

DESCRIPTION

Ag ALLOY SPUTTERING TARGET FOR FORMING ELECTROCONDUCTIVE
FILM, AND METHOD OF PRODUCING SAME

5

TECHNICAL FIELD

[0001]

The present invention relates to an Ag alloy sputtering target for forming a
conductive film such as a reflective electrode in an organic light-emitting diode (OLED)
10 element or a interconnection film in a touch panel, and a method of producing the same.

Priority is claimed on Japanese Patent Application No. 2013-048388, filed
March 11, 2013, the content of which is incorporated herein by reference.

BACKGROUND ART

15 [0002]

An OLED element is a light-emitting element using the principal in which a
voltage is applied between a positive electrode and a negative electrode formed on both
sides of an organic EL light-emitting layer, holes and electrons are respectively injected
into an organic EL film from the positive electrode and the negative electrode, and light
20 is emitted when the holes and the electrons are bonded to each other in the organic EL
light-emitting layer. In recent years, the OLED element has been attracting a great deal
of attention for use in display devices. Regarding the method of driving the OLED
element, there are a passive matrix method and an active matrix method. In the active
matrix method, since one or more thin film transistors are provided in each pixel,
25 switching can be performed at a high speed. Therefore, the active matrix method has an

advantage in increasing the contrast ratio and the definition and is a driving method capable of exhibiting the characteristics of the OLED element.

In addition, regarding the method of extracting light, there are a bottom emission method in which light is extracted from the transparent substrate side and a top emission
5 method in which light is extracted from the side opposite to the substrate. The top emission method having a high aperture ratio is advantageous in increasing luminance.

[0003]

A reflective electrode film in a top emission structure preferably has a high reflectance and a high corrosion resistance in order to efficiently reflect light emitted
10 from an organic EL layer. In addition, the reflective electrode film also preferably has a low resistance as an electrode. As the material described above, an Ag alloy and an Al alloy are known, and the Ag alloy is more suitable due to its high reflectance for visible light in order to obtain an OLED element having higher luminance. A sputtering method is employed for forming a reflective electrode film in an OLED element, and an
15 Ag alloy target is used (PTL 1).

[0004]

In response to an increase in the size of a glass substrate used for producing an OLED element, the size of an Ag alloy target used for forming a reflective electrode film has also increased. When sputtering is carried out by applying high power into a large
20 target, there is a problem in that a phenomenon called “splash”, which is caused by the abnormal electrical discharge of the target, occurs, and therefore molten fine particles are attached to the substrate thereby shorting between wires or electrodes, which decreases the yield of the OLED element. In a reflective electrode layer in the OLED element employing the top emission method, since the reflective electrode layer serves as a base
25 layer of an organic light-emitting layer, the reflective electrode layer is required to be

highly flat and it is necessary to further reduce an occurrence of the splash.

In order to solve the above-described problem, PTL 2 and 3 propose an Ag alloy target for forming a reflective electrode film in an OLED element which is capable of reducing the occurrence of the splash even when high power is applied to a target in accordance with an increase in the size of the target, and a method of producing the same.

CITATION LIST

PATENT LITERATURE

- 10 [0005]
[PTL 1] PCT International Publication No. WO2002/077317
[PTL 2] Japanese Unexamined Patent Application, First Publication No.
2011-100719
[PTL 3] Japanese Unexamined Patent Application, First Publication No.
15 2011-162876

SUMMARY OF INVENTION

TECHNICAL PROBLEM

- [0006]
20 According to the Ag alloy target for forming a reflective electrode film described in PTL 2 and 3, it is possible to reduce the occurrence of the splash even when high power is applied. However, in a large Ag alloy target, as the target is consumed, the number of arc discharges increases and thus there is a tendency that the number of splashes increases due to the arc discharge, which requires additional improvement.
25 In addition, the Ag alloy film is considered to be used in a conductive film such

as a lead-out interconnection of a touch panel in addition to the reflective electrode film for the OLED element. For example, when pure Ag is used as the interconnection film, migration occurs, and therefore a short-circuit defect tends to occur. Therefore, employing of the Ag alloy film is considered.

