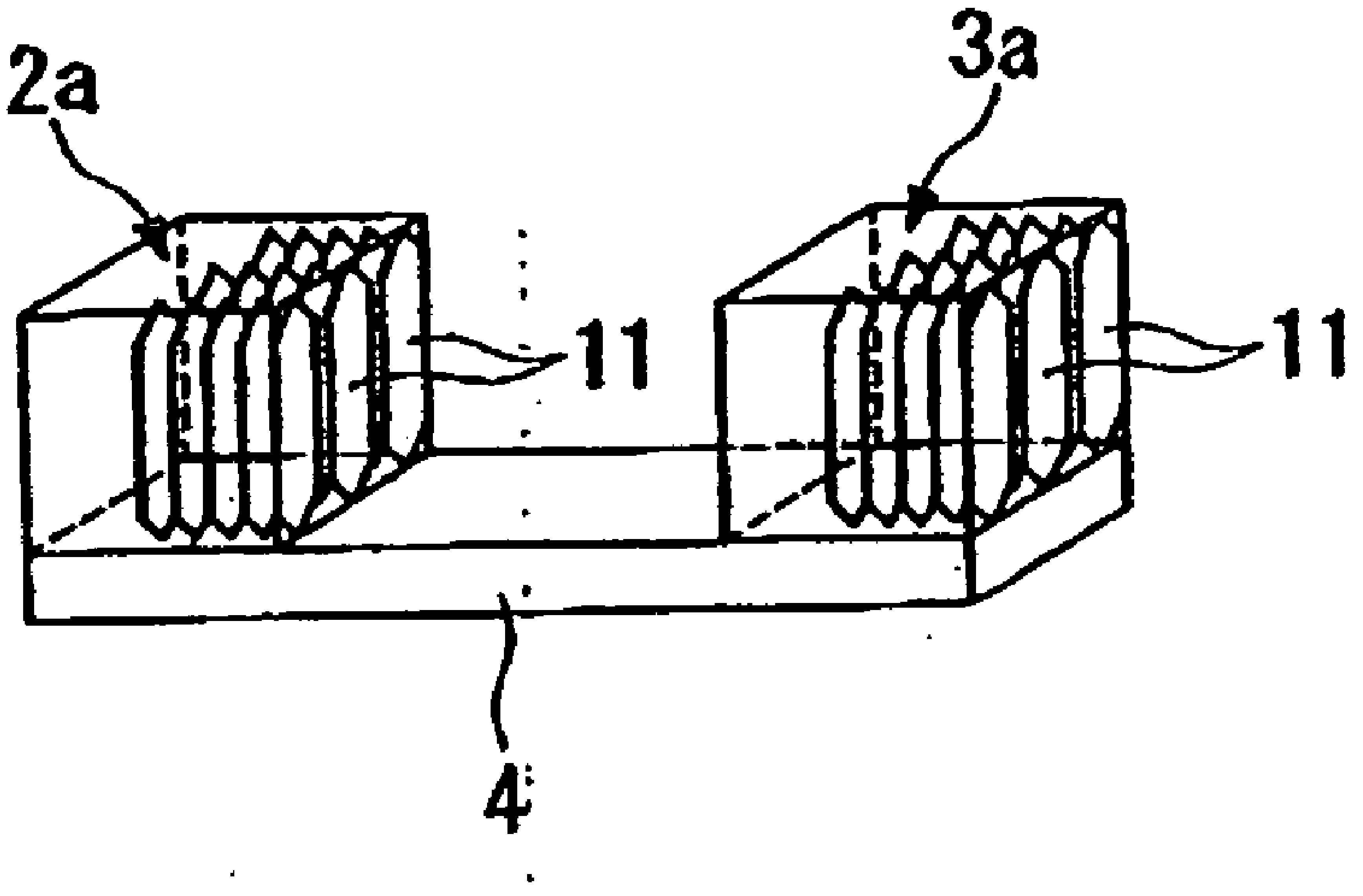


FIG. 24A

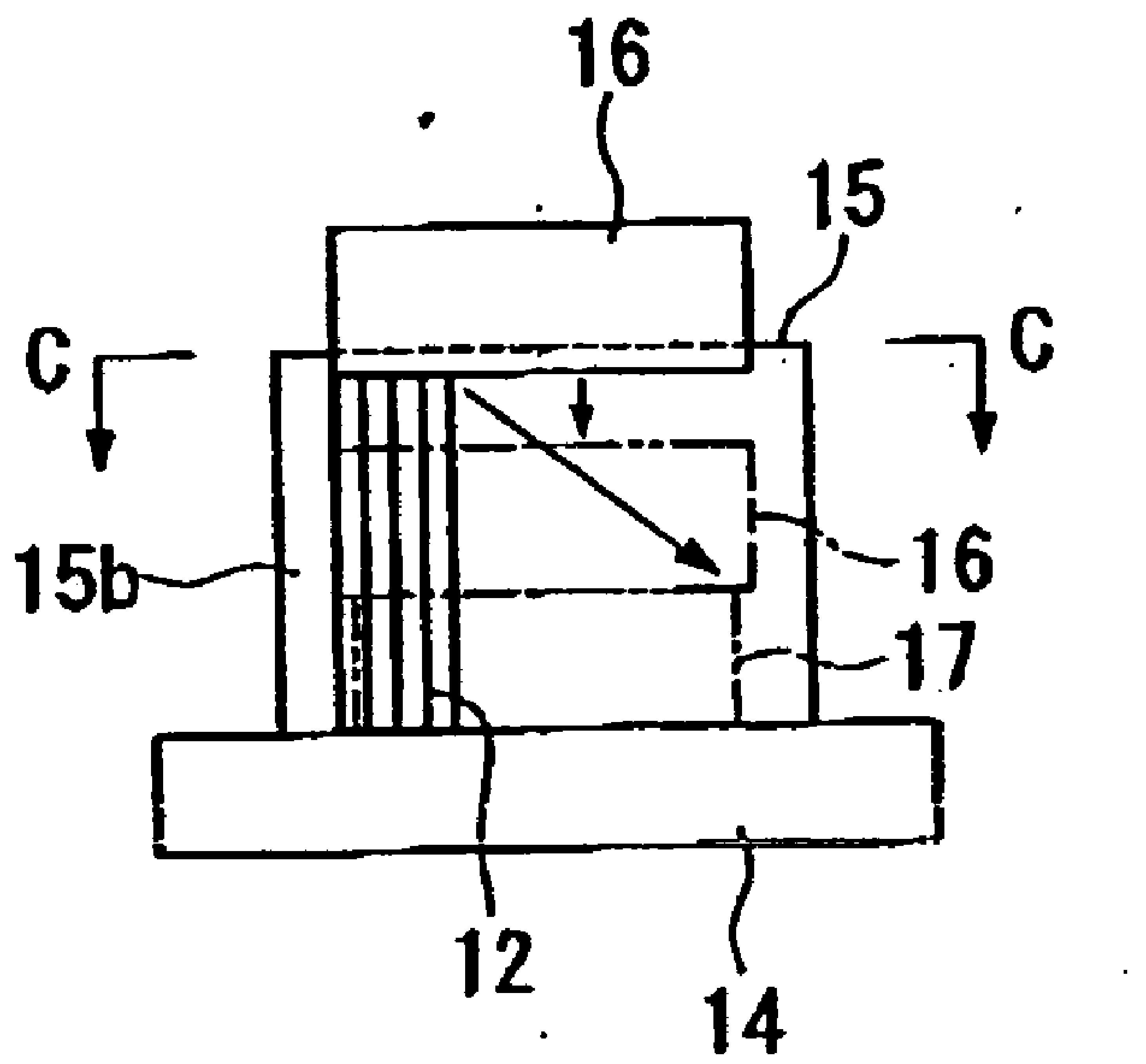


FIG. 24B

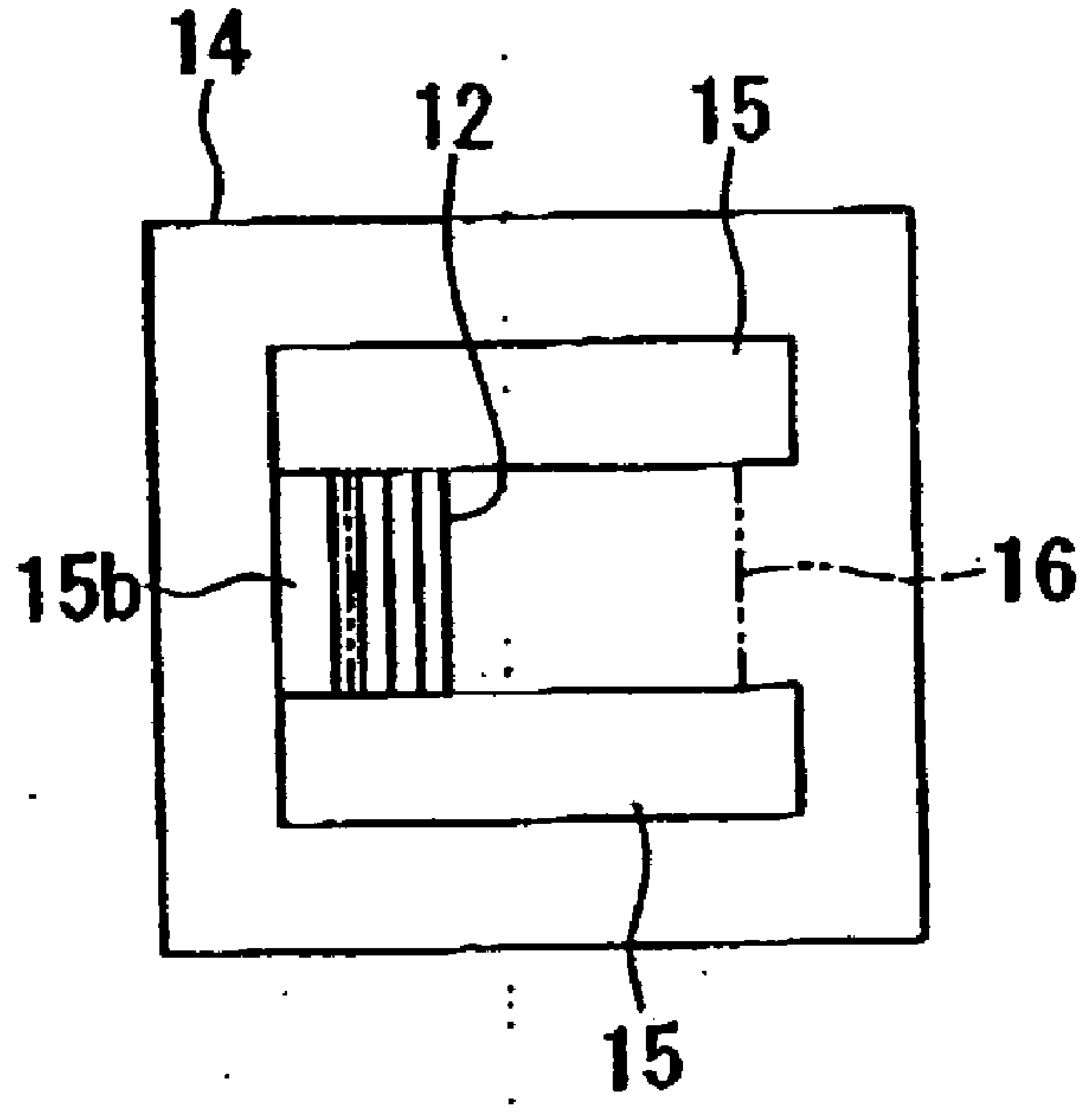


FIG. 25A

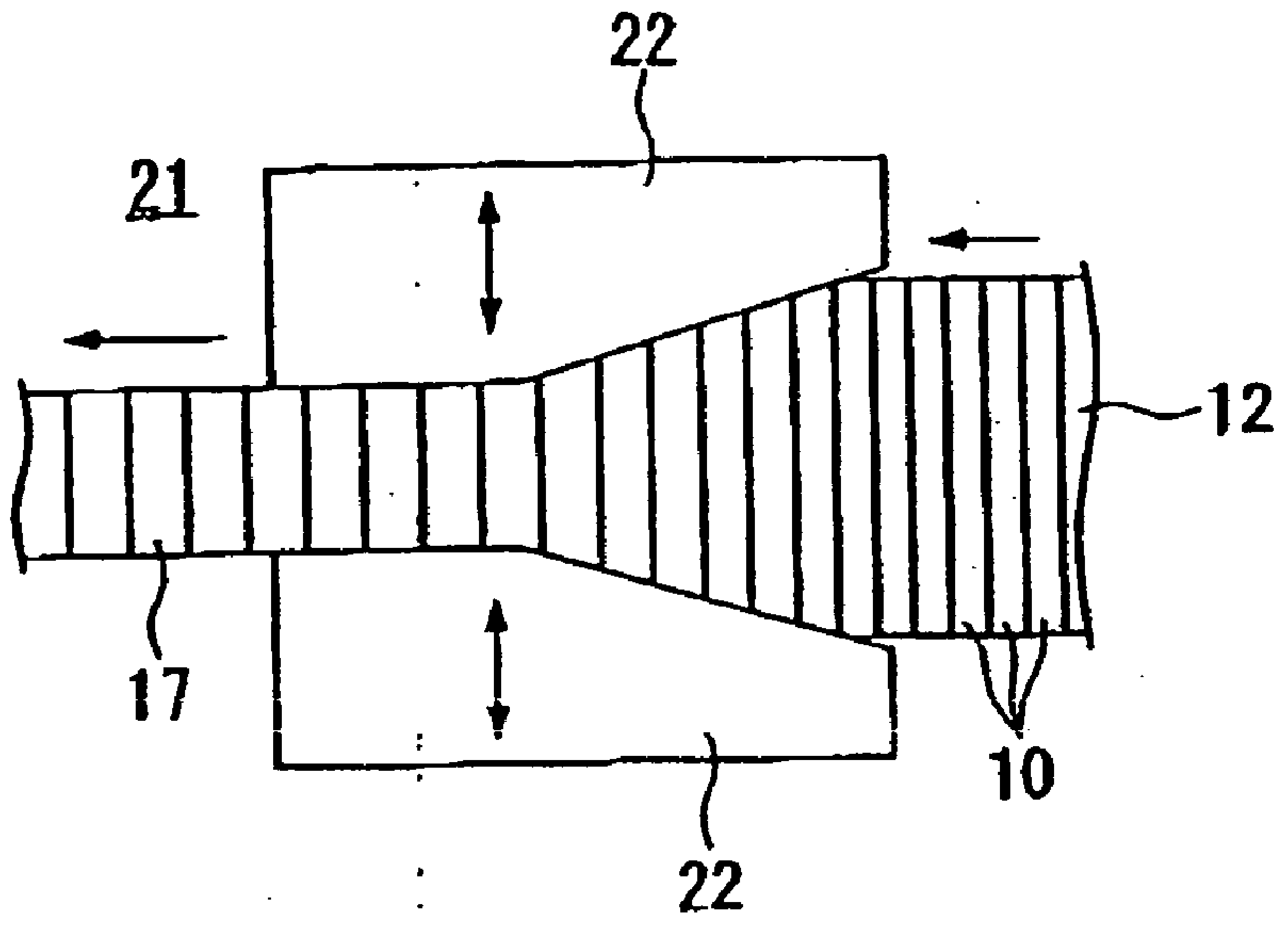


FIG. 25B

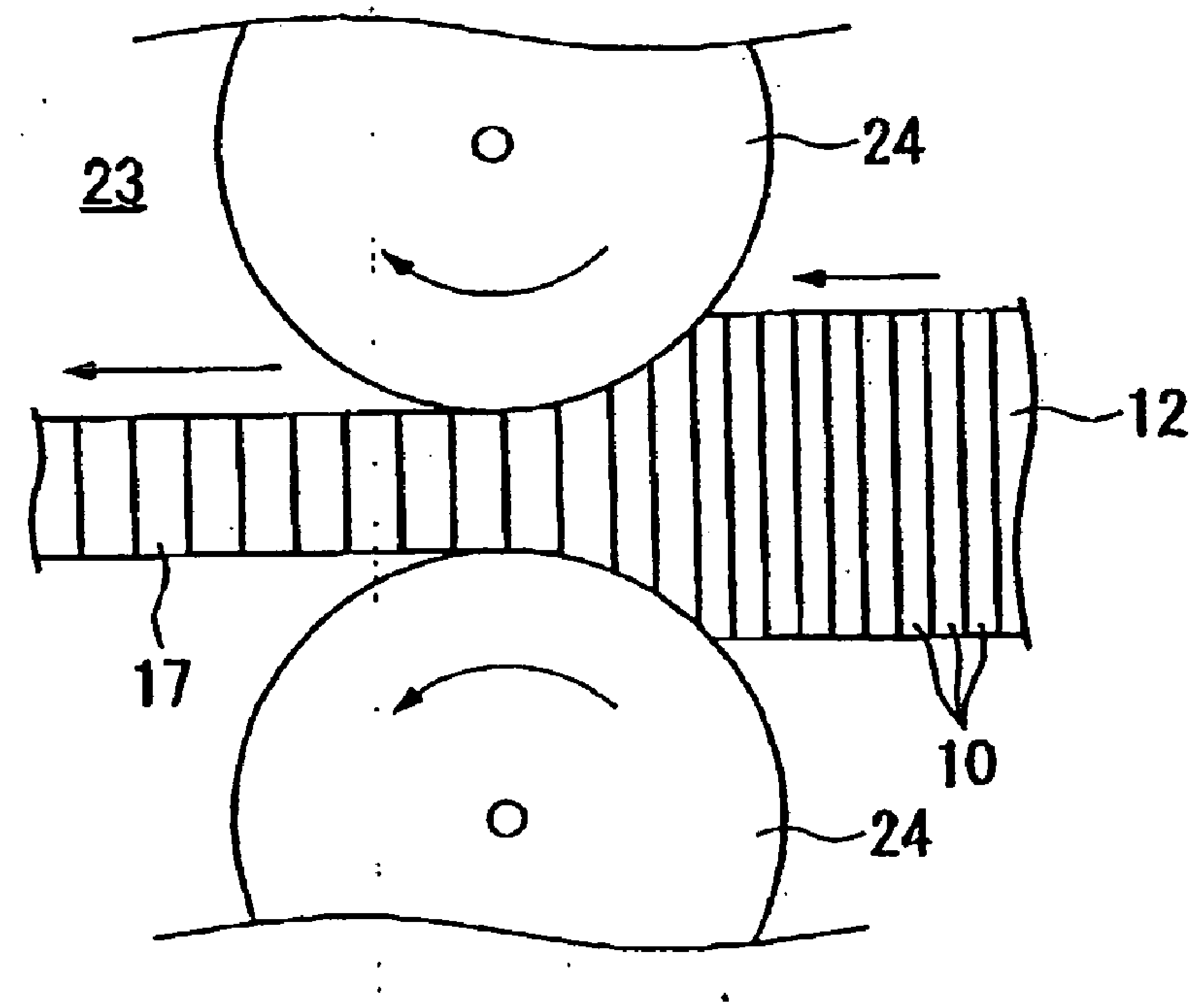


FIG. 26

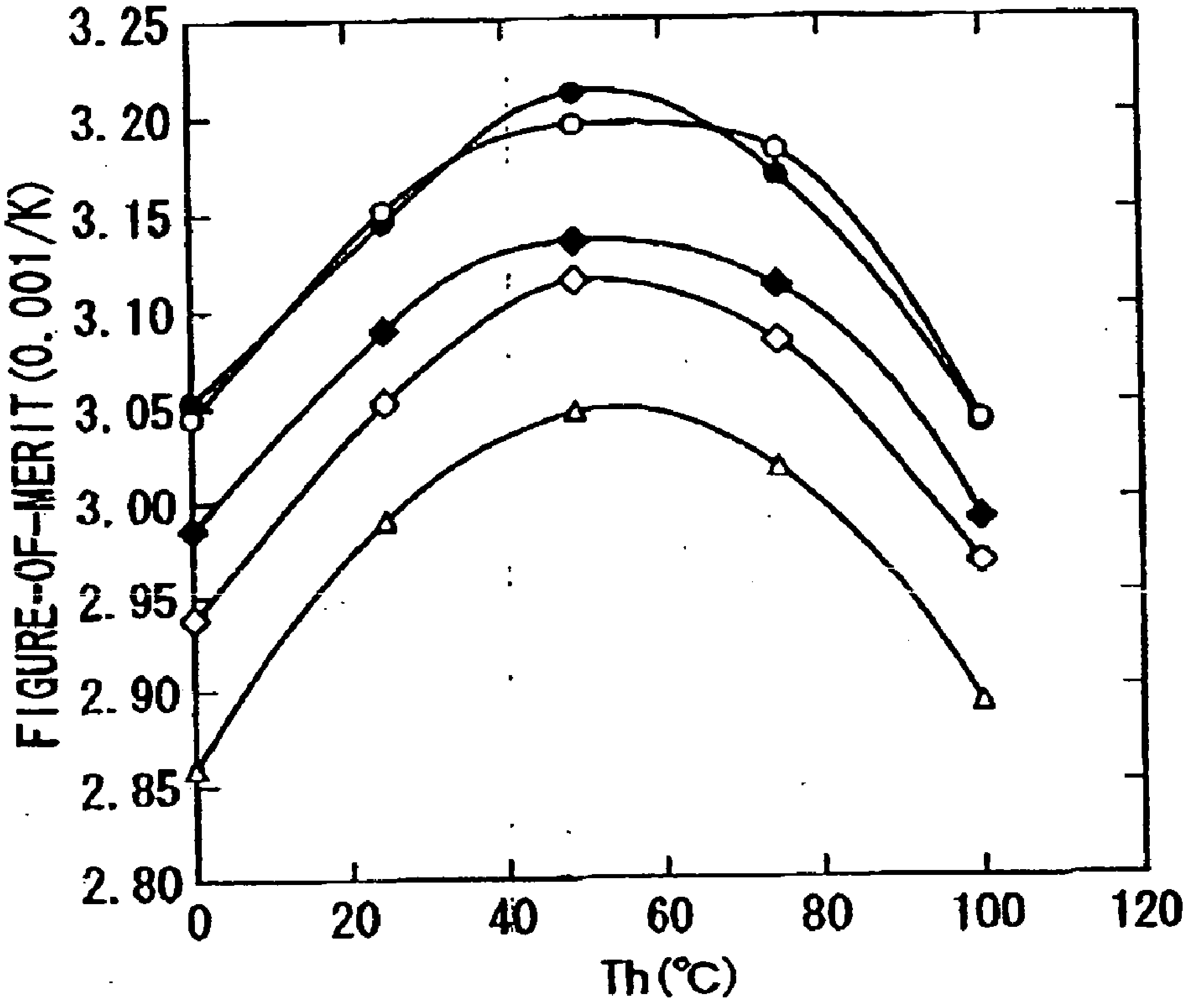
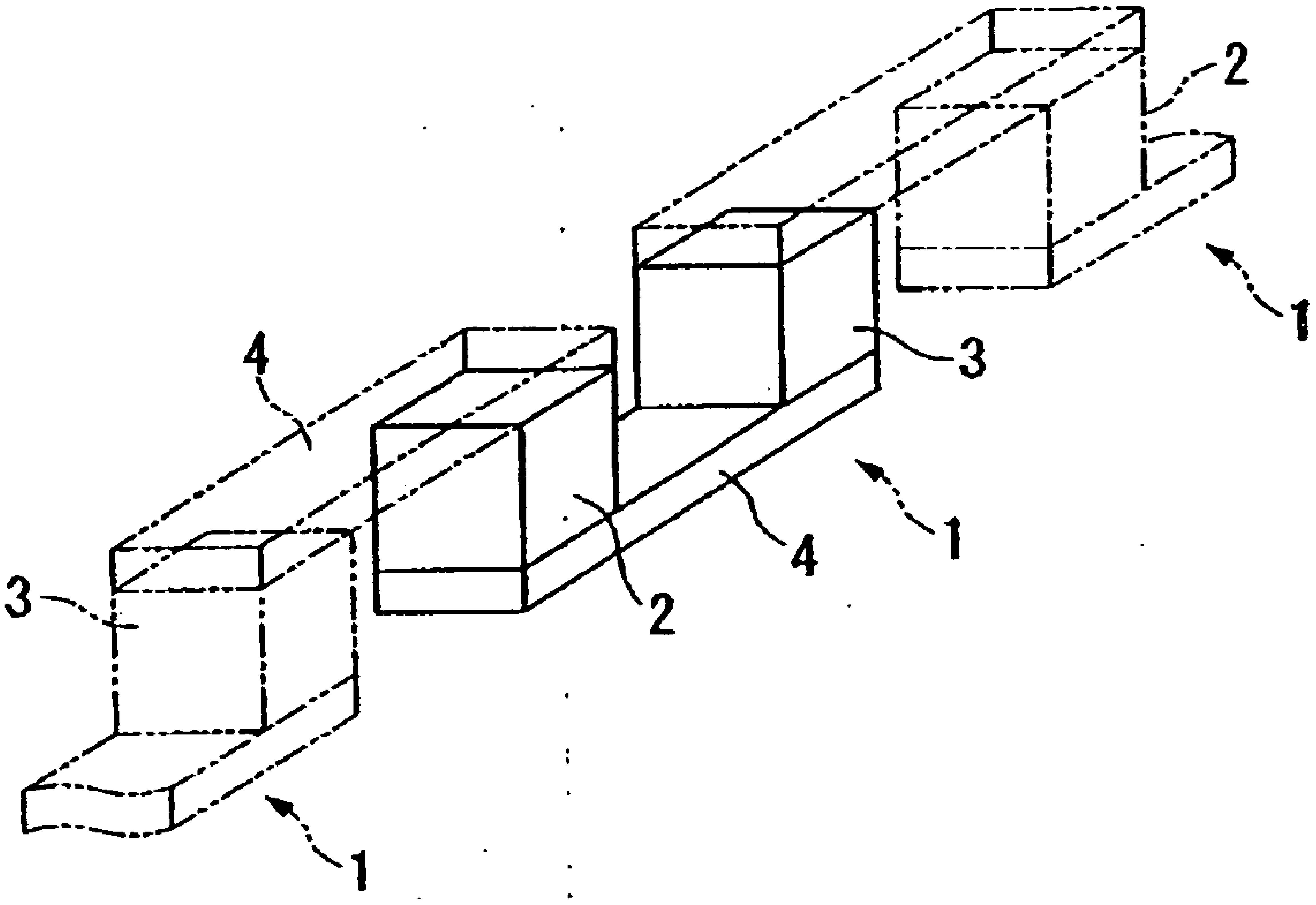

3.25
3.20
3.15
3.10
3.05
3.00
2.95
2.90
2.85
2.80
FIGURE-OF-MERIT (0.001/K)
0
20
40
60
80
100
120
Th(°C)

FIG. 27


2
1
4
3
3
1
2
4
1
1

THERMOELECTRIC SEMICONDUCTOR MATERIAL, THERMOELECTRIC SEMICONDUCTOR ELEMENT THEREFROM, THERMOELECTRIC MODULE INCLUDING THERMOELECTRIC SEMICONDUCTOR ELEMENT AND PROCESS FOR PRODUCING THESE

TECHNICAL FIELD

[0001] The present invention relates to a thermoelectric semiconductor material as well as to a thermoelectric semiconductor element, a thermoelectric module, and manufacturing method for same that are utilized for thermoelectric cooling, thermoelectric heating, thermoelectric power generation or the like.

BACKGROUND ART

[0002] Devices for carrying out thermoelectric cooling, thermoelectric heating and thermoelectric power generation using the thermoelectric properties of a thermoelectric semiconductor generally have a basic configuration where a plurality of thermoelectric modules **1** are aligned and connected in series, as shown schematically in the example of **FIG. 27**. In each of the thermoelectric modules **1**, a PN element pair is formed by joining a P type thermoelectric semiconductor element **2** to an N type thermoelectric semiconductor element **3** via a metal electrode **4**.

[0003] One type of thermoelectric semiconductor that forms above described thermoelectric semiconductor elements **2** and **3** uses a complex compound made of one or two elements selected from bismuth (Bi) and antimony (Sb) of 5B group, and one or two elements selected from tellurium (Te) and selenium (Se) of 6B group. The thermoelectric semiconductor is made of an alloy having a (Bi—Sb)$_2$(Te—Se)$_3$ based composition in which the ratio of a number of atoms of 5B group elements (Bi and Sb) to a number of atoms of 6B group elements (Te and Se) is 2:3.

[0004] Above-described alloy having a (Bi—Sb)$_2$(Te—Se)$_3$ based composition for forming the thermoelectric semiconductor, has a hexagonal strut and electrical and thermal anisotropy due to the crystal structure. It is known that by conveying electricity or heat in the <110> direction of the crystal structure, that is, along C face of the hexagonal structure, excellent thermoelectric performance can be obtained, in comparison with a case where electricity or heat is conveyed in the direction of c-axis.

[0005] Conventionally, raw alloys prepared so as to have the above-described desired composition are heated and melted to form molten alloys. Subsequently, using a directional solidification method, such as a zone melting method, while controlling the direction of the crystal growth so that the crystal has an excellent thermoelectric performance along the growth direction, a single crystalline or a polycrystalline ingot is manufactured as a thermoelectric semiconductor material. By a requited working of the ingot, such as cutting a portion having little irregularity in the composition from the ingot and working the cut portion, an element having an excellent properties is manufactured.

[0006] However, the ingots converted to single crystal using the zone melting method have significant cleavage due to their crystal structure. Therefore, when a thermoelectric semiconductor element is manufactured by slicing or the like of the ingot as a thermoelectric semiconductor material, there is a problem that the insufficient mechanical strength cause a reduction of yields by cracking or chipping. Therefore, it has been desired to improve thermoelectric performance along with increasing the strength of thermoelectric semiconductor materials for thermoelectric semiconductor elements.

[0007] In order to improve the strength and thermoelectric performance of thermoelectric semiconductors, one technique is proposed in which an ingot as a thermoelectric semiconductor material which has been manufactured in the same manner as described above by a directional solidification method, is worked by extrusion or roiling so as to apply shear force in the direction of C face of a hexagonal structure, and thereby improving the strength of the material (see, for example, Patent Document 1).

[0008] There has been proposed several method in view of general properties of polycrystalline metallic material as following: Crystal grains of polycrystalline metallic material show dispersive distribution of orientation, the metallic material exhibits isotropy. When the crystal grains are oriented in a specific direction as a result of a working such as plastic working, crystal anisotropy of individual crystal grains appears as macroscopic characteristics so that the metallic material as a whole exhibits anisotropy (for example, Non-Patent Document 1). By crushing raw alloy powder and sintering the powder, mechanical property of the material is improved in the sintered body. In the sintered body crystalline orientation is reduced, since the integration of randomly oriented powder grains during the sintering process orientates constituent crystals randomly. By rolling the sintered body in a direction (see, for example, Patent Document 2), by extrusion molding the sintered body (see, for example, Patent Documents 3 and 4), or by plastically deforming the sintered body (see, for example Patent Documents 5, 6, 7, 8, 9 and 10), uniformity of crystalline orientation of the sintered body is improved.

[0009] That is to say, by applying a pressing force on the above-described sintered body, and plastically deforming the sintered body, constituent crystals of the texture are plastically deformed and flattened in a direction perpendicular to the direction of pressing force, and thus, the crystals are oriented in such a manner that the cleavage plane are perpendicular to the direction of compression. In a rolling or a forging by an uniaxial compression, C face of the hexagonal structure is oriented in the direction perpendicular to the direction of compressing the sintered body (direction of pressing). In an extrusion molding, C face of the hexagonal structure is oriented along the direction of extrusion (direction of pressing). By this method, it is possible to prepare a thermoelectric semiconductor material in which crystals are oriented in a direction of excellent thermoelectric performance.

[0010] In general, the thermoelectric performance of the material used for the manufacture of a thermoelectric semiconductor is expressed by the following equation:

$$Z=\alpha^2\cdot\sigma/\kappa=\alpha^2/(\rho\cdot\kappa)$$

where Z is a Figure-of-Merit, α is the Seebeck coefficient, σ is electric conductivity, κ is thermal conductivity, and ρ is resistivity.