5 [0007]

The present invention has been made in consideration of the above-described circumstances, and an object thereof is to provide an Ag alloy sputtering target for forming a conductive film capable of further reducing the occurrence of arc discharge and splash, and a method of producing the same.

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SOLUTION TO PROBLEM

[0008]

As a result of extensive studies, the present inventors have obtained the following findings. For further suppressing an increase in the number of arc discharges as a target is consumed, it is effective to make crystal grains finer so as to have an average grain size of less than 30 μm and the dispersion in the grain size of 30% or less of the average grain size.

15

On the basis of the above-described findings, an Ag alloy sputtering target for forming a conductive film of the present invention is an Ag alloy sputtering target containing: 0.1 to 1.5 mass% in total of In and Sn which can be solid-solved in Ag; and the balance including Ag and inevitable impurities, in which an average grain size of crystal grains in an alloy is 1 μm or more and less than 30 μm , and a dispersion in a grain size of the crystal grains is 30% or less of the average grain size.

20

[0009]

25 In has effects of suppressing the crystal grain growth of the target and making

the crystal grains finer by solid-solving in Ag. Since In improves the hardness of the target, warpage during machining is suppressed. In improves the corrosion resistance and heat resistance of a film formed through sputtering.

Similar to In, Sn has effects of suppressing the crystal grain growth of the target and making the crystal grains finer by solid-solving in Ag. Since Sn improves the hardness of the target, warpage during machining is suppressed. Sn improves the corrosion resistance and heat resistance of a film formed through sputtering.

When the total amount of one or more of In and Sn is less than 0.1 mass%, the above-described effects cannot be obtained. When the total amount thereof exceeds 1.5 mass%, the reflectance and electric resistance of a film decrease.

The reason for setting the average grain size to 1 μm or more and less than 30 μm is as follows. An average grain size of less than 1 μm is unrealistic and causes an increase in manufacturing costs. When the average grain size is 30 μm or more, it becomes difficult to control the dispersion in the grain size and, consequently, the tendency for increasing the number of abnormal electrical discharges as the target is consumed during sputtering becomes significant.

When the dispersion in the grain size exceeds 30%, the tendency for increasing the number of abnormal electrical discharges as the target is consumed during sputtering, becomes significant.

[0010]

An Ag alloy sputtering target for forming a conductive film of the present invention is an Ag alloy sputtering target containing: 0.1 to 1.5 mass% in total of one or more of In and Sn which can be solid-solved in Ag; 0.1 to 2.5 mass% in total of one or more of Sb and Ga which can be solid-solved in Ag; and the balance including Ag and inevitable impurities, in which an average grain size of crystal grains in an alloy is 1 μm

or more and less than 30 μm , and a dispersion in a grain size of the crystal grains is 30% or less of the average grain size.

[0011]

Sb and Ga have effects of further suppressing the crystal grain growth by solid-solting in Ag. Sb and Ga further improve the corrosion resistance and heat resistance of a film formed through sputtering by solid-solting in Ag. Particularly, Ga improves the chloride resistance of a film. When the total amount thereof is less than 0.1 mass%, the above-described effect cannot be obtained. When the total amount thereof exceeds 2.5 mass%, the reflectance and electric resistance of a film decrease and a crack tends to occur during hot-rolling.

[0012]

In addition, a method of producing an Ag alloy sputtering target for forming a conductive film of the present invention is a method of producing an Ag alloy sputtering target by subjecting a melted and cast ingot to: a hot-rolling step; a cooling step; a cold-rolling step; a heat-treating step; and a machining step in this order, the ingot containing: 0.1 to 1.5 mass% in total of one or more of In and Sn; and the balance including Ag and inevitable impurities, in which the hot-rolling step includes one or more passes of finishing hot-rolling in which a rolling reduction per pass is 20 to 35%, a strain rate is 3 to 10/sec, and a temperature after the pass is 400 to 650°C, in the cooling step, the ingot is quenched to 200°C or lower at a cooling rate of 100 to 1000°C/min, the cold-rolling step is carried out so that a plate having a target thickness is obtained at an average value of the rolling reductions per pass throughout all cold-rolling passes of 10 to 30%, an average value of the strain rates throughout all the cold-rolling passes of 3 to 10/sec, and a total rolling reduction of 40 to 80%, and in the heat-treating step, the ingot is held at 350 to 550°C for 1 to 2 hours.

[0013]

A method of producing an Ag alloy sputtering target for forming a conductive film of the present invention is also a method of producing an Ag alloy sputtering target by subjecting a melted and cast ingot to: a hot-rolling step; a cooling step; a cold-rolling
5 step; a heat-treating step; and a machining step in this order, the ingot containing: 0.1 to 1.5 mass% in total of one or more of In and Sn; 0.1 to 2.5 mass% in total of one or more of Sb and Ga; and the balance including Ag and inevitable impurities, in which the hot-rolling step includes one or more passes of finishing hot-rolling in which a rolling reduction per pass is 20 to 35%, a strain rate is 3 to 10/sec, and a temperature after the
10 pass is 400 to 650°C, in the cooling step, the ingot is quenched to 200°C or lower at a cooling rate of 100 to 1000°C/min, the cold-rolling step is carried out so that a plate having a target thickness is obtained at an average value of the rolling reductions per pass throughout all cold-rolling passes of 10 to 30%, an average value of the strain rates throughout all the cold-rolling passes of 3 to 10/sec, and a total rolling reduction of 40 to
15 80%, and in the heat-treating step, the ingot is held at 350 to 550°C for 1 to 2 hours.

[0014]

The reason for setting the rolling reduction per pass to 20 to 35% in the finishing hot-rolling is as follows. At the rolling reduction per pass of less than 20%, the crystal grains are not made fine sufficiently. When an attempt is made to obtain the rolling
20 reduction per pass of more than 35%, the load applied to a rolling machine becomes excessive, which is unrealistic.

In addition, the reason for setting the strain rate to 3 to 10/sec is as follows. When the strain rate is less than 3/sec, the crystal grains are not made fine sufficiently and a mixed grains of fine crystal grains and coarse crystal grains tend to generate. The
25 strain rate of more than 10/sec causes the load applied to a rolling machine to become

excessive, which is unrealistic.

When the temperature after each pass is lower than 400°C, dynamic recrystallization becomes insufficient and a tendency of an increase in the dispersion in the grain size becomes significant. When the temperature after each pass is higher than 5 650°C, crystal grain growth proceeds and the crystal grains cannot be made fine.

In addition, when the ingot is quenched after the hot-rolling, the growth of the crystal grains is limited and it is possible to obtain a target having fine crystal grains.

The cooling rate of less than 100°C/min is not preferred since the growth of the crystal grains proceeds. The cooling rate of more than 1000°C/min does not contribute to 10 making the crystal grains further finer.

The reason for setting the average value of the rolling reductions per pass throughout all the cold-rolling passes to 10 to 30% in the cold-rolling is as follows. The average rolling reductions per pass of less than 10% is not preferred since the crystal grains are not made fine sufficiently and the dispersion in the grain size also increases.

15 When an attempt is made to obtain the rolling reduction per pass of more than 30%, the load applied to a rolling machine becomes excessive, which is unrealistic.

The reason for setting the average value of the strain rates throughout all the cold-rolling passes to 3 to 10/sec in the cold-rolling is as follows. At the average value of the strain rates of less than 3/sec, the crystal grains are not made fine sufficiently and a 20 mixed grains of fine grains and coarse grains tend to generate. The average value of the strain rates of more than 10/sec causes the load applied to a rolling machine to become excessive, which is unrealistic.

The reason for setting the total rolling reduction of the cold-rolling to 40 to 80% is as follows. At the total rolling reduction of less than 40%, the supply of strain energy

through the cold-rolling becomes insufficient and it becomes difficult to make the crystal grains fine through recrystallization and homogenize the crystal grains. In a case in which the total rolling reduction is more than 80%, it becomes difficult to carry out the hot-rolling in which a rolling reduction of the hot-rolling is 20% or more and a strain rate is 3 to 10/sec.