[0011] Accordingly, in order to increase the thermoelectric performance (Figure-of-Merit Z) of a thermoelectric semiconductor material, a raw alloy material in which the value of the Seebeck coefficient (α) or the electric conductivity (σ) is increased or the thermal conductivity (κ) is lowered, may be utilized. Judging from this, it should be possible to increase thermoelectric performance (Figure-of-Merit Z) by decreasing the grain sizes of crystals and reducing the conductivity (κ). However, in the above-described techniques using a powder produced by crushing an ingot of the raw alloy, the particle sizes of the powder is the grain sizes of crystals, therefore there is a limit to the miniaturiztion of crystal grains formed by crushing. Therefore, in order to improve the strength and thermoelectric performance of a thermoelectric semiconductor material, still another technique has been proposed. A raw alloy is melted into a molten alloy. A raw thermoelectric semiconductor material in a ribbon, foil piece or powder form is formed by a liquid quenching method such as rotational roll method in which the molten alloy is sprayed onto the surface of a rotational roll which is being rotated or a gas atomizing method in which the molten alloy is sprayed into a predetermined gas flow. At that time, microscopic crystal grains are formed within the texture of the raw thermoelectric semiconductor material, and high density strain and defects are introduced into the texture. After the raw thermoelectric semiconductor material is crushed into a powder, this raw thermoelectric semiconductor material in powder form is heat treated and solidified, and thereby a thermoelectric semiconductor material is manufactured. By this method, during the heat treatment or the solidification process, recrystallization of crystals occurs ling the distortion due to the defects as a driving force, and due to the presence of grain boundaries, the thermal conductivity (κ) is lowered and thermoelectric performance (Figure-of-Merit Z) is increased (see, for example, Patent Document 11).

[0012] As the rotational velocity of a rotational roll that is used to form a raw thermoelectric semiconductor material in a ribbon, foil piece or powder form by quenching a molten alloy, it is proposed to set a circumferential velocity to be 2 to 80 m/sec, so as to effectively generate microscopic crystals by quenching, and make the crystals grow in the direction of heat flow (see, for example, Patent Document 12). In this case, a sufficient quenching speed is not achieved when the circumferential velocity of the rotational roll is less than 2 m/sec, and a sufficient quenching speed is also not achieved when the circumferential velocity is 80 m/sec or greater.

[0013] As the heating conditions when the raw thermoelectric semiconductor material in a ribbon, foil or powder form is solidified and formed, it is proposed to maintain the material at a temperature from 200 to 400° C. or at a temperature from 400 to 600° C. for 5 to 150 minutes while applying pressure to the material (see, for example, Patent Document 13).

[0014] Another technique for increasing the thermoelectric performance of a thermoelectric semiconductor material is proposed, in which Ag is added to and mixed with a raw thermoelectric semiconductor material in a ribbon, foil piece or powder form that has been formed by quenching a molten alloy of a $(Bi—Sb)_2(Te—Se)_3$ based raw alloy, on a rotational roll. By subsequent sintering and solidification, Ag is distributed in the grain boundaries, so that resistivity ρ is lowered, and thus, an increase in the thermoelectric performance (Figure-of-Merit Z) can be achieved (see, for example, Patent Document 14).

[0015] It is known that in a rotational rolling method as the liquid quenching method, a molten alloy sprayed onto the surface of a rotational roll is cooled from contact surface with the rotational roll in the direction toward the outer periphery of the roll. Together with this quenching, the molten alloy solidifies in the direction of the film thickness. As a result, a raw thermoelectric semiconductor material in foil form is produced, in which C face, the base plane of the hexagonal structure of the crystal gains, stand in the direction of the film thickness.

[0016] Therefore, a technique for effectively using the orientation of the crystals of a raw thermoelectric semiconductor material that has been manufactured by the rotational rolling method is proposed, in which the raw thermoelectric semiconductor materials are layered in the direction of the film thickness, and are sintered while pressure is applied in the direction parallel to the direction of the film thickness, and thereby, a thermoelectric semiconductor material is manufactured (see, for example, Patent Document 15).

[0017] Furthermore, techniques for manufacturing a thermoelectric semiconductor material in which crystal orientation is improved have been proposed. In a technique, a layered body is produced by layering raw thermoelectric semiconductor materials manufactured by a rotational rolling method, and integrating the layered body layered in the direction of the film thickness by applying a in the direction parallel to the layering direction. During the pressing for integrating the layers in the direction parallel to the layering direction, crystal orientation of each layers are disordered at the interface of the layers. By applying pressure in the direction perpendicular to the layering direction of the layered body, such disorder of crystal orientation at the interface can be improved (see, for example, Patent Document 16). In another technique, a layered body is produced by layering raw thermoelectric semiconductor materials in foil powder form in the direction of the film thickness. Crystalline orientation of the layered body is improved by applying pressure in at least three directions perpendicular to the layering direction. Furthermore, the layered body, the crystalline orientation of which has been improved by the above-described application of pressure, is formed by extrusion molding in the direction parallel to the layering direction, and thereby uniformity in the orientation of the crystals is additionally increased (see, for example, Patent Document 17).

[0018] Recently, it has been desired for a thermoelectric transducing material to be provided with further improved performance and high reliability. Together with an increase in performance, an inclease in mechanical strength and excellence in workability are also desired. For example, when a thermoelectric semiconductor is used to cool a laser oscillator, N type and P type thermoelectric semiconductor elements having dimensions of no greater than 1 mm are used as modules. Accordingly, it is required a mechanical strength sufficient to make it possible for a thermoelectric semiconductor element of no greater than 1 mm in dimension to be sliced from an ingot of a thermoelectric semiconductor material without chipping.