In the heat-treating after the cold-rolling, when the temperature is lower than 350°C or the time is shorter than 1 hour, the recrystallization is insufficient and the dispersion in the grain size increases. When the temperature is higher than 550°C or the time is longer than 2 hours, crystal grain growth proceeds and the average grain size exceeds 30 μm .

ADVANTAGEOUS EFFECTS OF INVENTION

[0015]

According to the present invention, it is possible to obtain a target capable of further reducing arc discharge and splash even when high power is applied during sputtering. Through the sputtering using the target, a conductive film having a high reflectance and excellent durability can be obtained.

DESCRIPTION OF EMBODIMENTS

20 [0016]

Hereinafter, embodiments of the Ag alloy sputtering target for forming a conductive film of the present invention and the method of producing the same will be described. Unless otherwise described, “%” indicates mass% except for cases in which “%” simply indicates percentage.

25 [0017]

In the target, the target surface (a surface of the target which is subjected to sputtering) has an area of 0.25 m^2 or more. In the case of a rectangular target, at least one side has a length of 500 mm or more, and the upper limit of the length is preferably 3000 mm from the viewpoint of the handling of the target. The upper limit of the width is preferably 1700 mm from the viewpoint of the upper limit of the ordinary size that can be rolled in a rolling machine which is used in the hot-rolling step. In addition, the thickness of the target is preferably 6 mm or more from the viewpoint of the exchange frequency of the target, and is preferably 25 mm or less from the viewpoint of the discharge stability of magnetron sputtering.

[0018]

An Ag alloy sputtering target for forming a conductive film of a first embodiment is made of an Ag alloy containing: 0.1 to 1.5 mass% in total of one or more of In and Sn which can be solid-solved in Ag; and the balance including Ag and inevitable impurities, an average grain size of crystal grains in an alloy is $1 \text{ }\mu\text{m}$ or more and less than $30 \text{ }\mu\text{m}$, and a dispersion in a grain size of the crystal grains is 30% or less of the average grain size.

[0019]

Ag has an effect that imparts a high reflectance and low electric resistance to a reflective electrode film in an OLED element or an interconnection film in a touch panel which is formed through sputtering.

[0020]

Since In improves the hardness of the target, the occurrence of warpage during machining is suppressed. Particularly, the occurrence of warpage during the machining of a large target in which the area of the target surface is 0.25 m^2 or more, can be suppressed. In addition, In has an effect that improves the corrosion resistance and heat

resistance of a reflective electrode film in an OLED element which is formed through sputtering. This is because In has effects of: making the crystal grains in a film fine; decreasing the surface roughness of the film; increasing the strength of the crystal grains by being solid-solved in Ag; suppressing coarsening of the crystal grains due to heat, thereby suppressing an increase in the surface roughness of the film or suppressing a decrease in the reflectance due to the corrosion of the film. Therefore, in a reflective electrode film or an interconnection film formed using the Ag alloy sputtering target for forming a conductive film, the corrosion resistance and heat resistance of the film are improved, and therefore the film contributes to an increase in the luminance of an OLED element or the improvement in the reliability of interconnections in touch panels and the like.

Similar to In, Sn has effects of suppressing the crystal grain growth of the target and making the crystal grains finer by solid-solving in Ag. Since Sn improves the hardness of the target, warpage during machining is suppressed. Sn improves the corrosion resistance and heat resistance of a film formed through sputtering.

[0021]

When the total amount of one or more of In and Sn is less than 0.1 mass%, the above-described effect of the addition of In and Sn cannot be obtained. When the total amount thereof exceeds 1.5 mass%, the electrical resistance of the film increases, or the reflectance or corrosion resistance of a film formed through sputtering is, conversely, degraded, which is not preferable. Therefore, since the composition of a film depends on the composition of the target, the total amount of one or more of In and Sn which are contained in the Ag alloy sputtering target is set to 0.1 to 1.5 mass%. The total amount thereof is more preferably 0.2 to 1.0 mass%.