[List of Prior Art Documents]

(1) Patent Document 1: Japanese Unexamined Patent Application, First Publication No. H11-163422

(2) Pat Document 2: Japanese Unexamined Patent Application, First Publication No. S63-138789

(3) Patent Document 3: Japanese Unexamined Patent Application, First Publication No. 2000-124512

(4) Patent Document 4: Japanese Unexamined Patent Application, First Publication No. 2001-345487

(5) Patent Document 5: Japanese Unexamined Patent Application, First Publication No. 2002-118299

(6) Patent Document 6: Japanese Unexamined Patent Application, First Publication No. H10-178218

(7) Patent Document 7: Japanese Unexamined Patent Application, First Publication No. 2002-151751

(8) Patent Document 8: Japanese Unexamined Patent Application, First Publication No. H11-261119

(9) Patent Document 9: Japanese Unexamined Patent Application, First Publication No. H10-178219

(10) Patent Document 10: Japanese Unexamined Patent Application, First Publication No. 2002-111086

(11) Patent Document 11: Japanese Unexamined Patent Application, First Publication No. 2000-36627

(12) Patent Document 12: Japanese Unexamined Patent Application, First Publication No. 2000-286471

(13) Patent Document 13: Japanese Unexamined Patent Application, First Publication No. 2000-332307

(14) Patent Document 14: Japanese Unexamined Patent Application, First Publication No. H8-199291

(15) Patent Document 15: Japanese Patent Publication No. 2659309

(16) Patent Document 16: Japanese Unexamined Patent Application, First Publication No. 2001-53344

(17) Patent Document 17: Japanese Unexamined Patent Application, First Publication No. 2000-357821

[0019] (18) Non-Patent Document 1: "Elastic Constants of Al—Cu Alloys Containing Columnar Crystals" by Hiroshi Kato and Keiji Yoshikawa, Materials (Journal of the Society of Materials Science, Japan) Volume 30, No. 331, April 1981, p. 85.

[0020] There is a problem, however, in that the mechanical strength of a thermoelectric semiconductor material cannot be sufficiently enhanced, even when the thermoelectric semiconductor material is manufactured by plastically deforming an ingot of a thermoelectric semiconductor raw alloy, as shown in Patent Document 1.

[0021] At present, it is difficult to overcome the problem in which a single-crystal or directionally solidified ingot easily cracks along the cleavage plane of the material. Even though the orientation of the crystals is uniform, there are few methods for still increasing performance, because the manufacturing methods are limited.

[0022] Among techniques for manufacturing a polycrystalline thermoelectric semiconductor material, as shown in Patent Documents 2 to 10, by a technique for plastically deforming a sintered body by rolling, by an extrusion molding, or by upsetting forging of the sintered body formed by sintering of powder produced by crushing an ingot of an alloy material, it should be possible to enhance the mechanical strength of a thermoelectric semiconductor material. However, the size of the powder particles determine the diameter of the crystal grains in the powder of the ingot, and there is a limit to the miniaturization of the cry grains. Therefore, the thermoelectric semiconductor material is disadvantageous in reducing thermal conductivity (a) and the thermoelectric performance cannot be significantly enhanced. In addition, since the powder is sintered in a state in which each powder particles are randomly oriented, by the plastic deformation of the sintered body having such disordered crystalline orientation, it is difficult to enhance the crystalline orientation of a tenure of thermoelectric semiconductor material.

[0023] Furthermore, in the technique disclosed in Patent Document 11, electric conductivity (σ) is increased by heat treatment or sintering in order to remove defects within the grains, and thermal conductivity (κ) is reduced due to scattering of phonons of the crystal grain boundaries. However, the grain boundaries inevitably exist in a polycrystalline body. Therefore, at present, it is difficult to increase electric conductivity and to reduce thermal conductivity at the same time. In addition, there is a problem in that the electric resistance is lowered in the vicinity of grain boundaries where the impurities are concentrated, whereas inside of the grains which mainly make up the volume are converted to semiconductors, and thus, electric resistance increases.

[0024] As a rotational speed of the rotational roll for manufacturing a raw thermoelectric semiconductor material in foil or powder form, Patent Document 12 discloses that the circumferential velocity of a rotational roll may be set at 2 to 80 nm/sec. However, Patent Document 12 does not show any concrete processes for manufacturing a thermoelectric semiconductor material by solidifying and forming a raw thermoelectric semiconductor material in foil or powder form that has been manufactured by using a rotational roll of which the circumferential velocity has been set as described above.

[0025] As a heating condition for sintering a raw thermoelectric semiconductor material that has been manufactured by a liquid quenching method, Patent Document 13 discloses that the temperature may be set in a range from 200 to 60° C. This is the setting of a temperature condition that allows sintering without losing uniformity in the orientation of the crystals within the texture of the raw thermoelectric semiconductor material, but is totally different from the temperature range for the setting of the temperature when a raw thermoelectric semiconductor material is solidified and formed according to the present invention as described below where segregation, dropping of separated phase, liquid deposition, and the like of a Te rich phase having a low melting point are completely prevented during solidification forming of a raw thermoelectric semiconductor material.

[0026] By a technique, as proposed in Patent Document 14, for dispersing Ag in the crystal grain boundaries and lowering resistivity (ρ), and thereby, achieving an increase in the thermoelectric performance, Ag serves as a dopant in a $(Bi—Sb)_2(Te—Se)_3$ based thermoelectric semiconductor. Therefore, the technique includes a problem in that the added amount of Ag must be strictly adjusted, and also includes a problem of age deterioration.

[0027] In the technique described in Patent Document 15, raw thermoelectric semiconductor materials in foil forms manufactured by the rotational rolling method are layered in the direction of the film thickness and are solidified and formed. Therefore, there is a problem in which the crystal orientation of the layered raw thermoelectric semiconductor material is disordered when pressure is applied in the direction parallel to the direction of the film thickness.

[0028] When raw thermoelectric semiconductor materials in foil forms manufactured by a rotational rolling method are layered, and pressure is applied to the layered body in the direction perpendicular to the layering direction, and pressure is applied to layered body, as described in Patent Document 16, in a direction perpendicular to the layering direction, or as described in Patent Document 17, in at least three direction perpendicular to the layering direction, it should be possible to improve crystal orientation of the texture. In these case, an improvement of crystalline orientation is achieved by making the direction of C face of the hexagonal structure stand in the layering direction of the raw thermoelectric semiconductor material. However, the direction of c-axis of the hexagonal structure in each crystal grain cannot be uniformly oriented. Therefore the direction of c-axis of the hexagonal structure of the crystal grains cannot be uniformly oriented even when an extrusion molding is additionally and sequentially carried out by applying pressure in the layering direction, as described in Patent Document 17.

[0029] In conventional manufacturing methods for a polycrystalline thermoelectric semiconductor materials as described in Patent Documents 2 to 17, powders of ingots to be solidified and formed for the manufacture of a thermoelectric semiconductor material, and raw thermoelectric semiconductor materials in ribbon, foil, and powder form produced by a liquid quenching method have fine grain sizes. Therefore raw thermoelectric semiconductor materials have large specific surface area and their surfaces are easily oxidized. In addition, even when reduction process is carried out on each of the raw materials in order to prevent the surface oxidation, there are many operations to be added such as sealing a material in a mold without allowing contact with oxygen during sintering. Even when such additional operations are carried out, it is difficult to reduce influence of oxidization.

[0030] In addition, since each of the above-described raw materials has fine grain size, it is difficult to increase density of the material during sintering. For example, when a raw thermoelectric semiconductor material in fine foil form that has been manufactured by a rotational rolling method and is sintered at 475° C., the increase of density is only within a range of 98 to 991%. When a powder is sintered, reduction of density depends on the grain size, but is limited to approximately 95%. Therefore, there is a possibility that the electric conductivity being lowered.

[0031] Furthermore, in a general hot pressing, a fine powder is used in order to obtain the compact texture after sintering. It is known that bulk density increase with decreasing particle size of powder due to increasing amount, of air, but it is possible to gain a compact structure by applying pressure. Therefore, in the techniques described in Patent Documents 15 to 17, in which raw thermoelectric semiconductor materials in foil forms manufacture by rotational rolling methods are layered and subsequently solidified and formed, fine foils are used as the raw thermoelectric semiconductor materials. However, since the densification of sintered texture by hot press is a phenomena occurring as a result of powder flow and plastic deformation of powder particles, when fine foils of raw thermoelectric semiconductor materials are solidified, as described in Patent Documents 15 to 17, a large portion of each raw thermoelectric semiconductor material is plastically deformed and in a great number of portions, the original crystalline orientation of the foil is disordered, and an orientation of C face is easily disordered.

DISCLOSURE OF INVENTION

[0032] Therefore, an object of the present invention is to provide a thermoelectric semiconductor material having excellent crystalline orientation in the texture, reduced oxygen concentration, and enhanced thermoelectric performance, as well as to provide a thermoelectric semiconductor element using such a thermoelectric semiconductor material, a thermoelectric module using such a thermoelectric element, and manufacturing methods for same.

[0033] In order to achieve the above-described objects, the sent invention provides a thermoelectric semiconductor material which is produced by: layering and packing raw thermoelectric semiconductor materials made of a raw alloy having a predetermined composition of a thermoelectric semiconductor to form a layered body; solidifying and forming the layered body to form a compact; applying pressure to the compact in a uniaxial direction that is perpendicular or nearly perpendicular to the main layering direction of the raw thermoelectric semiconductor materials; and thereby applying shear force in a uniaxial direction that is approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials, and plastically deforming the compact.

[0034] When a raw alloys is contacted with the surface of a cooling member at the time of the manufacture of the thermoelectric semiconductor material, a raw thermoelectric semiconductor material is achieved, in which C face of the hexagonal structure of the crystal grains are oriented approximately parallel to the direction of the plate thickness. When the raw thermoelectric semiconductor materials are layered in the direction of the plate thickness to form a layered body, and then solidified and formed, the direction of extension of C face of the crystal grains is maintained to be oriented in the layering direction in the compact. Furthermore, when pressure is applied to the compact in such a manner that shear force is applied in a uniaxial direction approximately parallel to the main layering direction of the thermoelectric semiconductor, which is approximately similar to the extending direction of C face of the crystal grains and thereby the compact is plastically deformed, the crystal grains are flattened along the direction in which shear force is applied, and the extending direction of C face remain to be oriented in the direction of shear force during the plastic deformation. At the same time, the directions of c-axes of the crystal grains are oriented approximately parallel to the direction in which pressure is applied for the plastic deformation. Accordingly, in the texture of achieved thermoelectric semiconductor material, both the extending direction of C face and the direction of c-axis in the hexagonal structure of crystal grains are uniformly oriented, and therefore high thermoelectric performance can be obtained by setting current and heat to be conveyed in the extending direction of C face.

[0035] Accordingly, a thermoelectric semiconductor material having an excellent thermoelectric performance can be achieved by a manufacturing method for a thermoelectric semiconductor material comprising: melting a raw alloy having a predetermined composition of thermoelectric semiconductor; subsequently having the molten alloy contacted with a surface of a cooling member and thereby forming plate shaped raw thermoelectric semiconductor materials; layering the plate shaped raw thermoelectric semiconductor materials in a direction approximately parallel to a direction of the plate thickness and solidifying and forming the layered body into a compact; applying pressure to the compact in one of two axial directions which are crossing each other in a plane approximately perpendicular to the main layering direction of the raw thermoelectric semiconductor materials, while preventing deformation of the compact in the other axial direction; and thereby applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials, and plastically deforming the compact to form a thermoelectric semiconductor material.

[0036] In addition, when a thermoelectric semiconductor material has a compound phase comprising: complex compound semiconductor phase having a predetermined stoichiometric composition of a compound thermoelectric semiconductor, and a Te rich phase in which excess Te is added to the above composition, crystal grain boundaries exist in the thermoelectric semiconductor material, and crystal strain is generated due to the presence of the compound phase of complex compound semiconductor phase and the Te rich phase. By the introduction of crystal strain, thermal conductivity can be lowered, and therefore, the Figure-of-Merit can be increased as a result of the lowering of thermal conductivity.

[0037] Furthermore, when a thermoelectric semiconductor material is produced by: adding excess Te to a predetermined stoichiometric composition of a compound thermoelectric semiconductor to form a raw alloy; layering and packing plate shaped raw thermoelectric semiconductor materials made of the raw alloy to form a layered body; solidifying and forming the layered body to form a compact; applying pressure to the compact in an axial direction perpendicular or nearly perpendicular to the main layering direction of the raw thermoelectric semiconductor materials; and thereby applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials, and plastically deforming the compact, the thermoelectric semiconductor material is provided with excellent crystalline orientation in which both extending direction of C face and direction of c-axes of the hexagonal structure of the crystal grains are approximately uniformly oriented. In addition, due to the presence of the compound phase of complex compound semiconductor phase and the Te rich phase, thermal conductivity can be lowered, and therefore, the Figure-of-Merit can be further increased.

[0038] Accordingly, a manufacturing method for a thermoelectric semiconductor material, in which a raw alloy is controlled to have a composition where an excess Te is added to the predetermined stoichiometric composition of a compound thermoelectric semiconductor can provide a thermoelectric semiconductor having excellent crystalline orientation, a compound phase of complex compound semiconductor phase and the Te rich phase, and a high Figure-of-Merit.

[0039] In the above described method, a P type thermoelectric semiconductor material having high thermoelectric performance can be produced by controlling the raw alloy to have a composition in which excess Te is added to a $(Bi—Sb)_2Te_3$ based stoichiometric composition, concretely, by controlling the raw alloy to have a composition in which 0.1 to 5% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 7 to 10 atomic % of Bi, 30 to 33 atomic % of Sb, and 60 atomic % of Te.

[0040] On the other hand, a N type thermoelectric semiconductor material having high thermoelectric performance as described above can be produced by controlling the raw alloy to have a composition in which excess Te is added to a $Bi_2(Te—Se)_3$ based stoichiometric composition, concretely, by controlling the raw alloy to have a composition where 0.01% to 10% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 40 atomic % of Bi, 50 to 59 atomic % of Te, and 1 to 10 atomic % of Se.

[0041] Furthermore, when the solidification forming of the raw thermoelectric semiconductor materials is carried out by applying pressure and by heating to a temperature no less than 380° C. and no higher than 500° C., the thermoelectric semiconductor material can be solidified and formed in a state in which the Te rich phase in the raw thermoelectric semiconductor material is prevented from being converted to liquid phase, or the Te rich liquid phase is controlled to be a small amount. Therefore, a P type or N type thermoelectric semiconductor material can be formed, having a multi phase structure of the P type or N type complex compound semiconductor phase dispersing microscopic Te rich phases including an excess Te in the above semiconductor composition.

[0042] Moreover, in the manufacturing method, when a molten alloy of the raw alloy is contacted with the surface of a cooling member to form a plate shaped raw thermoelectric semiconductor material, the cooling rate of the molten alloy during solidification may be controlled to a rate by which 90% or more of the thickness of the plate shaped raw thermoelectric semiconductor material is not quenched. Concretely, a rotational roll may be used as the cooling member, and when the plate shaped raw thermoelectric semiconductor material is formed by supplying the molten alloy of the raw alloy to the surface of such cooling member, the rotational roll may be rotated at a rate at which the thickness of the raw thermoelectric semiconductor material is controlled to be at least no less than 30 μm. By this method, microscopic crystal nuclei are formed on the side of contact surface of the molten raw alloy and the cooling member, and the molten alloy can be slowly solidified so that, from the nuclei, large crystal grains grow in the direction of the thickness, and the raw thermoelectric semiconductor material can be formed to have a thickness of no less than 30 μm. At at time, the crystal grains can be grown in such a manner that C face of the hexagonal structure of the crystals extend in the direction of thickness, approximately throughout the entire thickness of the raw thermoelectric semiconductor material. When the raw alloy is made to have a composition including excess Te, in the $(Bi—Sb)_2Te_3$ based P type complex compound semiconductor phase or in the $Bi_2(Te—Se)_3$ based N type complex compound semiconductor phase, the Te rich phases including excess Te in each of the above compositions can be microscopically dispersed as separated phase without being converted to amorphous phase. Thus, the Te rich phase precipitate as hetero phase or nucreate as hetero phase nuclei within crystal grains or in grain boundaries of the complex compound semiconductor, and thereby a raw thermoelectric semiconductor material having crystal strain can be achieved.

[0043] In addition, the raw thermoelectric semiconductor material has a great thickness and a large width as a result of solidification from molten raw alloy under slow cooling rate. Therefore, each raw thermoelectric semiconductor material may have large volume, and therefore may have a small specific surface area compared with a powder or the like of fine sizes. Therefore, the possibility of surface oxidization is reduced, and thereby, lowering of the electric conductivity of the raw thermoelectric semiconductor material can be prevented.

[0044] In the above described method, when heating during solidification forming of a raw thermoelectric semiconductor material is performed by multiple step method, the layered raw thermoelectric semiconductor material can be heated in such a manner that the entire body reaches a desired temperature for solidification and formation even when the heating position by the heat source is biased during heating raw thermoelectric semiconductor material for solidification and formation. Therefore, the compact formed through solidification forming of a raw thermoelectric semiconductor material can be made homogeneous throughout the entire body, and therefore, the thermoelectric semiconductor material manufactured by plastic deformation of the compact can be made homogeneous throughout the entire body. In addition, when the raw alloy is controlled to have a composition containing excess Te, the above excess component can be dissolved at the grain boundaries, and thus, the junction at the grain boundaries can be improved.

[0045] In addition, when the plastic deformation process comprises one or more omnidirectional hydrostatic pressure process, the occurrence of buckling can be prevented and an uniform deformation rate can be obtained during the plastic deformation of the compact. Therefore, a texture of the thermoelectric semiconductor material formed by the above described plastic deformation can be homogenized.

[0046] A thermoelectric semiconductor element may be cut out from the above described thermoelectric semiconductor material having excellent crystalline orientation in which both the extending direction of C face and the direction of c-axis of the hexagonal structure of the crystal grains are uniformly oriented. When the cut surface of thermoelectric semiconductor element include, as a contact surface with an electrode, a plane approximately perpendicular to the uniaxial direction of shear force application during the plastic deformation of compact to form the thermoelectric semiconductor material, it is possible to convey a current or heat in the direction approximately parallel to the extending direction of C face of the crystal grains. Therefore, the thermoelectric performance of the thermoelectric semiconductor element can be enhanced.

[0047] Accordingly, by a manufacturing method for a thermoelectric semiconductor element, in which a thermoelectric semiconductor material is cut to form a thermoelectric semiconductor element so that an approximately perpendicular plane to the uniaxial direction of shear force application during the plastic deformation of compact may be used as a contact sure with an electrode, the above described thermoelectric semiconductor element having enhanced thermoelectric performance can be achieved.

[0048] A P type thermoelectric element and an N type thermoelectric semiconductor element may be formed as above described thermoelectric semiconductor elements having a high thermoelectric performance. A PN element pair may be formed by joining, via a metal electrode, the P type and N type thermoelectric semiconductor elements arranged so that the elements are align in the direction perpendicular to the axial direction of pressure application during plastic deformation of compact for forming a thermoelectric semiconductor material, and also perpendicular to the direction of shear force by the pressure application. A thermoelectric semiconductor module may be made to have the configuration provided by the PN element pair. In such a thermoelectric semiconductor module, a stress caused by expansion or contraction of the metal electrode accompanied with temperature deviation during the use of the thermoelectric module can be applied to each of the P type and N type thermoelectric semiconductor elements in the direction parallel to C face of the hexagonal structure of the respective crystal grains. Therefore, even when the metal electrode expands or contracts, interlayer peeling of the crystals in the texture of the thermoelectric semiconductor elements can be prevented, strength and durability of the thermoelectric module can be enhanced.