[0022]

In addition, an Ag alloy sputtering target for forming a conductive film of a second embodiment contains 0.1 to 1.5 mass% in total of one or more of In and Sn which can be solid-solved in Ag; 0.1 to 2.5 mass% in total of one or more of Sb and Ga which can be solid-solved in Ag, and the balance including Ag and inevitable impurities, in which an average grain size of crystal grains in an alloy is 1 μm or more and less than 30 μm , and a dispersion in a grain size of the crystal grains is 30% or less of the average grain size.

[0023]

In the second embodiment, Sb and Ga have an effect of further suppressing crystal grain growth by being solid-solved in Ag. Sb and Ga further improve the corrosion resistance and heat resistance of a film formed through sputtering.

Particularly, Ga improves the chloride resistance of a film. In a case in which a film formed through sputtering is used for a lead-out interconnection in a touch panel, since the touch panel is operated by being touched with a finger, the interconnection film needs to have resistance against a chlorine component contained in sweat from a human body. By adding Ga, the chloride resistance of the interconnection film becomes excellent.

When the total amount of Sb and Ga is less than 0.1 mass%, the above-described effect cannot be obtained. When the total amount thereof exceeds 2.5 mass%, the reflectance and electric resistance of a film decrease and a crack tends to occur during hot-rolling.

[0024]

In the embodiment of each of the above-described compositions, the average grain size of Ag alloy crystal grains in the Ag alloy sputtering target is 1 μm or more and less than 30 μm . Setting the average grain size of the Ag alloy crystal grains to less

than 1 μm is unrealistic and causes an increase in manufacturing costs. In addition, since it is difficult to produce homogeneous crystal grains and the dispersion in the grain size becomes great, during high-power sputtering, abnormal electrical discharge and splash are likely to occur. On the other hand, when the average grain size is 30 μm or more, it becomes difficult to control the dispersion in the grain size and, consequently, as the target is consumed during sputtering, the sputtering surface becomes more uneven due to the difference in the sputtering rate caused by the difference in the crystal orientations of the respective crystal grains. Therefore, during high-power sputtering, abnormal electrical discharge and splash are likely to occur.

[0025]

The average grain size of the Ag alloy crystal grains is measured as described below.

Cuboid specimens with each side of about 10 mm are taken from 16 positions on the sputtering surface of the target which are equally separated from each other.

Specifically, the target is divided into 16 sections (4 vertical sections $\times$ 4 horizontal sections), and specimens are taken from the central portion of each section. Since the large target is assumed in the present embodiment, the large target having a 500 $\times$ 500 (mm) or larger sputtering surface, the area of the target surface of 0.25 m^2 or more, the method of taking specimens from a rectangular target ordinarily used as a large target is described. However, it is needless to say that the present invention also exhibits an effect in reducing the occurrence of splash in a round target. At this time, the sputtering surface of the target is equally divided into 16 sections and specimens are taken according to the method of taking specimens from a large rectangular target.

Next, the sputtering surface of each specimen is polished. At this time, the

surface is polished using waterproof paper of #180 to #4000 and then is buffed using 3 μm to 1 μm abrasive grains.

Furthermore, the surface of each specimen is etched so that grain boundaries become visible with an optical microscope. As an etching fluid, a liquid mixture of hydrogen peroxide water and ammonia water is used, the surface is immersed in the etching fluid at room temperature for 1 to 2 seconds, and the grain boundaries are caused to appear. Next, in each specimen, a photograph is taken using an optical microscope at a magnification of 200 times, 500 times, or 1000 times. As the magnification of the photograph, a magnification at which the number of crystal grains can be easily counted, is selected.

On each photograph, four line segments of 60 mm are perpendicularly and transversely drawn in a lattice shape at intervals of 20 mm and the number of crystal grains cut by the respective straight lines is counted. A crystal grain at the end of the line segment is counted as 0.5. The average cut length L (μm) is obtained using $L=60000/(M \cdot N)$ (where M represents the actual magnification and N represents the average value of the numbers of the cut crystal grains).

Next, the average grain size d (μm) of the specimen is computed from the obtained average cut length L (μm) using $d=(3/2) \cdot L$.