[0049] Accordingly, the thermoelectric module having enhanced durability and strength can be achieved by a manufacturing method for a thermoelectric module comprising: preparing P type and N type thermoelectric semiconductor elements as above described thermoelectric semiconductor elements; arranging the P type and N type thermoelectric semiconductor elements so that the elements are aligned in the direction perpendicular to the axial direction of pressure application during plastic deformation of a compact, and also perpendicular to the direction of shear force by the pressure application; joining the P type and N type elements via a metal electrode to form a PN element pair.

[0050] According to the present invention as described above, excellent effects can be obtained as following:

[0051] (1) A thermoelectric semiconductor material is produced by: layering and packing plate shaped raw thermoelectric semiconductor materials made of a raw alloy having a predetermined composition of a thermoelectric semiconductor to form a layered body; solidifying and forming the layered body to form a compact; plastically deforming the compact by applying pressure to the compact in a uniaxial direction that is perpendicular or nearly perpendicular to the main layering direction of the raw thermoelectric semiconductor material, and thereby applying shear force in a uniaxial direction that is approximately parallel to the main layering direction of the raw thermoelectric semiconductor material. In such a thermoelectric semiconductor elements, it is possible to enhance the strength by applying additional pressure to plastically deforming the compact which is formed by solidifyication forming of plate shaped raw thermoelectric semiconductor materials. At the same time, not only the extending direction of C face, but also the direction of c-axis of the hexagonal structure in the crystal gains in the texture can be uniformly oriented, and highly excellent crystalline orientation can be achieved. Therefore, by setting the direction in which current and heat are conveyed in the extending direction of C face of the crystal grains, thermoelectric performance can be enhanced.

[0052] (2) Accordingly, the above described thermoelectric semiconductor material may be achieved by a manufacturing method of a thermoelectric semiconductor material comprising: melting a raw alloy having a predetermined composition of thermoelectric semiconductor; subsequently having the molten alloy contacted with the surface of a cooling member and thereby forming plate shaped raw thermoelectric semiconductor materials; layering the plate shaped raw thermoelectric semiconductor materials in a direction approximately parallel to the direction of the plate thickness to form a layered body; solidifying and forming the layered body to form a compact; applying pressure to the compact in one of two axial directions which are crossing each other in a plane approximately perpendicular to the main layering direction of the raw thermoelectric semiconductor materials, while preventing deformation of the layered by in the other axial direction; and thereby applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials, and plastically deforming the layered body to form a thermoelectric semiconductor material.

[0053] (3) In a thermoelectric semiconductor material having a compound phase comprising: complex compound semiconductor phase having a predetermined stoichiometric composition of a compound thermoelectric semiconductor, and a Te rich phase in which excess Te is added to the above composition, crystal grain boundaries exist in the thermoelectric semiconductor material, and crystal strain is generated due to the presence of the compound phase of complex compound semiconductor phase and the Te rich phase. By the introduction of crystal stain, thermal conductivity can be lowered, and therefore, the Figure-of-Merit can be increased as a result of the lowering of thermal conductivity.

[0054] (4) In a thermoelectric semiconductor material produced by: adding excess Te to the predetermined stoichiometric composition of a compound thermoelectric semiconductor to form a raw alloy; layering and packing plate shaped raw thermoelectric semiconductor materials made of the raw alloy to form a layered body; solidifying and forming the layered body to form a compact; applying pressure to the compact in an axial diction perpendicular or nearly perpendicular to the main layering direction of the raw thermoelectric semiconductor materials; and thereby applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials, and plastically deforming the compact, the thermoelectric semiconductor material is provided with excellent crystalline orientation in which both extending direction of C face of the hexagonal structure of the crystal grains and direction of c-axes of the crystal grains are approximately uniformly oriented. In addition, due to the presence of the compound phase of complex compound semiconductor phase and the Te rich phase, thermal conductivity can be lowered, and therefore, the Figure-of-Merit can be further increased.

[0055] (5) Accordingly, a thermoelectric semiconductor having above described excellent crystalline orientation, a compound phase of complex compound semiconductor phase and the Te rich phase, and a high Figure-of-Merit can be achieved by a manufacturing method for a thermoelectric semiconductor material, comprising controlling a raw alloy to have a composition in which excess Te is added to the predetermined stoichiometric composition of a compound thermoelectric semiconductor.

[0056] (6) In the above described method, a P type thermoelectric semiconductor material having high thermoelectric performance can be produced by controlling the raw alloy to have a composition in which excess Te is added to a $(Bi—Sb)_2Te_3$ based stoichiometric composition, concretely, by controlling the raw alloy to nave a composition where 0.1% to 5% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 7 to 10 atomic % of Bi, 30 to 33 atomic % of Sb, and 60 atomic % of Te.

[0057] (7) On the other band, a N type thermoelectric semiconductor material having above described high thermoelectric performance can be produced by controlling the raw alloy to have a composition where excess Te is added to a $Bi_2(Te—Se)_3$ based stoichiometric composition, concretely, by controlling the raw alloy to have a composition where 0.01% to 10% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 40 atomic % of Bi, 50 to 59 atomic % of Te, and 1 to 10 atomic % of Se.

[0058] (8) Furthermore, by carrying out solidification forming of the raw thermoelectric semiconductor material by applying pressure along with heating the raw material to a temperature no less than 380° C. and no higher than 500° C., the thermoelectric semiconductor material can be solidified and formed in a state in which the Te rich phase in the raw thermoelectric semiconductor material is prevented from being converted to liquid phase, or the Te rich liquid phase is controlled to be a small amount. Therefore, a P type or N type thermoelectric semiconductor material can be formed, having a multi phase structure of the P type or N type complex compound semiconductor phase dispersing microscopic Te rich phases including an excess Te in the above semiconductor composition.

[0059] (9) Moreover, in the manufacturing method, when a molten alloy of the raw alloy is contacted with the surface of a cooling member to form a plate shaped raw thermoelectric semiconductor material, the cooling rate of the molten alloy during solidification may be controlled to a rate at which 90% or more of the thickness of the plate shaped raw thermoelectric semiconductor material is not quenched.

Concretely, a rotational roll may be used as the cooling member, and when the plate shaped raw thermoelectric semiconductor material is formed by supplying the molten alloy of the raw alloy to the surface of such cooling member, the rotational roll may be rotated at a rate at which the thickness of the raw thermoelectric semiconductor material is controlled to be at least no less than 30 μm. By this method, microscopic crystal nuclei are formed on the side of contact sure of the molten raw alloy and the cooling member, and the molten alloy can be slowly solidified so that, from the nuclei, large crystal grains grow in the direction of the thickness, and the raw thermoelectric semiconductor material can be formed to have a thickness of no less than 30 μm. At that time, the crystal grains can be grown in such a manner that C face of the hexagonal structure of the crystals extend in the direction of thickness, approximately throughout the entire thickness of the raw thermoelectric semiconductor material. When the raw alloy is made to have a composition including excess Te, in the $(Bi—Sb)_2Te_3$ based P type complex compound semiconductor phase or in the $Bi_2(Te—Se)_3$ based N type complex compound semiconductor phase, the Te rich phases including an excess Te in each of the above compositions can be microscopically dispersed as separated phase without being converted to amorphous phase. Thus, a Te rich phase precipitate as hetero phase or nucleate as hetero phase nuclei within crystal grains or in grain boundaries of the complex compound semiconductor, and thereby a raw thermoelectric semiconductor material having crystal strain can be achieved.

[0060] In addition, the raw thermoelectric semiconductor material has a large thickness and a large width as a result of solidification from molten raw alloy under slow cooling rate. Therefore, each raw thermoelectric semiconductor material may have large volume, and therefore may have a small specific surface area compared with a powder or the like of fine sizes. Therefore, the possibility of surface oxidization is reduced, and thereby, lowering of the electric conductivity of the raw thermoelectric semiconductor material can be prevented.

[0061] (10) In the above described method, when heating during solidification and forming process of a raw thermoelectric semiconductor material is performed by multiple step method, the layered raw thermoelectric semiconductor material can be heated in such a manner that the entire body reaches a desired temperature for solidification forming even when the heating position by the heat source is biased during heating raw thermoelectric semiconductor material for solidification forming. Therefore, the compact formed through solidification forming of a raw thermoelectric semiconductor material can be made homogeneous throughout the entire body, and therefore, the thermoelectric semiconductor material manufactured by plastic deformation of the compact can be made homogeneous throughout the entire body. In addition, when the raw alloy is controlled to have a composition containing excess Te, the above excess component can be dissolved at the grain boundaries, and thus, the junction at the gain boundaries can be improved

[0062] (11) In addition, when the plastic working process in the method comprises one or more omnidirectional hydrostatic pressure process, the occurrence of buckling can be prevented and an uniform deformation rate can be obtained during the plastic deformation of the compact. Therefore, a texture of the thermoelectric semiconductor material formed by the above described plastic deformation can be homogenized.

[0063] (12) A thermoelectric semiconductor element may be cut out from the above described thermoelectric semiconductor material having excellent crystalline orientation in which both the extending direction of C face and the direction of c-axis of the hexagonal structure of the crystal grains are uniformly oriented. When the cut surface of thermoelectric semiconductor element include, as a contact surface with an electrode, a plane approximately perpendicular to the uniaxial direction of shear force application during the plastic deformation of a compact to form the thermoelectric semiconductor material, it is possible to convey a current or heat in the direction approximately parallel to the extending direction of C face of the crystal grains. Therefore, the thermoelectric performance of the thermoelectric semiconductor element can be enhanced

[0064] (13) Accordingly, the above described thermoelectric semiconductor element having enhanced thermoelectric performance can be achieved by a manufacturing method for a thermoelectric semiconductor element, comprising slicing a thermoelectric semiconductor material to form a thermoelectric semiconductor element so that an approximately perpendicular plane to the weal direction of shear force application during the plastic deformation of a compact may be used as a contact surface with an electrode.

[0065] (14) A P type thermoelectric element and an N type thermoelectric semiconductor element may be formed as above described thermoelectric semiconductor elements having a high the thermoelectric performance. A PN element pair may be formed by joining, via a metal electrode, the P type and N type thermoelectric semiconductor elements arranged so that the elements are aligned in the direction perpendicular to the axial direction of pressure application during plastic deformation of a compact for forming a thermoelectric semiconductor material, and also perpendicular to the direction of shear force by the pressure application. A thermoelectric semiconductor module may be made to have the configuration provided by the above described PN element pair. In such a thermoelectric semiconductor module, a stress caused by expansion or contraction of the metal electrode accompanied with temperature deviation during the use of the thermoelectric module can be applied to each of the P type and N type thermoelectric semiconductor elements in the direction parallel to C face of the hexagonal structure of the respective crystal grains. Therefore, even when the metal electrode expands or contracts, interlayer peeling of the crystals in the texture of the thermoelectric semiconductor elements can be prevented, strength and durability of the thermoelectric module can be

[0066] (15) Accordingly, the thermoelectric module having enhanced durability and strength can be achieved by a manufacturing method for a thermoelectric module comprising: preparing P type and N type thermoelectric semiconductor elements as above described thermoelectric semiconductor elements; arranging the P type and N type thermoelectric semiconductor elements so that the elements are aligned in the direction perpendicular to the axial direction of pressure application during plastic deformation of a compact, and also perpendicular to the direction of shear force by the pressure application; joining the P type and N type elements via a metal electrode to form a PN element pair.

BRIEF DESCRIPTION OF THE DRAWINGS

[0067] **FIG. 1** is a flow chart showing an embodiment of manufacturing method for a thermoelectric semiconductor material according to the present invention.

[0068] **FIG. 2** is a diagram schematically showing a device used in the slow cooling foil manufacturing process of **FIG. 1**.

[0069] **FIG. 3** is a schematic perspective diagram showing a raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process of **FIG. 1**.

[0070] **FIG. 4** is a graph showing the correlation between the thickness of a raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process of **FIG. 1** and the circumferential velocity of the cooling roll.

[0071] **FIG. 5** is a graph showing the correlation between the width of the raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process of **FIG. 1** and the circumferential velocity of the cooling roll.

[0072] **FIG. 6A** is a photograph showing the cross section of the structure of a raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process of **FIG. 1**;

[0073] **FIG. 6B** is a photograph of the structure of a raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process of **FIG. 1** showing a surface of the raw thermoelectric semiconductor material opposite to the contact surface with a rotational roll.

[0074] **FIG. 7A** is a schematic perspective diagram showing a compact formed in the solidification forming process of **FIG. 1**.

[0075] **FIG. 7B** is a perspective diagram of a compact formed in a solidification forming process of **FIG. 1** schematically showing the layered structure of a raw thermoelectric semiconductor material.

[0076] **FIG. 7C** is an enlarged perspective diagram showing a partial cross section of a compact shown in **FIG. 7B**.

[0077] **FIG. 8A** is a diagram showing a plastic working device used in the plastically deforming process of **FIG. 1** and is a schematic cross sectional side view of the device in the initial state before plastically deforming the compact.

[0078] **FIG. 8B** is a diagram showing the device of **FIG. 8A** as viewed along the line A-A in the direction of the arrows;

[0079] **FIG. 8C** is a diagram showing a plastic working device used in the plastically deforming process of **FIG. 1** and is a schematic cross sectional side view of the device in a state in which a thermoelectric semiconductor material is formed by plastic deformation of a compact.

[0080] **FIG. 8D** is a diagram corresponding to **FIG. 8B** showing another type of the plastic working device used in the plastically deforming process of **FIG. 1** and is provided with a ring for fixing the position.

[0081] **FIG. 9A** is a schematic perspective diagram showing a thermoelectric semiconductor material formed in the plastically deforming process of **FIG. 1**.

[0082] **FIG. 9B** is a perspective diagram schematically showing the crystalline orientation of a thermoelectric semiconductor material formed in the plastically deforming process of **FIG. 1**;

[0083] **FIG. 10** is a graph showing the correlation between the circumferential velocity of the cooling roll in the slow cooling foil manufacturing process of **FIG. 1** and the thermal conductivity of the thermoelectric semiconductor material formed in the plastically deforming process of **FIG. 1** using a raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process.

[0084] **FIG. 11** is a graph showing the correlation between the circumferential velocity of the cooling roll in a slow cooling foil manufacturing process of **FIG. 1** and the electric conductivity of a thermoelectric semiconductor material that is formed in the plastically deforming process of **FIG. 1** using a raw thermoelectric semiconductor material formed in this slow cooling foil manufacturing process.

[0085] **FIG. 12** is a graph showing the correlation between the circumferential velocity of the cooling roll in a slow cooling foil manufacturing process of **FIG. 1** and the Seebeck coefficient of a thermoelectric semiconductor material formed in a plastically deforming process of **FIG. 1** using the raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process.

[0086] **FIG. 13** is a graph showing the correlation between the circumferential velocity of a cooling roll in a slow cooling foil manufacturing process of **FIG. 1** and the carrier concentration of the thermoelectric semiconductor material formed in the plastically deforming process of **FIG. 1** using a raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process.

[0087] **FIG. 14** is a graph showing the correlation between the circumferential velocity of the cooling roll in the slow cooling foil manufacturing process of **FIG. 1** and the Figure-of-Merit of the thermoelectric semiconductor material formed in the plastically deforming process of **FIG. 1** using the raw thermoelectric semiconductor material formed in this slow cooling foil manufacturing process;

[0088] **FIG. 15** is a graph showing the correlation between the thickness and the oxygen concentration of the raw thermoelectric semiconductor material formed in a slow cooling foil manufacturing process of **FIG. 1**.

[0089] **FIG. 16** is a graph showing the correlation between the width and oxygen concentration of the raw thermoelectric semiconductor material that is formed in a slow cooling foil manufacturing process of **FIG. 1**.

[0090] **FIG. 17** is a graph showing the correlation between the circumferential velocity of the cooling roll in a slow cooling foil manufacturing process of **FIG. 1** and the oxygen concentration of the raw thermoelectric semiconductor material formed in the slow cooling foil manufacturing process.

[0091] **FIG. 18** is a graph showing the correlation between the oxygen concentration in the raw thermoelectric semiconductor material that is manufactured in the slow cooling foil manufacturing process of **FIG. 1** and the Figure-of-Merit of the thermoelectric semiconductor material formed using the raw thermoelectric semiconductor material.

[**0092**] **FIG. 19** is a flow chart showing another embodiment of a manufacturing method for the thermoelectric semiconductor material according to the present invention;

[**0093**] **FIG. 20A** is a diagram showing a plastic working device used for an omnidirectional hydrostatic pressure process of **FIG. 19** and is a schematic cross sectional side view of the device in the initial state before the plastic deformation of a compact.

[**0094**] **FIG. 20B** is a diagram showing the device of **FIG. 20A** as viewed along line B-B in the direction of the arrows.

[**0095**] **FIG. 20C** is a diagram showing the plastic working device used for an omnidirectional hydrostatic pressure process of **FIG. 19** and is a schematic cross sectional side view of the device in a state in which omnidirectional hydrostatic pressure is applied to a compact that has been plastically deformed by a predetermined amount.

[**0096**] **FIG. 21** is a schematic perspective diagram showing steps of the manufacturing method for a thermoelectric semiconductor element of the present invention, and showing a state for slicing a thermoelectric semiconductor material, a sliced wafer, and a thermoelectric semiconductor element cut out from a wafer.

[**0097**] **FIG. 22** is a schematic perspective diagram showing an embodiment of a thermoelectric module according to the present invention.

[**0098**] **FIG. 23** is a schematic perspective diagram showing a comparative example for a thermoelectric module of **FIG. 22**.

[**0099**] **FIG. 24A** is a schematic cross sectional side view showing another example of a plastic working device used in a plastically deforming process of **FIG. 1**.

[**0100**] **FIG. 24B** is a diagram showing the device of **FIG. 24A** along line C-C in the direction of the arrows.

[**0101**] **FIG. 25A** is a schematic diagram showing an example of the plastically deforming process of **FIG. 1** by another device, and showing a state in which a compact is plastically deformed by a high pressure press.

[**0102**] **FIG. 25B** is a schematic diagram showing an example of the plastically deforming process of **FIG. 1** by another device, and showing a state in which a compact is plastically deformed by a rolling device.

[**0103**] **FIG. 26** is a graph showing the results of the comparison of the thermoelectric performance of a thermoelectric module manufactured by the manufacturing method of the present invention with that of a thermoelectric module manufactured by another manufacturing method.

[**0104**] **FIG. 27** is a perspective diagram schematically showing an example of a conventional thermoelectric module.

BEST MODE FOR CARRYING OUT THE INVENTION

[**0105**] In the following embodiments of the present invention are explained with reference to the drawings.