The average value of the average grain sizes of the specimens sampled from 16 positions as described above is used as the average grain size of Ag alloy crystal grains in the target.

[0026]

When the dispersion in the grain size of the Ag alloy crystal grains is 30% or less of the average grain size of the Ag alloy crystal grains, it is possible to more reliably

reduce the occurrence of the splash during sputtering. The dispersion in the grain size is computed as follows. An average grain size having the maximum absolute value of the deviation from the average grain size ($|[(\text{the average grain size of one position out of the 16 positions}) - (\text{the average grain size of the 16 positions})]|$), is specified out of the 16 average grain sizes obtained at the 16 positions, and then the dispersion is computed using the specified average grain size as described below.

$$\frac{|[(\text{The specified average grain size}) - (\text{the average grain size of the 16 positions})]|}{(\text{the average grain size of the 16 positions})} \times 100 (\%)$$

[0027]

Next, a method of producing an Ag alloy sputtering target for forming a conductive film of the present embodiment will be described.

For the Ag alloy sputtering target for forming a conductive film of the first embodiment, Ag having a purity of 99.99 mass% or more and In and Sn having a purity of 99.9 mass% or more are used as raw materials.

First, Ag is melted in a high vacuum or inert gas atmosphere, and a predetermined amount of one or more of In and Sn are added to the obtained molten Ag so that the total amount reaches 0.1 to 1.5 mass%. After that, by melting the components in a vacuum or inert gas atmosphere, a melted and cast ingot of an Ag alloy containing 0.1 to 1.5 mass% in total of one or more of In and Sn and the balance including Ag and inevitable impurities is prepared.

Here, with regard to the melting of Ag, it is preferable that an atmosphere is set to a vacuum atmosphere at once, Ag is melted in an atmosphere substituted with Ar, and then In and Sn is added to a molten metal of Ag in the Ar atmosphere, from the viewpoint of stabilizing a composition ratio of In and Sn to Ag.

[0028]

For the Ag alloy sputtering target for forming a conductive film of the second embodiment, Ag having a purity of 99.99 mass% or more and In, Sn, Sb, and Ga having a purity of 99.9 mass% or more are used as raw materials. One or more of In and Sn are
5 added to the molten Ag so that the total amount reaches 0.1 to 1.5 mass%, and one or more of Sb and Ga are added so that the total amount reaches 0.1 to 2.5 mass%. In this case as well, Ag is melted in a high vacuum or inert gas atmosphere and a predetermined amount of In, Sn, Sb, and Ga are added to the obtained molten Ag, and then the components are melted in a vacuum or inert gas atmosphere.

10 [0029]

In addition, the above-described melt and casting is desirably carried out in a vacuum or inert gas-substituted atmosphere, while it is also possible to use a melting furnace in the atmosphere. In a case in which a melting furnace in the atmosphere is used, the melt and casting is carried out, while the surface of the molten metal is sprayed
15 with an inert gas or is covered with a carbon-based solid sealing material such as wood coal. Thereby, it is possible to reduce the amount of oxygen or non-metallic inclusions in the ingot.

As the melting furnace, an induction heating furnace is preferred for purpose of homogenization of the components.

20 In addition, it is efficient and desirable to cast the molten alloy using a rectangular mold so as to obtain a cuboid ingot, while it is also possible to work a cylindrical ingot cast using a round mold so as to obtain a substantially cuboid ingot.

[0030]

The obtained cuboid ingot is heated, is hot-rolled to a predetermined thickness,
25 and then is subjected to quenching, cold-rolling, and heat-treating.

In this case, the conditions for the finishing hot-rolling in the final phase of the hot-rolling, the cold-rolling after the quenching, and the heat-treating are important. By setting the conditions appropriately, it is possible to produce an Ag alloy plate in which the crystal grains are fine and homogeneous.

5 Specifically, in the finishing hot-rolling, the rolling reduction per pass is set to 20 to 35%, the strain rate is set to 3 to 10/sec, and the rolling temperature after each rolling pass is set to 400 to 650°C. The hot-rolling includes one or more passes of the finishing hot-rolling. The total rolling reduction throughout the entire hot-rolling is set to, for example, 40% or more.