[**0106**] FIGS. **1** to **18** show an embodiment of manufacturing method for a thermoelectric semiconductor material according to the present invention. As shown in the flow chart of **FIG. 1**, basically the thermoelectric semiconductor material is manufactured by: preparing an alloy by mixing, in a predetermined ratio, respective metals composing a raw alloy of a thermoelectric semiconductor; melting the metals to form a molten alloy; slowly cooling the molten alloy by an undermentioned cooling method at a rate at which 90% or more of the thickness of the raw thermoelectric semiconductor material is not quenched; solidifying the molten alloy to form a thin plate shaped foils (slow cooling foils) as raw thermoelectric semiconductor materials; after layering and packing the slow cooling foils produced as raw thermoelectric semiconductor materials so that the foils are layered in a mold, in the direction of plate thickness, solidification forming the layered foils under an undermentioned predetermined heating condition to form a compact; next, plastically deforming the compact by applying a load in such a manner that a shear stress is applied in an uniaxial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor material, and thereby manufacturing a thermoelectric semiconductor material.

[**0107**] Concrete manufacturing methods for an N type thermoelectric semiconductor material and an N type semiconductor element are described as follows.

[**0108**] Firstly, to prepare a stoichiometric composition of a raw alloy of an N type thermoelectric semiconductor in a component mixing process I, Bi, Se and Te are weighed so that the raw alloy contains 40 atomic % of Bi, 1 to 10 atomic % of Se, and 50 to 59 atomic % of Te. The weighed metals are mixed to obtain a $Bi_2(Te—Se)_3$ based composition. Furthermore excess Te is aided so that 0.01 to 10% by weight of Te is contained in the entire $Bi_2(Te—Se)_3$ based component, and thus an alloy having a nonstoichiometric composition with excess Te is prepared. At that time, a predetermined amount of dopant for forming an N type thermoelectric semiconductor, such as Hg, Ag, Cu or a halogen dopant, may be added.

[**0109**] Next, in a slow cooling foil manufacturing process II, as shown in **FIG. 2**, a metal mixture that has been mixed and prepared in the above-described component mixing process I is put into a melting crucible **6** made of quartz. The crucible is introduced into a container **5** which can hold a low oxygen concentration atmosphere such as a reduction gas atmosphere, an inert gas atmosphere or a vacuum. The crucible is heated by a heating coil **7** so as to melt the metal to form a molten alloy **8**. After that, the molten alloy **8** is supplied to the surface of a rotational roll **9** such as a water cooled roll. The rotational roll act as cooling member and the molten alloy is solidified. So as to form slow cooling foils as raw thermoelectric semiconductor materials **10** of at least 30 μm or more in thickness, the molten alloy is supplied from a nozzle which has a predetermined diameter, for example 0.5 mm, and is provided at the bottom of the melting crucible **6**, to the surface of the rotational roll **9** rotating at a slow rate at which the circumference velocity is no higher than 5 m/sec, and thereby the molten alloy is solidified. By this process, slow cooling foils as raw thermoelectric semiconductor materials **10** in thin plate shaped forms arm manufactured as shown in **FIG. 3**.

[**0110**] It is preferable to set the rotational velocity of the rotational roll **9** so that the circumferential velocity is no higher than 2 m/sec. When the circumference velocity of the rotational roll **9** is set to be no higher than 5 m/sec, as it is obviously shown in the graph of **FIG. 4**, the thickness of the slow cooling foil manufactured as a raw thermoelectric semiconductor material **10** can be made as thick as 30 μm or more. In addition, when molten alloy **8** is solidified on the surface of the rotational roll **9** to form the raw thermoelectric semiconductor material **10**, the molten alloy can be solidified at a rate by which 90% or more of the thickness of the raw thermoelectric semiconductor material is not quenched. Therefore, as shown in **FIG. 3**, crystal grains **11** formed in the texture of the raw thermoelectric semiconductor material **10** may have a length extending throughout entire thickness of the slow cooling foil as the raw thermoelectric semiconductor material **10**, and thus, raw thermoelectric semiconductor material **10** having an excellent crystalline orientation can be formed. Furthermore, when the circumferential velocity of rotational roll **9** is set to be no greater than 2 m/sec, the thickness of raw thermoelectric semiconductor material **10** can be effectively increased to a value of no less than approximately 70 μm. Thus lengths of crystal grains **11** can be additionally increased, and the crystalline orientation can be further improved. In addition, as described above, when the rotational speed of rotational roll **9** is set so that the circumferential velocity becomes no greater than 5 m/sec, as it is obvious from the graph shown in **FIG. 5**, the width of the slow cooling foils manufactured as the raw thermoelectric semiconductor materials **10** can be increased, and the volumes of each raw thermoelectric semiconductor material **10** can be increased.

[**0111**] Crystal grains **11** in the texture of raw thermoelectric semiconductor material **10** are schematically illustrated as hexagons in **FIG. 3**. These hexagons do not show the actual crystal lattice in the hexagonal structure of the above-described crystal grains **11**, but for convenience in explanation, schematically show the direction of C face of the hexagonal structure of the crystal grains **11** by the hexagons, and in addition, by the flattened direction of the hexagons, schematically indicate the direction in which crystal grains **11** are flattened, that is, the direction in which the crystal grains are oriented. This can be applied to the following figures.

[**0112**] As a result of this, molten alloy **8** of the raw alloy is supplied to the rotational roll **9** and is slowly cooled, and thereby is slowly and sequentially cooled from the contact surface with the rotational roll toward the outer periphery of the roll, that is in the direction of the thickness of molten alloy **8**. As a result, as shown in **FIG. 3**, the crystal structures of the complex compound semiconductor phases of Bi_2Te_3 and Bi_2Se_3 are respectively solidified and crystallized, in which extending direction of C face of the hexagonal structure of crystal grains **11** are mainly oriented in the direction of the plate thickness (the direction shown by arrow t in the figure). At the same time, since Te is added to the above molten alloy **8** so that excess Te is added to the $Bi_2(Te—Se)_3$ based stoichiometric composition, Te rich phases including excess Te in the composition of Bi_2Te_3 or Bi_2Se_3 are microscopically dispersed as a non-amorphous separated phase in the crystal grains and grain boundaries of the respective complex compound semiconductor phases of Bi_2Te_3 and Bi_2Se_3. Thus a raw thermoelectric semiconductor material **10** that is thought to have a structure dispersing microscopic Te-rich phase, that is, a structure having crystal strain by precipitation of hetero phase (Te-rich pahse) or by nucleation of hetero pahse nuclei within crystal grains and grain boundaries of the $Bi_2(Te—Se)_3$ based complex compound semiconductor, can be achieved.

[**0113**] **FIGS. 6A and 6B** show scanning electron microscope (SEM) images of a texture of raw thermoelectric semiconductor material **10** manufactured by the above-described slow cooling foil mating process II. **FIG. 6A** shows a cross section of the raw thermoelectric semiconductor material **10**. In this figure, contact surface with the rotational roll **9** is placed on the upper side. **FIG. 6B** shows the surface structure of the raw thermoelectric semiconductor material **10** opposite to the contact surface with the rotational roll.

[**0114**] As is clear from the **FIG. 6A**, raw thermoelectric semiconductor materials **10** having a thickness of no less than 30 μm can be formed in the slow cooling foil manufacturing process II. The contact surface with the rotational roll **9** shows fine crystal gains formed by quenching of molten alloy **8** by the contact with the rotational roll **9**. These fine crystal grains are formed only in the surface region on the side of the contact surface with the rotational roll **9**, whereas other than the surface region having the fine crystal grains, in the region of 90% or more of the thickness, large crystal grams **11** oriented in the direction of the plate thickness throughout the entire thickness of the plate can be formed.

[**0115**] In addition, as is clear from **FIG. 6B**, the raw thermoelectric semiconductor material **10** have a textual structure in which crystal grains **11***a* of hetero phases (Te rich phases) are generated within the grains and grain boundaries of crystal grains **11** of the $Bi_2(Te—Se)_3$ based complex compound semiconductor or the like, which are flattened and oriented so as to extend in direction of the plate thickness. Powder particles of small grain sizes mixed in the raw thermoelectric semiconductor materials **10** manufactured by the slow cooling foil manufacturing process II may be removed in advance by sieving, before the raw thermoelectric semiconductor materials being sent to the following solidification forming process III.

[**0116**] Next, in the solidification forming process III, the slow cooling foils of raw thermoelectric semiconductor materials **10** manufactured by the slow cooling foil manufacturing process II are layered in the direction approximately parallel to the direction of the plate thickness (the direction of arrow t) and are packed in a mold, not shown, within a container (not shown) that can hold a low oxygen concentration atmosphere such as a reduction gas atmosphere, an inert gas atmosphere or a vacuum of 10 Pa or less. After that, the foils are sintered and pressurized and are solidified and formed to have a predetermined form. For example, a rectangular solid shaped compact **12** having a predetermined width corresponding to a spacing between restricting members **15** in a plastic working device **13** used in the after-mentioned plastically deforming process IV is manufacturing as shown in **FIGS. 7A, 7B**, and 7C.

[**0117**] **FIG. 7B** schematically shows a layered structure of the slow cooling foils of a raw thermoelectric semiconductor material **10** as a basic configuration of the structure of the compact **12**. **FIG. 7C** shows an enlarged view of the layered structure of raw thermoelectric semiconductor materials **10** of the **FIG. 7B**.

[**0118**] As conditions for the above-described sintering process along with applying predetermined pressure, for example, pressure of no less than 14.7 MPa, and heat is applied in a manner such that the Te rich phase existing in the thermoelectric semiconductor material manufactured in the above-described slow cooling foil manufacturing process II is prevented from complete segregation, formation of deferent phase, or liquid phase precipitation. Since the Te-rich phase have a possibility to form a liquid phase at a temperature of approximately 420° C., sintering is carried out by heating to a temperature condition of no higher than 500° C., preferably no lower than 420° C. and no higher than 450° C., and keeping at the temperature for about 5 seconds to 5 minutes.

[0119] The lower limit of the temperature condition in the sintering is no lower than 380° C. This is because the density of compact **12** does not increase when the sintering temperature is lower than 380° C.

[0120] At the time of the above-described sintering, multi step heating is carried out so that the entirety of the object for sintering can be approximately uniformly heated to the predetermined sintering temperature without causing heterogeneous temperature distribution in the object.

[0121] In the multi step heating, when an object for sintering is heated to the predetermined sintering temperature using a predetermined heating source, not shown, heating step is controlled to comprise one or periods, for example, for no less than 10 seconds, of stopping heating by the heat source for a predetermined period of time, or of temporally changing the heating by the heat source so that the heating rate of the object of sintering is slowed down, and thereby homogenizing the temperature of the whole object for sintering by heat conduction during the above-described stopping heating or slowing heating rate periods. After homogenizing the temperature of the whole body in the process of heating, by further heating the object for sintering, the object is heated almost homogeneously to the final temperature, as the sintering temperature.

[0122] Accordingly, by homogenizing the temperature of the entire object for sintering in the process of heating, even though the heating position by the heat source is biased, uneven temperature distribution can be restrained when the temperature reaches the sintering temperature. In this case, as a heating device (heating furnace) for the sintering, conventional hot pressing, energized hot pressing or pulse energized hot pressing may be used. In addition, the above-described periods for stopping heating, or slowing the heating rate are not limited to 10 seconds or higher, but may be arbitrarily set depending on the heating ability of the heat source, the size of the object for sintering, or the like.

[0123] The slow cooling foils as raw thermoelectric semiconductor materials **10** formed in the above-described slow cooling foil manufacturing process II have large widths and thicknesses, and therefore, their layered body have a large volume and many interstices. By layering and subsequently sintering along with pressing the raw thermoelectric semiconductor materials **10** in the solidification forming process III, atoms of the respective raw thermoelectric semiconductor materials **10** migrate so as to fill in the interstices between the raw thermoelectric semiconductor materials **10**. Together with the migration of atoms, the respective raw thermoelectric semiconductor materials **10** are plastically deformed so as to make contact with each other and fill in the interstices between the raw thermoelectric semiconductor materials **10**. Therefore, raw thermoelectric semiconductor materials **10** which are made to make contact with each other through the plastic deformation are joined to each other via the interfaces.

[0124] At that time, although the deformation of raw thermoelectric semiconductor menials **10** slightly disarrange the orientation of C face of crystal grains **11** that have been oriented approximately in the direction of plate thickness of the raw thermoelectric semiconductor material **10**, that disordering does not cause a volumetric breakdown of the whole body. Accordingly, as shown in **FIG. 7B**, in the slow cooling foils of raw thermoelectric semiconductor material **10** constructing the compact **12**, the orientation of crystal grains **11** is maintained as same as the crystalline orientation (in the direction of arrow t) of a single piece of raw thermoelectric semiconductor material **10** shown in **FIG. 3**. Therefore, it is possible to prevent the possibility of mass breakdown of the orientation of C face of the crystal grains, which could not be avoided in prior art, in which very fine raw thermoelectric semiconductor materials were sintered.

[0125] In addition, in the formation of the compact **12**, slow cooling foils of raw thermoelectric semiconductor material **10** having a large thickness and large width are layered in the direction approximately parallel to the direction of the plate thickness, and subsequently solidified and formed. Therefore, the interstices between the raw thermoelectric semiconductor materials **10** can be easily reduced, and it becomes possible to increase density of the compact **12** to approximately 99.8% or higher of the density of an ideal crystal structure of the complex compound semiconductor of the same composition.

[0126] Furthermore, no or only little amount of Te rich phase in the raw thermoelectric semiconductor material **10** is converted to a liquid phase during sintering. Therefore, the compact **12** is formed so as to maintain the teal structure of a complex compound semiconductor phase having the composition of Bi_2Te_3 and Bi_2Se_3 dispersing microscopic Te rich phases including excess Te in the above-described compositions. In addition, together with heating during the sintering process, the Te rich phases partially occur in the interfaces between the slow cooling foils as raw thermoelectric semiconductor materials **10**.

[0127] After that, in the plastically deforming process IV, a plastic working device **13** is prepared to comprise an air-tight container, not shown, that can hold a low oxygen concentration atmosphere, for example, having partial pressure of oxygen no higher than 0.2 Pa by a reduction gas atmosphere, an inert gas atmosphere or a vacuum. In such a container, as shown in **FIGS. 8A, 8B**, and **8**C, a pair of restricting members **15** in plate form having approximately parallel surfaces opposed to each other are placed intervening a predetermined spacing at either side of a base **14**. The spacing corresponds to the width of the above-described compact **12** (dimension of the compact **12** in one axial direction of the two axial directions crossing in a plane perpendicular to the main layering direction of raw thermoelectric semiconductor material **10** forming the compact **12**). Inner side of the restricting members **15** placed in the lateral direction, a punch **16** is placed so that it can slide in the upward and downward directions. In addition, by a vertical driving unit, not shown, along with being added with a load, the punch **16** can be lowered from the upper position above the restricting members **15** placed in the lateral direction to the lower position inside between the restricting members **15**. Heating units are provided to predetermined positions of the base **14**, restricting members **15**, and punch **16**. As shown in **FIG. 8A**, in a state where the punch **16** is pulled up to the upper position above the restricting members **15**, the compact **12** formed in the solidification forming process III is placed in the center portion between the restricting members **15** so that the longitudinal direction of this compact **12** is vertically directed. At the same time, the compact **12** is arranged so that the layering direction of the raw thermoelectric semiconductor materials **10** forming the compact **12** (direction of arrow t, same as the direction of the plate thickness of the raw thermoelectric semiconductor material **10**) is set to be parallel to the restricting members **15** placed in the lateral direction, and both sides of the compact in the direction of the width are placed so as to make contact with the inner surfaces of the restricting members **15** placed in the lateral direction. Next, along with heating the compact **12** at a temperature that is no higher than 470° C., preferably no higher than 450° C. by the heating units, pressure of a predetermined load is applied to the compact **12** by lowering the punch **16** by the vertical driving unit as shown in two-dot chain lines of **FIG. 8A**. As a result, as shown in **FIG. 8C**, the compact **12** is plastically deformed so as to be expanded in a uniaxial direction parallel to the layering direction of raw thermoelectric semiconductor materials **10**, and a thermoelectric semiconductor material **17** of rectangular solid is manufactured.

[0128] In the above-described plastic working device **13**, when a pressing force is applied from above to compact **12** by punch **16**, since deformation of the compact **12** in the direction of its width is restricted by the restricting members **15** placed in the lateral direction, deformation of the compact **12** is allowed only in the direction parallel to the restricting members **15**, that is to say, in the layering direction of raw thermoelectric semiconductor materials **10** (in the direction of arrows t), and therefore a shear force is applied in a uniaxial direction parallel to the layering direction. As a result, in the slow cooling foils of raw thermoelectric semiconductor material **10** constructing the compact **12** before the above-described plastic deformation, interfaces of layers are deformed and adjacent layers are integrated to each other. Crystal grains being oriented so that C face of the hexagonal structure extend in the direction parallel to the direction of the plate thickness of raw thermoelectric semiconductor materials **10** in the compact **12**, are plastically deformed to be flattened in the direction in which the shear force is applied, and are oriented so that the cleavage planes are perpendicular to the direction of the pressure.

[0129] Accordingly, as shown in **FIG. 9A**, in the texture of thermoelectric semiconductor materiel **17** formed after the plastically deforming of the compact **12**, crystal grains are oriented as schematically shown in **FIG. 9B**. The crystal grains **11** are respectively deformed so that C face of the hexagonal structure extends in the expanding direction of the compact **12**, that is to say, in the direction parallel to the layering direction of raw thermoelectric semiconductor materials **10** in the compact **12** before the deformation (in the direction of arrows t). At the same time, most of the crystal grains **11** are oriented so that the direction of c-axes are aligned in the direction of compression (in the direction of arrows p) in the plastically forming process. The hexagons in **FIG. 9B** only indicate the orientation of the crystal grains **11**, but do not reflect the actual sizes of the crystal grains **11**.

[0130] During the plastically deformation of the compact **12** in the plastic wowing device **13**, strong outward sums is applied to the restricting members **15** placed in the lateral direction. Therefore, as show in **FIG. 8D**, a fixing position ring **15***a* may be provided so as to surround the outer periphery of the restricting members **15** placed in the lateral direction. By this configuration, the stress that is applied to the restricting members **15** placed in the lateral direction may be endured by the fixing position ring **15***a*.

[0131] As described above, in the N type thermoelectric semiconductor material **17** of the present invention, by slowly cooling and solidifying molten raw alloy **8** using rotational roll **9**, crystal grins **11** are oriented in the direction of the plate thickness, and made long to extending throughout entire plate thickness, and thereby have an improved crystalline orientation. In addition raw thermoelectric semiconductor materials **10** have a structure in which Te rich phases are precipitated, as hetero phase low melting point, in the crystal grains or grain boundaries. Along with maintaining the crystalline orientation and the textual structure comprising $Bi_2(Te—Se)_3$ based complex compound semiconductor phases dispersing the above-described Te-rich phase, the raw thermoelectric semiconductor materials **10** are solidified and formed to form the compact. The compact is expanded only in a uniaxial direction approximately parallel to the direction of the plate thickness of the raw thermoelectric semiconductor material **10**, that is, the layering direction of the raw thermoelectric semiconductor material **10**. Because of the above-described configuration, in the N type thermoelectric semiconductor material, crystal strain is generated by the presence of the hetero phase within crystal grains and grain boundaries, as well as by the presence of grin boundaries. By the generation of the crystal strain, thermal conductivity can be reduced. In addition, since the directions of c-axes and extending directions of C face of the hexagonal structure of the crystal grains **11** are approximately uniformly oriented throughout the entire body of the thermoelectric semiconductor material **17**, thermoelectric performance (of which the Figure-of-Merit is Z) can be enhanced by setting the direction for conveying a current and heat to the extending direction of C face of the crystal grains **11**.

[0132] As shown in **FIG. 4**, the circumferential velocity of rotational roll **9** is set at a rate as low as 5 m/sec, so that raw thermoelectric semiconductor materials **10** having thickness of no less than 30 μm can be achieved. By using a rotational roll of the above-described low speed rotation, the thermal conductivity (κ) of manufactured thermoelectric semiconductor material **17** can be increased compared to the case using raw thermoelectric semiconductor material **10** made by the rotational roll **9** of high rotational speed. As shown in **FIG. 10**, the above description is clearly shown in the relationship, between the rotational speed of rotational roll **9** during the manufacture of slow cooling foils as raw thermoelectric semiconductor materials **10**, and the thermal conductivity (κ) of the thermoelectric semiconductor material **17** manufactured from the raw thermoelectric semiconductor materials **10** through the above-described process.

[0133] In addition, as shown in **FIG. 11**, as it is clearly indicated by the relationship between the rotational speed of rotational roll **9** during manufacturing slow cooling foils as raw thermoelectric semiconductor materials **10** and electric conductivity (σ) of manufactured thermoelectric semiconductor material **17**, by using a rotational roll of the low rotational speed like the above described value, electric conductivity (σ) of manufactured thermoelectric semiconductor material **17** can be increased, compared to the case using raw thermoelectric semiconductor materials **10** produced by a rotational roll **9** of high rotational speed.

[**0134**] Furthermore, as shown in **FIG. 12**, as it is clearly indicated from the relationship between the rotational speed of the rotational roll **9** during manufacturing the slow cooling foils as raw thermoelectric semiconductor materials **10** and the Seebeck coefficient (α) of manufactured thermoelectric semiconductor material **17**, by using a rotational roll of the low rotational speed like the above described value, the Seebeck coefficient (α) of manufactured thermoelectric semiconductor material **17** can be increased, compared to the case using raw thermoelectric semiconductor materials **10** produced by a rotational roll **9** of high rotational speed.

[**0135**] Moreover, as shown in **FIG. 13**, as it is clearly indicated from the relationship between the rotational speed of rotational roll during manufacturing slow cooling foils as raw thermoelectric semiconductor materials **10** and the concentration of the carriers of manufactured thermoelectric semiconductor material **17**, by using a rotational roll of the low rotational speed like the above described value, the concentration of the carriers of manufactured thermoelectric semiconductor material **17** can be increased, compared to the case using raw thermoelectric semiconductor materials **10** produced by a rotational roll **9** of high rotational speed.

[**0136**] Accordingly, as shown in **FIG. 14**, as it is clearly indicated from the relationship between the rotational speed of the rotational roll **9** during manufacturing slow cooling foils as the raw thermoelectric semiconductor materials **10** and the Figure-of-Merit (Z) of manufactured thermoelectric semiconductor material **17**,

[**0137**] in the thermoelectric semiconductor material **17** manufactured, through the above-described procedures, from the raw thermoelectric semiconductor material **10** that has been manufactured by the rotational roll **9** of slow speed, the Figure-of-Merit (Z) is increased compared to the case using the raw thermoelectric semiconductor materials **10** produced by a rotational roll **9** of high rotational speed.

[**0138**] Furthermore, as shown in **FIG. 4**, in the above-described thermoelectric semiconductor material **17** according to the present invention, the thickness of the slow cooling foils manufactured as raw thermoelectric semiconductor materials **10** can be increased by slowing the rotational speed of rotational roll **9**, and thereby the specific surface area can be reduced. As a result, as it is clear from **FIG. 15** showing a relationship between the thickness of slow cooling foils as raw thermoelectric semiconductor materials **10** and the oxygen concentration, measured by an infrared absorption method, contained in the raw thermoelectric semiconductor materials **10**, oxidization of raw thermoelectric semiconductor materials **10** can be restricted and the oxygen concentration in thermoelectric semiconductor material **17** manufactured from the raw thermoelectric semiconductor materials **10** can be reduced.

[**0139**] In addition, as shown in **FIG. 5**, the width of the slow cooling foils manufactured as the raw thermoelectric semiconductor materials **10** can be increased by slowing the rotational speed of rotational roll **9**, and thereby the specific surface area can be reduced. As a result, as it is clear from **FIG. 16** showing the relationship between the width of slow cooling foils as raw thermoelectric semiconductor materials **10**, and the oxygen concentration, measured by an infrared absorption method, contained in the raw thermoelectric semiconductor materials **10**, oxidization of the raw thermoelectric semiconductor materials **10** can be restricted in the same manner as described above, and the oxygen concentration in manufactured thermoelectric semiconductor material **17** can be reduced.

[**0140**] Accordingly, as it is clear from **FIG. 17** showing the relationship between the rotational speed of the rotational roll **9** and the oxygen concentration in thermoelectric semiconductor material **17**, the oxygen concentration contained in manufactured thermoelectric semiconductor material **17** can be reduced by slowing the rotational speed of the rotational roll **9**. Therefore, it is possible to prevent lowering of the electric conductivity (σ) due to oxidation.

[**0141**] Therefore, as it is clear **FIG. 18** showing the relationship between the oxygen concentration in slow cooling foils as raw thermoelectric semiconductor materials **10**, and the Figure-of-Merit, by reducing the oxygen concentration contained in manufactured thermoelectric semiconductor material **17**, the thermoelectric performance of the thermoelectric semiconductor material **17** can be increased.

[**0142**] The electric conductivity (σ) and the Seebeck coefficient (α) of the above-described manufactured N type thermoelectric semiconductor material **17** can be controlled, by adjusting the ratio of Te to Se in the $Bi_2(Te—Se)_3$ based composition, which is the standard for N type thermoelectric semiconductor compositions.

[**0143**] **FIG. 19** is a flow chart showing another embodiment of a manufacturing method for a thermoelectric semiconductor material of the present invention. In this embodiment, in plastically deforming process IV during the manufacturing procedure of a thermoelectric semiconductor material in the same manner as described above, when a compact **12** is pressed, and a shear force is applied in a uniaxial direction parallel to the layering direction of the slow cooling foils of the raw thermoelectric semiconductor materials **10**, so that the compact is plastically deformed to a predetermined form, one or more times of omnidirectional hydrostatic pressure process IV-2 may be carried out during the process of the uniaxial shear force applying process IV-1 for plastically deforming an object, for example, at the time in which ratio of deformation is low. In the omnidirectional hydrostatic pressure process IV-2, during the plastic deformation of the compact **12**, deformation of the compact **12** is temporarily restricted by contact with planes placed in the direction of deformation, and at that state, a pressure is continuously applied over a given period of time.

[**0144**] Accordingly, when the above-described omnidirectional hydrostatic pressure process IV-2 is carried out, as shown in **FIGS. 20A, 20D**, and **20**C, within a plastic working device **13** having similar configuration as shown in **FIGS. 8A, 8B**, and **8**C, a pair of front and rear restricting members **18**, each having approximately parallel surface opposed to each other intervening a predetermined spacing are provided at positions between restricting members **15** at the lateral sides so as to form a configuration in which the space between the above-described restricting members **15** placed in the lateral direction is closed on the anteroposterior sides. When a compact **12** formed in solidification forming process III is placed in the center portion of the inside between the above-described restricting members **15** placed in the lateral direction so that the layering direction of the raw thermoelectric semiconductor materials **10** constructing the compact **12** is parallel to the surfaces of restricting members **15** placed in the lateral direction, a predetermined gap is formed between the above-described compact **12** and front and rear restricting members **18** so as to provide a space for deformation of the compact. In addition, a punch **16***a* having a plane form corresponding to the space surrounded by the above-described restricting members **15** and **18** at lateral and anteroposterior sides, is provided so as to be moveable in the upward and downward directions within the above-described space by a vertical driving unit, not shown. Furthermore, heating units, not shown, are provided at predetermined positions on base **14**, restricting members **15** and **18**, and punch **16***a*. Along with preparing a plastic working device **13***a* having above-described configuration, a plastic working device **13** shown in **FIGS. 8A, 8B**, and **9**C, is also prepared.

[**0145**] When a plastic working process IV is carried out, firstly, as shown in **FIGS. 20A and 20B**, compact **12** formed in solidification forming process III is placed in the center portion between restricting members **15** placed in the lateral direction in the plastic working device **13***a*. After that, temperature conditions and pressure conditions are adjusted as same as in the above-decribed plastically deforming process IV, and punch **16***a* is lowered by the vertical driving unit so that pressure is applied to the compact **12** from above by the lowering punch **16***a*. Then, as shown by two-dot chain lines in **FIG. 20A**, since the two sides in the direction of the width of the compact **12** are restricted by restricting members **15** placed in the lateral direction, shear force is applied in a uniaxial anteroposterior direction approximately parallel to the layering direction of the raw thermoelectric semiconductor materials **10** forming the compact. As a result, the compact is plastically deformed and flattened in the anteroposterior direction. Thus, a uniaxial shear force applying process IV-1 is carried out. After that, plastic deformation continues in the anteroposterior direction, ad thereby, as shown in **FIG. 20C**, the plastically deformed body of the compact **12** is made to be contacted with the front and rear restricting members **18**. In this state, when further pressure is applied from above by the punch **16***a*, the deformed body of the compact **12** is restricted by the restricting members **15** placed in the lateral direction at two sides in the direction of the width, and also restricted by restricting members **18** at two sides in the anteroposterior direction, and thereby prevented from deformation. Therefore, pressure provided by the punch **16***a* is applied to the deformed body of the compact **12** as omnidirectional hydrostatic pressure. As described above, the omnidirectional hydrostatic pressure process IV-2 is carried out.

[**0146**] After that, the plastically deformed body of compact **12** which has been expanded (plastically deformed) in the anteroposterior direction until it contacts front and rear restricting members **18**, is taken out from the plastic working device **13***a*, and the plastically deformed body of the compact **12** is placed in the center portion between restricting members **15** placed in the lateral direction of plastic working device **13** in the same manner as described in reference to **FIGS. 8A, 8B**, and **8**C. After that, punch **16** is lowered so as to press further the plastically deformed body of the above-described compact **12** from above, and thereby, the plastically deformed body of the compact **12** is further expanded by applying a shear force in the anteroposterior direction, which is an uniaxial direction approximately parallel to the layering direction of raw thermoelectric semiconductor materials **10** constructing the compact **12** before plastic deformation. Thus, the uniaxial shear force applying process IV-1 is carried out, and thermoelectric semiconductor material **17** is manufactured.

[**0147**] The above-described omnidirectional hydrostatic pressure process IV-2 may be carried out two or more times. In this case a plurality of plastic working devices **13***a*, in which the distance between front and rear restricting members **18** increases step by step, are prepared and the devices are sequentially used from the one having smallest distance between front and rear restricting members **18** is the smallest to the one having the largest distance between front and rear restricting members **18**. Pressure is applied to the compact **12** formed in solidification forming process III from above by lowering the punch **16***a* in the same manner as described above, and thus, a shear force is applied in a uniaxial direction approximately parallel to the layering direction of raw thermoelectric semiconductor materials **10**. As a result, the compact is plastically deformed so that the amount of deformation from the initial state sequentially increases. After that, omnidirectional hydrostatic pressure is applied in a state in which deformation is restricted by front and rear restricting members **18**, and finally, the compact may be plastically deformed so as to expand in the anteroposterior direction by the plastic working device **13** not having the front and rear restricting members **18**.

[**0148**] In this case, by caring out the above-described omnidirectional hydrostatic pressure process IV-2 on a compact **12** during plastic deformation in the uniaxial shear force applying process IV-1, the density of the above-described compact **12** during plastic deformation can be increased. Therefore, a possibility of occurrence of buckling is prevented in the compact **12** on which the plastically deforming process is finally cared out in the plastic working device **13**. In addition, two end portions of the compact **12** in the anteroposterior direction, which are the end portions in the direction of plastic deformation, are pressed against front and rear restricting members **18**, and thereby, the forms of the two end pons in the anteroposterior direction, of the compact **12** are adjusted at a stage during plastic deformation. Thus, the deformation rate of the compact **12** can be made uniform, and therefore, it is possible to enhance the homogeneity of the texture of manufactured thermoelectric semiconductor material **17**.

[**0149**] When the omnidirectional hydrostatic pressure process IV-2 is carried out, due to the contact of the end portions of the compact **12** in the anteroposterior direction with front and rear restricting members **18**, there is a possibility that the orientation of C face of crystal grains **11** may be slightly disordered in the end portions of the compact **12** in the anteroposterior direction. Whereas, finally in plastic working device **13**, a shear force is applied in a uniaxial direction approximately parallel to the layering direction of raw thermoelectric semiconductor material **10** constructing the compact **12** so that the compact is expanded without restriction in the anteroposterior direction.

Therefore, it is possible to uniformly align the direction of C face and the direction of c-axis of crystal grains **11** even in the end portions in the anteroposterior direction of manufactured thermoelectric semiconductor material **17**.

[0150] Furthermore, in a manufacturing method for a thermoelectric semiconductor material of the present invention, as shown in **FIG. 19**, a stress stain processing process V is provided as the process after the above-described plastically deforming process IV. In the stress strain processing process V, the thermoelectric semiconductor material **17**, manufactured and plastically deformed into a predetermined form in plastically deforming process IV may be maintained at a predetermined temperature, for example at a temperature from 350° C. to 500° C., for a predetermined period of time, for example, for 30 minutes to 24 hours so that dislocations or vacancies of crystal lattice are reduced or reconstructed as a result of heat treatment. As a result, stress strain which is generated as a result of the plastic deformation in the plastically deforming process IV and remains in the structure of thermoelectric semiconductor material **17** may be eliminated. It is clear that the same effects can be obtained in the stress strain processing process V even when the temperature condition is maintained for 24 hours or more.

[0151] Moreover, a defect concentration controlling process VII may be provided as the process after the above-described stress strain processing process VI. By holding the thermoelectric semiconductor material **17**, from which residual stress strain has been removed in the above-described stress strain processing process VI, at a predetermined temperature for a predetermined period of time in the defect concentration controlling process VII, the concentration of defects in the thermoelectric semiconductor material **17** may be changed, and therefore, the electric conductivity (σ) and the Seebeck coefficient (α) may be controlled.

[0152] The thermoelectric semiconductor material **17** manufactured in the plastically deforming process IV retains a stricture of raw thermoelectric semiconductor materials **10** constructing the compact **12**, namely $Bi_2(Te—Se)_3$ based complex compound semiconductor including hetero phases (Te rich phases) in the crystal grains or in the grain boundaries. Since the excess Te is a component of the $Bi_2(Te—Se)_3$ based thermoelectric semiconductor, when the above-described thermoelectric semiconductor material **17** is heat treated, the excess Te reacts with the main component of $Bi_2(Te—Se)_3$ based semiconductor, and fill in the defects of the main component. When a slight amount of dopant such as Ag is introduced in the main component, performance changes largely. Such dopant has a large influence even when it is distributed in the grain boundaries. Performance may change largely, if the dopant diffuse into the main component portion by the use at a high temperature or by a heat treatment. It is considered that the change in the concentration of defects in thermoelectric semiconductor material **17** due to the excess Te can provide effects which cancel or accelerate the effects of the dopant.

[0153] Next, as manufacturing method for a thermoelectric semiconductor element according to the present invention, a case in which N type thermoelectric semiconductor element **3***a* is manufactured using N type thermoelectric semiconductor material **17** manufactured in accordance with the embodiments shown in FIGS. **1** to **18** is described in the following.

[0154] In this case, in the N type thermoelectric semiconductor material **17**, the extending direction of C face and the direction of c-axis of the hexagonal structure of crystal grains **11** are uniformly aligned throughout the entire structure. Therefore, considering the orientation of crystal grains **11** having uniform orientation, thermoelectric semiconductor element **3***a* is formed by being cut out from the material, so that the direction in which a current and heat are conveyed can be set in the extending direction of C face in the hexagonal structure of crystal **11**.

[0155] In the N type thermoelectric semiconductor material **17**, as shown in **FIG. 9B**, C face of the hexagonal structure in each crystal grain extends in the direction of expansion of the compact **12** during plastic deformation (direction of arrow t), and c-axis is oriented approximately in the direction of pressure (direction of arrow p) during the plastic deformation. Therefore, first as shown in the upper portion of **FIG. 21**, at predetermined spacing position in the direction of expansion of the compact **12** during the plastic deformation (direction of arrow t), the thermoelectric semiconductor material **17** is sliced along a plane perpendicular to the direction of expansion, and a wafer **19** is cut out, as shown in the middle of **FIG. 21**.

[0156] As a result, C face of the hexagonal structure of crystal grains **11** is oriented in the direction of the thickness of the above-described wafer **19**.

[0157] Next, a conductive material processed surfaces **20** are formed by processing the both ends of the wafer **19**, for example, by a plating process by a plating device, not shown. Subsequently, as shown by two-dot chain lines in the middle portion of FIG. **21**, the wafer **19** processed with conductive material is cut along two planes: a plane perpendicular to the direction (direction of arrow p) in which compact **12** is pressed during the manufacture of the thermoelectric semiconductor material **17**; and a plane defined by two axes of the direction of pressing (direction of arrow p) and the direction of expansion (direction of arrow t) during the manufacture of the thermoelectric semiconductor material **17**. Thus, a rectangular solid form, as shown in the lower portion of **FIG. 21** is cut out (diced), and thereby the N type thermoelectric semiconductor element **3***a* is manufactured.

[0158] As a result, the above-described N type thermoelectric semiconductor element **3***a* has a crystal structure in which, as shown in the lower portion of **FIG. 21**, C face of the hexagonal structure of crystal grains **11** extends throughout long length in the direction (as shown by arrow t in the figure, the same direction as the direction of expansion of the thermoelectric semiconductor material **17** during the manufacture) of a pair of opposing surfaces **20** which are processed with a conductive material. The pair of the surface **20** correspond to conductive material processed surfaces **20** of the wafer **19** processed with a conductive material. In addition, c-axes of crystal grains **11** extend in the direction of pressing (direction of arrow p in the figure) during the manufacture of the thermoelectric semiconductor material **17** among the two axial directions perpendicular to the conductive material processed surface **20**.

[0159] Accordingly, by attaching a metal electrode (not shown) to the above-described conductive material processed surface **20**, an N type thermoelectric semiconductor element **3***a* having excellent thermoelectric performance can be obtained, by making the element to have a textual structure in which the direction of c-axis, as well as the direction of C face of the hexagonal structure of the crystal grains **11** are uniformly oriented, and allowing the current and heat to be applied in the direction of C face of the hexagonal structure of the above-described crystal grains **11**.

[0160] Next, a case in which a P type thermoelectric semiconductor material is manufactured is described. In this case, to prepare a stoichiometric composition of a raw alloy of an P type thermoelectric semiconductor in a component mixing process I shown in **FIG. 1**, Bi, Sb and Te are weighed so that the raw alloy contains 7 to 10 atomic % of Bi, 30 to 33 atomic % of Sb, and 60 atomic % of Te. The weighed metals are mixed to obtain a $(Bi—Se)_2 Te_3$ based composition. Furthermore an excess Te is aided so that 0.1 to 5% by weight of Te is contained in the entire $(Bi—Se)_2 Te_3$ based component, and thus an alloy having excess Te is prepared. At that time, a predetermined amount of dopant for forming a P type thermoelectric semiconductor, such as Ag or Pb may be added.

[0161] Subsequently, in the same manner as in the case for manufacturing above-described N type thermoelectric semiconductor material **17**, in slow cooling foil manufacturing process II using a device shown in **FIG. 2**, molten alloy **8** of the metal mixture that has been mixed in the above-described component preparing process I is supplied from a nozzle of melting crucible **6**, having a diameter of 0.5 mm to a surface of rotational roll **9** slowly rotating at a circumferential velocity of 5 m/sec or less, preferably at a circumferential velocity of 2 m/sec or less, so as to be slowly cooled and solidified, and thereby, plate shaped raw thermoelectric semiconductor materials **10** (slow cooling foil) are manufactured.

[0162] The circumferential velocity of rotational roll **9** is set at 5 m/sec or less, preferably 2 m/sec or less. By using such velocity, in the same manner as in the case for forming the N type raw thermoelectric semiconductor material **10**, the slow cooling foils are manufactured to have a thick thickness of 30 μm or more, preferably, the slow cooling foils are formed to have a thickness of no less than 70 μm, and thereby, raw thermoelectric semiconductor materials **10** having an excellent crystalline orientation and large crystal grains **11** extending throughout almost entire plate thickness can be obtained. At the same time, the widths of the slow cooling foils manufactured as raw thermoelectric semiconductor material **10**, are increased, the volume of a single piece of the raw thermoelectric semiconductor material **10** is increased, and thereby the specific surface area of the piece can be reduced.

[0163] As a result, in the same manner as the above-described N type raw thermoelectric semiconductor material **10**, when the P type raw thermoelectric semiconductor material **10** is cooled on rotational roll **9**, the crystal structures of the complex compound semiconductor phases of Bi_2Te_3 and Sb_2Te_3 are respectively solidified and crystallized, in which crystalline orientation is aligned in the direction of the plate thickness. At the same time, Te rich phases including excess Te in the composition of Bi_2Te_3 or Sb_2Te_3 are microscopically dispersed as a non-amorphous separated phase in the crystal grains and grain boundaries of the Hive complex compound semiconductor phases of Bi_2Te_3 and Sb_2Te_3. Thus a raw thermoelectric semiconductor material **10** that is thought to have a structure having crystal strain by precipitation of hetero phase (Te-rich phase) or by nucleation of hetero phase nuclei within crystal grains and grain boundaries of the $(Bi—Sb)_2Te_3$ based complex compound semiconductor, can be achieved. In this raw thermoelectric semiconductor material **10**, in the same manner as that shown in **FIG. 3**, crystal grains **11** extend in approximately the direction of the plate thickness, and the crystal grains have a length almost corresponding to the plate thickness. Powder particles may be removed in advance by sieving from the raw thermoelectric semiconductor materials, before the following solidification forming process III.

[0164] Subsequently, in solidification forming process III, slow cooling foils of P type raw thermoelectric semiconductor materials **10** manufactured in the slow cooling foil manufacturing process II, are layered in the direction approximately parallel to the direction of the plate thickness, and are packed in a mold, not shown. After that, the layered body is sintered under the same pressure and temperature conditions by a multistage heating method in the same manner as the manufacturing process of compact **12** having the N type composition. As a result, the layered raw thermoelectric semiconductor materials **10** are plastically worked, solidified and formed so that the respective pieces of raw thermoelectric semiconductor materials **10** are made to make contact with each other and the interstices between the raw thermoelectric semiconductor materials are eliminated. Thus, a compact **12** in rectangular solid form in the same manner as those shown in **FIGS. 7A, 7B**, and 7C is manufactured.

[0165] As a result, no or only little limited amount of Te rich phases which have been formed in the P type raw thermoelectric semiconductor material **10** are converted to liquid phases during sintering. Therefore, the compact **12** is formed maintain a structure comprising complex compound semiconductor phases having the composition of Bi_2Te_3 and Sb_2Te_3 microscopically dispersing Te rich phases containing excess Te in the above-described compositions.

[0166] Subsequently, in a plastically deforming process IV, in the same manner as in the case for manufacturing the N type thermoelectric semiconductor material **17**, using a plastic working device **13** as shown in **FIGS. 8A, 8B, 8**C, and **8**D, along with hating the compact **12** at a temperature no higher than 500° C., preferably, no higher than 350° C., the compact is plastically deformed so as to expand in a uniaxial direction approximately parallel to the layering direction of the raw thermoelectric semiconductor materials **10**, and thereby, P type thermoelectric semiconductor material **17** is manufactured. The above-described temperature condition for heating is varied depending on the excessive amount of Te, and the processing temperate is increased with decreasing amount of excess Te.

[0167] As a result, by applying shear force only in the layering direction of raw thermoelectric semiconductor materials **10**, in the same manner as those shown in **FIGS. 9A and 9B**, crystal grains **11** oriented in the direction of the plate thickness of the raw thermoelectric semiconductor material **10** in the compact **12** are plastically deformed so as to be flatted in the uniaxial direction in which the shear force is applied. In addition, the cleavage planes are oriented so as to be approximately perpendicular to the direction in which pressure is applied, and the compact is deformed so that C face of the hexagonal structure of each crystal grain **11** is extended in the direction of expansion (direction of arrow t in **FIGS. 9A and 9B**). At the same time, a P type thermoelectric semiconductor material **17** in which c-axes of most of crystal grains **11** are oriented in the direction of compression (direction of arrow p in **FIGS. 9A and 9B**) during the plastic deformation is formed.

[**0168**] Accordingly, in the P type thermoelectric semiconductor material **17**, crystal strain is generated by the presence of the hetero phase within crystal grains and grain boundaries, as well as by the presence of grain boundaries. By the generation of the crystal strain, thermal conductivity (**1***c*) can be reduced. In addition, since the directions of c-axes and extending directions of C face of the hexagonal structure of the crystal grains **11** are approximately uniformly oriented, thermoelectric performance (of which the Figure-of-Merit is Z) can be enhanced by setting the direction for conveying a current and heat to the extending direction of C face of the crystal grains **11**.

[**0169**] Moreover, since the P type raw thermoelectric semiconductor material **10** is manufactured to have a large thickness and a large width, and therefore, have a small specific surface area, and is solidified and formed to manufacture P type thermoelectric semiconductor material **17**, the oxygen concentration contained in the thermoelectric semiconductor material **17** can be reduced. Thus, a reduction in the electric conductivity (σ) due to oxidation can be prevented. By this reduction, an the thermoelectric performance of thermoelectric semiconductor material **17** can also be improved.

[**0170**] The electric conductivity (σ) and the Seebeck coefficient (α) of the P type thermoelectric semiconductor material **17** can be controlled by adjusting the amounts of Bi and Sb in the $(Bi—Sb)_2Te_3$ based composition, which is the standard of the composition of P type semiconductors. In addition, during the manufacturing process of the P type thermoelectric semiconductor material **17**, omnidirectional hydrostatic pressure process IV-2 in plastically deforming process IV shown in **FIG. 19** may be carried out. In addition, stress stain processing process V and defect concentration controlling process VI may be carried out as a post process of the plastically deforming process IV.

[**0171**] Next, a case in which P type thermoelectric semiconductor element **2***a* is manufactured using the P type thermoelectric semiconductor material **17** manufactured by the above-described method is described.

[**0172**] In this case, also in the above-described P type thermoelectric semiconductor material **17**, in the same manner as N type thermoelectric semiconductor material **17** shown in **FIGS. 9A and 9B**, throughout entire textual structure, C face of the hexagonal structure of most of crystal grains **11** extend in the direction of expansion of the compact **12** during the plastic deformation (direction of arrow t in **FIGS. 9A and 9B**), and the c-axes are almost oriented in the direction of the pressure during the plastic deformation (direction of arrow p in **FIGS. 9A and 9B**). Therefore, in the same manner as in manufacturing method for N type thermoelectric semiconductor element **3***a* shown in **FIG. 21**, firstly, as shown in the upper portion of **FIG. 21**, at predetermined spacing position in the direction of expansion of the compact **12** during the plastic deformation (direction of arrow t), the thermoelectric semiconductor material **17** is sliced along a plane perpendicular to the direction of expansion, and thereby a wafer **19** is cut out, as shown in the middle of **FIG. 21**. After that conductive material processed surfaces **20** are formed by processing both end surfaces in the direction of thickness of the wafer **19** with conductive material. Subsequently, by cutting the wafer **19**, a P type thermoelectric semiconductor element **2***a* of a rectangular solid form can be manufactured in the same manner as the N type thermoelectric semiconductor element **3***a* shown in the lower portion of **FIG. 21**.

[**0173**] As a result, the P type thermoelectric semiconductor element **2***a* has, in the same manner as the above-described N type thermoelectric semiconductor element **3***a*, a crystal structure in which C face of the hexagonal structure of crystal grains **11** extends throughout long length in the direction of a pair of opposing surface **20** which are processed with a conductive material. In addition, c-axes of crystal grains **11** extend in the direction of pressing (direction of arrow p) during the manufacture of the thermoelectric semiconductor material **17** among the two axial directions perpendicular to the conductive material processed surface **20**. Therefore the P type thermoelectric semiconductor element has an excellent thermoelectric performance.

[**0174**] As another embodiment of the present invention, a thermoelectric module that uses P type and N type thermoelectric semiconductor elements **2***a* and **3***a* that have been manufacture in accordance with the above-described method of the present invention, and manufacturing method of the thermoelectric module are described.

[**0175**] **FIG. 22** shows thermoelectric module **1***a* of the present invention, which comprises a PN element pair as in the same manner as a conventional thermoelectric module **1** shown in **FIG. 27**. In the formation of the PN element pair, the P type thermoelectric semiconductor element **2***a* and N type thermoelectric semiconductor element **3***a* respectively manufactured by the method of the present invention are arranged so that the elements are aligned in the direction perpendicular both to the extending direction of C face and the direction of c-axis of hexagonal structure of the crystal grains **11**. Conductive material processed surfaces of the thermoelectric semiconductor elements **2***a* and **3***a* opposed to each other in the extending direction of C face of the crystal grains are joined via a metal electrode **4**.

[**0176**] As a result, in the above-described thermoelectric module **1***a* of the present invention, current and heat can be conveyed in the extending direction of C face of the crystal grains **11** of the P type thermoelectric semiconductor element **2***a* and N type thermoelectric semiconductor element **3***a*, in which the extending direction of C face and the direction of c-axis of crystal gains **11** are approximately uniformly oriented. Therefore, thermoelectric module **1***a* having an excellent thermoelectric performance can be achieved.

[**0177**] In addition, when thermoelectric cooling, thermoelectric heating, thermoelectric power generation, and the like are carried out using the above-described thermoelectric module **1***a*, expansion or contraction of the metal electrode **4** accompany temperature deviation. Therefore, to adjacent P type and N type thermoelectric semiconductor elements **2***a* and **3***a* joined via a metal electrode **4**, stress is applied in the direction in which the elements come close to each other, or move away from each other. While in the above-described thermoelectric module, when a PN element pair is formed as shown in **FIG. 22**, adjacent thermoelectric semiconductor elements **2**_a_ and **3**_a_ joined via a metal electrode **4** are arranged in the same plane as the direction of C face of crystal grains **11**. Terefore, stress caused by expansion or contraction of the metal electrode **4** can be applied to respective crystal grains **11** only in the direction parallel to C plan. Accordingly, even when the stress is applied, interlayer peeling of the crystal grains **11** in the hexagonal structure in the respective structures of thermoelectric semiconductor elements **2**_a_ and **3**_a_ can be prevented, and thus, the damage to the thermoelectric semiconductor elements **2**_a_ and **3**_a_ due to cleavage can be prevented, and therefore, strength and durability of the them thermoelectric module **1**_a_ can be enhanced. When a PN elemental pair is formed, as a comparative example as shown in **FIG. 23**, by aligning the P type and N type thermoelectric semiconductor elements **2**_a_ and **3**_a_ in the direction of c-axis in the hexagonal structure of crystal grains **11**; and joining respective thermoelectric semiconductor elements **2**_a_ and **3**_a_ via metal electrode **4**, the caused by expanding or contracting deformation of the metal electrode **4** due to thermal deviation is applied respectively to the thermoelectric semiconductor elements **2**_a_ and **3**_a_ in the direction of c-axes of crystal grains **11**. Accordingly, the stress works to peel the layers in the hexagonal structure of these crystal grains **11**. In such a case, the damage to thermoelectric semiconductor elements **2**_a_ and **3**_a_ due to cleavage may be easily occur. Such occurrence of damage can be prevented in the above-described thermoelectric module **1**_a_ of the present invention.

[0178] The present invention is not limited only to the above-described embodiments. In the solidification forming process III in the manufacturing method for a thermoelectric semiconductor material, the above description shows a processing condition for solidifying and forming (sintering) the raw thermoelectric semiconductor material **10** at a temperature no lower than 380° C. and no higher than 500° C., preferably, a no lower than 420° C. and no higher than 450° C., is maintained for 5 seconds to 5 minutes. While, it is also possible to sinter raw thermoelectric semiconductor materials **10** for a long period of time at a temperature no higher than 400° C.

[0179] When temperature conditions and heating time may be set so that segregation, dropping of separated phase, and liquid phase precipitation, or the like of the Te rich phases having a low melting point and are dispersed in complex compound semiconductor phases do not completely occur, it is possible to form a compact **12** through plastic deformation by applying pressure, rolling, or by extrusion. As a plastically processing device **13** used in plastically deforming process TV, a structure having a punch **16** which can be raised and lowered inside between restricting members **15** placed in the lateral direction is described. In this case, the compact **12** is placed in the middle portion inside the restricting members **15** placed in the lateral direction, and this compact **12** is pressed from above by punch **16**, and thereby, the above-described compact **12** is expanded toward the two anteroposterior sides in a uniaxial direction parallel to the layering direction of raw thermoelectric semiconductor material **10**. While, as shown in **FIGS. 24A and 24B**, the plastically working device **13** may have a configuration in which an additional restricting member **15**_b_ is provided in a position on one side of the base **14** between restricting members **15** placed in the lateral direction to restrict the deformation (expansion) of compact **12** in forward and backward direction in one direction. In this case, when compact **12** is plastically deformed, compact **12** is firstly placed so as to be contacted with the restricting members **15** placed in the lateral direction and the restricting member **15**_b_. Subsequently, the compact **12** is pressed from above by punch **16** as shown by two-dot chain lines in the upper portion of **FIG. 21**. As a result, the compact **12** is expanded only in one direction opposite to the restricting member **15**_b_. Plastically working device **13**_a_ used in omnidirectional hydrostatic pressure process IV-2 shown in **FIGS. 20A, 20B**, and **20C** may be provided with a fixing position ring **15**_a_ same as that shown in **FIG. 8D**, on the outer periphery of restricting members **15** placed in the lateral direction and front and rear restricting members **18**. In this case, during the plastic deformation of the compact **12**, stress applied in the direction to the outside of the above-described restricting members **15** and **18** is received by the fixing position ring. When omnidirectional hydrostatic pressure process IV-2 is carried out two or more times, instead of preparing a plurality of plastically working device **13**_a_ having different spacing between front and rear restricting members **18**, it is also possible to use a plastic working device **13**_a_ in which positions of front and rear restricting members **18** may be set to have selective spacing. While a composition of raw alloy for thermoelectric semiconductors is, in either case of P type or N type, described to have excess Te added to stoichiometric composition of the thermoelectric semiconductor complex compound, it is also possible to add as excess composition, any element selected from Bi, Se, and Sb element instead of Te to the stoichiometric composition of the thermoelectric semiconductor complex compound. A manufacturing method for a thermoelectric semiconductor material, a thermoelectric semiconductor element, and a thermoelectric module according to the present invention may be applied to the raw alloy having the stoichiometric composition of the thermoelectric semiconductor complex compound to which an excess Te is not added. In this case, improvement of thermoelectric performance can be expected due to an improvement of orientation of crystal grains **11** in the texture of thermoelectric semiconductor material **17**. While $Bi_2(Te—Se)_3$ based, three element based composition was described as a stoichiometric composition of raw alloy for N type thermoelectric semiconductor, it is also possible to apply a manufacturing method for a thermoelectric semiconductor material, a thermoelectric semiconductor element, or a thermoelectric module to a raw alloy having a Bi_2Te_3 based, two element based, stoichiometric composition or a four element based stoichiometric composition comprising $(Bi—Sb)_2Te_3$ based composition added with small amount of Se. While $(Bi—Sb)_2Te_3$ based, three element based composition was described as a stoichiometric composition of P type thermoelectric semiconductor complex compound, it is also possible to apply a manufacturing method for a thermoelectric semiconductor material, a thermoelectric semiconductor element, or a thermoelectric module to a raw alloy having a four element based stoichiometric composition comprising $Bi_2(Te—Se)_3$ based composition added with small amount of Sb. In the above description, plastically working device **13** and **13**_a_ are used when a thermoelectric semiconductor material **17** is manufactured through plastic deformation by applying a shear force to a compact **12** in which slow cooling foils of raw thermoelectric semiconductor materials **10** are layered in the direction of the plate thickness and are solidified and formed, in a uniaxial direction approximately parallel to the layering direction of the above-described thermoelectric semiconductor element **10**. A high pressure pressing device **21** with a pair of dies **22** that are moveable in the direction in which they come close to each other or they move away from each other as shown in **FIG. 25A**, or a rolling device **23** provide with a roller **24** as shown in **FIG. 25B** may be used to press the compact **12** in a uniaxial direction perpendicular to the layering direction while moving the compact in the main layering don of raw thermoelectric semiconductor materials **10**. In this case, since a friction is applied in the direction perpendicular to both the layering direction of the raw thermoelectric semiconductor material **10** and the direction of pressure application, the compact is not spread or even if it spreads, amount of deformation is limited to small value. Therefore, restricting members are not specifically required. Of course, a variety of modifications can be applied to the embodiments within the scope that does not deviate from the gist of the present invention.

EXAMPLE

[0180] A thermoelectric module **1***a* was manufactured by forming a PN element pair of P type and N type thermoelectric semiconductor elements **2***a* and **3***a* manufactured by a manufacturing method for a thermoelectric semiconductor element of the present invention. The thermoelectric performance of the module was compared with that of a thermoelectric module manufactured in accordance with another method.

[0181] As a result, the Figure-of-Merit, shown by solid circle ● and open circle o in **FIG. 26**, were obtained as the thermoelectric performance of thermoelectric module **1***a* manufactured in accordance with the present invention.

[0182] The result indicates, it was found that high thermoelectric performance is gained according to the invention.

[0183] As a result, thermoelectric module of the present invention indicates high thermoelectric performance in comparison with a case in which a P type thermoelectric semiconductor element and an N type thermoelectric semiconductor element are both manufactured only by conventional hot pressing of a raw thermoelectric semiconductor material according (shown by open triangle A in **FIG. 26**), and a case in which N type thermoelectric semiconductor element **2***a* is manufactured by a manufacturing method for a thermoelectric semiconductor element of the present invention, while a P type thermoelectric semiconductor element is manufactured only by hot pressing of a raw thermoelectric semiconductor material (shown by open diamond ◇ and solid diamond ♦ in **FIG. 26**).

1. A thermoelectric semiconductor material produced by:

layering and packing plate shaped raw thermoelectric semiconductor materials made of a raw alloy having a predetermined composition of a thermoelectric semiconductor to form a layered body;

solidifying and forming the layered body to form a compact;

applying pressure to the compact in a uniaxial direction that is perpendicular or nearly perpendicular to a main layering direction of the raw thermoelectric semiconductor materials; and thereby

applying a shear force in a axial direction that is approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials; and

plastically deforming the compact.

2. A thermoelectric semiconductor material having a compound phase comprising:

complex compound semiconductor phase having a predetermined stoichiometric composition of a compound thermoelectric semiconductor, and

a Te rich phase in which excess Te is added to the stoichiometric composition.

3. A thermoelectric semiconductor material produced by:

adding excess Te to a predetermined stoichiometric composition of a compound thermoelectric semiconductor to form a raw alloy;

layering and packing plate shaped raw thermoelectric semiconductor materials made of the raw alloy to form a layered body;

solidifying and forming the layered body to form a compact;

applying pressure to the compact in an axial direction perpendicular or nearly perpendicular to a main layering direction of the raw thermoelectric semiconductor materials; and thereby

applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials; and

plastically deforming the compact.

4. The thermoelectric semiconductor material according to claim 2, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $(\mathrm{Bi}\text{—}\mathrm{Sb})_2\mathrm{Te}_3$ based composition.

5. The thermoelectric semiconductor material according to claim 3, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $(\mathrm{Bi}\text{—}\mathrm{Sb})_2\mathrm{Te}_3$ based composition.

6. The thermoelectric semiconductor material according to claim 2, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $\mathrm{Bi}_2(\mathrm{Te}\text{—}\mathrm{Se})_3$ based composition.

7. The thermoelectric semiconductor material according to claim 3, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $\mathrm{Bi}_2(\mathrm{Te}\text{—}\mathrm{Se})_3$ based composition.

8. A thermoelectric semiconductor element produced by:

layering and packing plate shaped raw thermoelectric semiconductor materials made of a raw alloy having a predetermined composition of a thermoelectric semiconductor to form a layered body;

solidifying and forming the layered body to form a compact;

applying pressure to the compact in an axial direction perpendicular or approximately perpendicular to a main layering direction of the raw thermoelectric semiconductor materials; and thereby applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials; and

plastically deforming the compact to form a thermoelectric semiconductor material;

cutting out a thermoelectric semiconductor element from the thermoelectric semiconductor material so that a plane approximately perpendicular to the uniaxial direction in which the shear force is applied during the plastic deformation of the compact can be used as a contact surface with an electrode.

9. The thermoelectric semiconductor element according to claim 8 wherein the plate shaped raw thermoelectric semiconductor material have a compound phase comprising:

a complex compound semiconductor phase having a predetermined stoichiometric composition of a compound thermoelectric semiconductor; and

a Te rich phase including excess Te in the stoichiometric composition.

10. The thermoelectric semiconductor element according to claim 9, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $(Bi—Sb)_2Te_3$ based composition.

11. The thermoelectric semiconductor element according to claim 9, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $Bi_2(Te—Se)_3$ based composition.

12. A thermoelectric module comprising a PN element pair produced by:

layering and packing respectively plate shaped raw thermoelectric semiconductor materials made of a raw alloy comprising a composition of P type thermoelectric semiconductor, and plate shaped raw thermoelectric semiconductor materials made of a raw alloy comprising a composition of N type thermoelectric semiconductor to form layered bodies;

solidifying and forming the layered bodies to form compacts;

applying pressure to the compacts having the compositions of P type and N type thermoelectric semiconductor in an axial direction perpendicular or approximately perpendicular to a main layering direction of the raw thermoelectric semiconductor materials; and thereby

applying shear force in an axial direction approximately parallel to the main layer direction of the raw thermoelectric semiconductor materials; and

plastically deforming the compacts to form P type and N type thermoelectric semiconductor materials;

cutting out P type and N type thermoelectric semiconductor elements from the P type and N type thermoelectric semiconductor materials so that planes approximately perpendicular to the uniaxial direction in which the shear force is applied during the plastic deformation of the compacts can be used as contact surfaces with an electrode;

arranging the P type and N type thermoelectric semiconductor elements so that the elements are aligned in the direction perpendicular to the axial direction of pressure application during plastic deformation of the compacts, and also perpendicular to the direction of shear force by the pressure application;

joining the P type and N type elements via a metal electrode.

13. The thermoelectric module according to claim 12, wherein the plate shaped P type and N type raw thermoelectric semiconductor materials respectively have a compound phase comprising:

complex compound semiconductor phase having a predetermined stoichiometric composition of a compound thermoelectric semiconductor; and

a Te rich phase in which excess Te is added to the stoichiometric composition.

14. The thermoelectric module according to claim 13, wherein the stoichiometric composition of the P type compound thermoelectric semiconductor is a $(Bi—Sb)_2Te_3$ based composition.

15. A thermoelectric module according to claim 13, wherein the stoichiometric composition of the N type compound thermoelectric semiconductor is a $Bi_2(Te—Se)_3$ based composition.

16. A manufacturing method for a thermoelectric semiconductor material comprising:

melting a raw alloy having a predetermined composition of a thermoelectric semiconductor;

having the raw alloy to be contacted with a surface of a cooling member to form plate shaped raw thermoelectric semiconductor materials;

layering and packing the plate shaped raw thermoelectric semiconductor materials to form a layered body;

solidifying and forming the layered body to form a compact;

applying pressure to the compact in one of two axial directions which are crossing each other in a plane approximately perpendicular to the main layering direction of the raw thermoelectric semiconductor materials, while preventing deformation of the compact in the other axial direction; and thereby

applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials; and

plastically deforming the compact to form a thermoelectric semiconductor material.

17. The manufacturing method for a thermoelectric semiconductor material according to claim 16, wherein the raw alloy has a composition in which excess Te is added to a predetermined stoichiometric composition of a compound thermoelectric semiconductor.

18. The manufacturing method for a thermoelectric semiconductor material according to claim 17, wherein the raw alloy comprises a composition in which 0.1 to 5% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 7 to 10 atomic % of Bi, 30 to 33 atomic % of Sb, and 60 atomic % of Te.

19. The manufacturing method for a thermoelectric semiconductor material according to claim 17, wherein the raw alloy comprises a composition in which 0.01 to 10% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 40 atomic % of Bi, 50 to 59 atomic % of Te, and 1 to 10 atomic % of Se.

20. The manufacturing method for a thermoelectric semiconductor material according to claim 17, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

21. The manufacturing method for a thermoelectric semiconductor material according to claim 18, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; thing the raw material at a temperature no lower than 380° C. and no higher than 500° C.

22. The manufacturing method for a thermoelectric semiconductor material according to claim 19, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by along with applying pressure; heating the raw material at a temperate no lower dm 380° C. and no higher than 500° C.

23. The manufacturing method for a thermoelectric semiconductor material according to claim 16, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

24. The manufacturing method for a thermoelectric semiconductor material according to claim 17, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

25. The manufacturing method for a thermoelectric semiconductor material according to claim 18, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

26. The manufacturing method for a thermoelectric semiconductor material according to claim 19, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

27. The manufacturing method for a thermoelectric semiconductor material according to claim 20, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

28. The manufacturing method for a thermoelectric semiconductor material according to claim 21, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

29. The manufacturing method for a thermoelectric semiconductor material according to claim 22, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

30. The manufacturing method for a thermoelectric semiconductor material according to claim 16, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

31. The manufacturing method for a thermoelectric semiconductor material according to claim 17, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

32. The manufacturing method for a thermoelectric semiconductor material according to claim 18, when a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

33. The manufacturing method for a thermoelectric semiconductor material according to claim 19, why a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

34. The manufacturing method for a thermoelectric semiconductor material according to claim 20, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

35. The manufacturing method for a thermoelectric semiconductor material according to claim 21, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

36. The manufacturing method for a thermoelectric semiconductor material according to claim 22, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

37. A manufacturing method for a thermoelectric semiconductor element, comprising:

melting a raw alloy having a predetermined composition of a thermoelectric semiconductor;

having the raw alloy to be contacted with a surface of a cooling member to form plate shaped raw thermoelectric semiconductor materials;

layering and packing in approximately layered form the plate shaped raw thermoelectric semiconductor materials to form a layered body;

solidifying and forming the layered body to form a compact;

applying presume to the compact in one of two axial directions which are crossing each other in a plane approximately perpendicular to the main layering direction of the raw thermoelectric semiconductor materials, while preventing deformation of the compact in the other axial direction; and thereby

applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials; and

plastically deforming the compact to form a thermoelectric semiconductor material; and

cutting out a thermoelectric semiconductor element from the thermoelectric semiconductor material so that a plane approximately perpendicular to the uniaxial direction in which the shear force is applied during the plastic deformation of the compact can be used as a contact surface with an electrode.

38. The manufacturing method for a thermoelectric semiconductor element according to claim 37, wherein the raw alloy has a composition in which excess Te is added to a predetermined stoichiometric composition of a compound thermoelectric semiconductor.

39. The manufacturing method for a thermoelectric semiconductor element according to claim 38, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $(Bi—Sb)_2Te_3$ based composition.

40. The manufacturing method for a thermoelectric semiconductor element according to claim 39, when in the raw alloy comprises a composition in which 0.1 to 5% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 7 to 10 atomic % of Bi, 30 to 33 atomic % of Sb, and 60 atomic % of Te.

41. The manufacturing for a thermoelectric semiconductor element according to claim 38, wherein the stoichiometric composition of the compound thermoelectric semiconductor is a $Bi_2(Te—Se)_3$ based composition.

42. The manufacturing meted for a thermoelectric semiconductor element according to claim 41, wherein the raw alloy comprises a composition in which 0.01 to 10% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 40 atomic % of Bi, 50 to 59 atomic % of Te, and 1 to 10 atomic % of Se.

43. The manufacturing method for a thermoelectric semiconductor element according to claim 37, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

44. The manufacturing method for a thermoelectric semiconductor element according to claim 38, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temper no lower than 380° C. and no higher than 500° C.

45. The manufacturing method for a thermoelectric semiconductor element according to claim 39, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

46. The manufacturing method for a thermoelectric semiconductor element according to claim 40, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

47. The manufacturing method for a thermoelectric semiconductor element according to claim 41, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

48. The manufacturing method for a thermoelectric semiconductor element according to claim 42, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

49. The manufacturing method for a thermoelectric semiconductor element according to claim 37, wherein, when the molten raw alloy is contacted with a surf of a cooling member so as to form plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

50. The manufacturing method for a thermoelectric semiconductor element according to claim 38, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

51. The manufacturing method for a thermoelectric semiconductor element according to claim 39, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shad raw thermoelectric semiconductor material is not quenched.

52. The manufacturing method for a thermoelectric semiconductor element according to claim 40, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

53. The manufacturing method for a thermoelectric semiconductor element according to claim 41, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

54. The manufacturing method for a thermoelectric semiconductor element according to claim 42, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

55. The manufacturing method for a thermoelectric semiconductor element according to claim 43, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

56. The manufacturing method for a thermoelectric semiconductor element according to claim 44, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

57. The manufacturing method for a thermoelectric semiconductor element according to claim 45, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

58. The manufacturing method for a thermoelectric semiconductor element according to claim 46, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

59. The manufacturing method for a thermoelectric semiconductor element according to claim 47, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

60. The manufacturing method for a thermoelectric semiconductor element according to claim 48, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

61. The manufacturing method for a thermoelectric semiconductor element according to claim 37, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

62. The manufacturing method for a thermoelectric semiconductor element according to claim 38, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

63. The manufacturing method for a thermoelectric semiconductor element according to claim 39, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

64. The manufacturing method for a thermoelectric semiconductor element according to claim 40, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

65. The manufacturing method for a thermoelectric semiconductor element according to claim 41, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

66. The manufacturing method for a thermoelectric semiconductor element according to claim 42, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

67. The manufacturing method for a thermoelectric semiconductor element according to claim 43, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate sped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

68. The manufacturing method for a thermoelectric semiconductor element according to claim 44, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

69. The manufacturing method for a thermoelectric semiconductor element according to claim 45, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

70. The manufacturing method for a thermoelectric semiconductor element according to claim 46, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 um or greater.

71. The manufacturing method for a thermoelectric semiconductor element according to claim 47, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

72. The manufacturing method for a thermoelectric semiconductor element according to claim 48, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

73. A manufacturing method for a thermoelectric module comprising:

melting a raw alloy having a composition of P type thermoelectric semiconductor, and a raw alloy having a composition of N type thermoelectric semiconductor respectively;

having the each raw alloy to be contacted with a surface of a cooling member to form plate shaped raw thermoelectric semiconductor materials having a composition of P type thermoelectric semiconductor and plate shaped raw thermoelectric semiconductor materials having a composition of N type thermoelectric semiconductor respectively;

having the P type and N type raw thermoelectric semiconductor materials layered approximately parallel in a direction of plate thickness to form layered bodies;

solidifying and forming the layered bodies to form compacts;

applying pressure to each of the compacts having the compositions of P type and N type thermoelectric semiconductor in one of two axial directions which are crossing each other in a plane approximately perpendicular to the main layering direction of the raw thermoelectric semiconductor materials, while preventing deformation of the compact in the other axial direction; and thereby

applying shear force in an axial direction approximately parallel to the main layering direction of the raw thermoelectric semiconductor materials; and

plastically deforming the comes to form P type and N type thermoelectric semiconductor materials;

cutting out P type and N type thermoelectric semiconductor elements from the P type and N type thermoelectric semiconductor materials so that a plane approximately perpendicular to the uniaxial direction in which the shear force is applied during the plastic deformation of the compact can be used as a contact surface with an electrode;

arranging the P type and N type thermoelectric semiconductor elements so that the elements are aligned in the direction perpendicular to the axial direction of pressure application during plastic deformation of a compact, and also perpendicular to the direction of shear force by the pressure application;

joining the P type and N type elements via a metal electrode to form a PN element pair.

74. The manufacturing method for a thermoelectric module according to claim 73, wherein the raw alloy of each of the P type and N type thermoelectric semiconductors has a composition in which excess Te is added to a predetermined stoichiometric composition of a compound thermoelectric semiconductor.

75. The manufacturing method for a thermoelectric module according to claim 74, wherein the stoichiometric composition of the P type compound thermoelectric semiconductor is a $(Bi—Sb)_2Te_3$ based composition.

76. The manufacturing method for a thermoelectric module according to claim 75, wherein the raw alloy of the P type thermoelectric semiconductor comprises a composition in which 0.1 to 5% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 7 to 10 atomic % of Bi, 30 to 33 atomic % of Sb, and 60 atomic % of Te.

77. The manufacturing method for a thermoelectric module according to claim 74, wherein the stoichiometric composition of the N type compound thermoelectric semiconductor is a $Bi_2(Te—Se)_3$ based composition.

78. The manufacturing method for a thermoelectric module according to claim 77, wherein the raw alloy of the N type thermoelectric semiconductor wherein the raw alloy comprises a composition in which 0.01 to 10% of excess Te is added to the stoichiometric composition of a compound thermoelectric semiconductor comprising 40 atomic % of Bi, 50 to 59 atomic % of Te, and 1 to 10 atomic % of Se.

79. The manufacturing method for a thermoelectric module according to claim 74, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

80. The manufacturing method for a thermoelectric module according to claim 75, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

81. The manufacturing method for a thermoelectric module according to claim 76, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

82. The manufacturing method for a thermoelectric module according to claim 77, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperate no lower than 380° C. and no higher than 500° C.

83. The manufacturing method for a thermoelectric module according to claim 78, wherein solidification forming of the raw thermoelectric semiconductor materials is carried out by: along with applying pressure; heating the raw material at a temperature no lower than 380° C. and no higher than 500° C.

84. The manufacturing method for a thermoelectric module according to claim 73, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shad raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

85. The manufacturing method for a thermoelectric module according to claim 74, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

86. The manufacturing method for a thermoelectric module according to claim 75, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

87. The manufacturing method for a thermoelectric module according to claim 76, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor material, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

88. The manufacturing method for a thermoelectric module according to claim 77, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

89. The manufacturing method for a thermoelectric module according to claim 78, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

90. The manufacturing method for a thermoelectric module according to claim 79, where, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

91. The manufacturing method for a thermoelectric module according to claim 80, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

92. The manufacturing method for a thermoelectric module according to claim 81, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

93. The manufacturing method for a thermoelectric module according to claim 82, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

94. The manufacturing method for a thermoelectric module according to claim 83, wherein, when the molten raw alloy is contacted with a surface of a cooling member so as to form the plate shaped raw thermoelectric semiconductor materials, the molten alloy is cooled and solidified at a rate at which 90% or more of a thickness of the formed plate shaped raw thermoelectric semiconductor material is not quenched.

95. The manufacturing method for a thermoelectric module according to claim 73, wherein a rotational roll is used as the cooling member and is rotated at a rate at which the thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

96. The manufacturing method for a thermoelectric module according to claim 74, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 sun or greater.

97. The manufacturing method for a thermoelectric module according to claim 75, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

98. The manufacturing method for a thermoelectric module according to claim 76, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

99. The manufacturing method for a thermoelectric module according to claim 77, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

100. The manufacturing method for a thermoelectric module according to claim 78, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

101. The manufacturing method for a thermoelectric module according to claim 79, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

102. The manufacturing method for a thermoelectric module according to claim 80, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the su of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

103. The manufacturing method for a thermoelectric module according to claim 81, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

104. The manufacturing method for a thermoelectric module according to claim 82, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

105. The manufacturing method for a thermoelectric module according to claim 83, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

106. The manufacturing method for a thermoelectric module according to claim 84, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

107. The manufacturing method for a thermoelectric module according to claim 85, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

108. The manufacturing method for a thermoelectric module according to claim 86, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

109. The manufacturing method for a thermoelectric module according to claim 87, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

110. The manufacturing method for a thermoelectric module according to claim 88, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

111. The manufacturing method or a thermoelectric module according to claim 89, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

112. The manufacturing method for a thermoelectric module according to claim 90, wherein a rotational roll is used as the cooling member and is red at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

113. The manufacturing method for a thermoelectric module according to claim 91, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

114. The manufacturing method for a thermoelectric module according to claim 92, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

115. The manufacturing method for a thermoelectric module according to claim 93, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

116. The manufacturing method for a thermoelectric module according to claim 94, wherein a rotational roll is used as the cooling member and is rotated at a rate at which thickness of the plate shaped raw thermoelectric semiconductor material formed by supplying the molten raw alloy to the surface of the cooling member and cooling and solidifying the molten alloy is at least 30 μm or greater.

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