10 The finishing hot-rolling refers to a rolling pass having a strong influence on the grain size of a rolled plate, includes the final rolling pass, and may be considered to include the last three rolling passes as necessary.

In addition, the strain rate ε (sec^{-1}) can be defined as the following expression.

[0031]

15 [Expression 1]

$$\varepsilon = \frac{2\pi n}{60\sqrt{r'}} \cdot \sqrt{\frac{R}{H_0}} \cdot \ln\left(\frac{1}{1-r'}\right)$$

[0032]

In the above-described expression, H_0 represents the thickness (mm) of a ingot at the entry side of rolling roll, n represents the rotation speed (rpm) of the rolling roll, R represents the radius (mm) of the rolling roll, and r represents the rolling reduction (%) and $r'=r/100$.

20

When the rolling reduction per pass is set to 20 to 35% and the strain rate is set to 3 to 10/sec, the ingot is strongly worked using a large amount of energy at a relatively

low temperature. Thereby, the mixed presence of coarse crystal grains is prevented and it is possible to generate fine and homogeneous crystal grains through dynamic recrystallization as a whole. At a rolling reduction per pass of less than 20%, the crystal grains are not made fine sufficiently. When an attempt is made to obtain a rolling
 5 reduction of greater than 35%, the load applied to a rolling machine becomes excessive, which is unrealistic. In addition, at a strain rate of less than 3/sec, the crystal grains are not made fine sufficiently and a mixed grains of fine crystal grains and coarse crystal grains tend to generate. A strain rate of greater than 10/sec causes the load applied to a rolling machine to become excessive, which is unrealistic.

10 [0033]

When the rolling temperature after each pass is set to 400 to 650°C which is relatively low as the temperature for hot-rolling, the coarsening of the crystal grains is suppressed. At a rolling temperature of lower than 400°C, dynamic recrystallization becomes insufficient and a tendency of an increase in the dispersion in the grain size
 15 becomes significant. When the temperature after each pass is higher than 650°C, crystal grain growth proceeds and the average crystal grain size exceeds 30 μm .

This final finishing hot-rolling is carried out once to multiple times as necessary.

Regarding the more preferred range of the final finishing rolling, it is preferable that the rolling reduction per pass be 25 to 35%, the strain rate be 5 to 10/sec, the rolling
 20 temperature after each pass be 500 to 600°C, and 3 or more passes of the finishing hot-rolling be carried out.

The rolling initiation temperature may not be 400 to 650°C and the rolling initiation temperature and the pass schedule are set so that the temperature at the end of each pass in the finishing hot-rolling in the final phase reaches 400 to 650°C.

[0034]

In addition, after the above-described hot-rolling, the ingot is quenched from a temperature from 400 to 650°C to a temperature of 200°C or lower at a cooling rate from 100 to 1000°C/min. This quenching suppresses the growth of the crystal grains and
5 therefore, it is possible to obtain a rolled plate including fine crystal grains. At a cooling rate of less than 100°C/min, an effect that suppresses the growth of the crystal grains is poor. A cooling rate of greater than 1000°C/min does not contribute to making the crystal grains further finer. As the quenching method, the rolled plate may be showered with water for approximately 1 minute.

10 [0035]

Next, the cold-rolling is carried out so that the plate having the target thickness is obtained at an average value of the rolling reductions per pass throughout all the cold-rolling passes of 10 to 30% and an average value of the strain rates throughout all the cold-rolling passes of 3 to 10/sec.

15 When the rolling reduction per pass of the cold-rolling is less than 10%, the crystal grains are not made fine sufficiently and the dispersion in the grain size also increases, which are not preferable. When an attempt is made to obtain a rolling reduction so that the rolling reduction per pass exceeds 30%, the load applied to a rolling machine becomes excessive, which is unrealistic.

20 When the rolling strain rate of the cold-rolling is less than 3/sec, the crystal grains are not made fine sufficiently and a mixed grains of fine crystal grains and coarse crystal grains tend to generate. A strain rate of greater than 10/sec causes the excessive load applied to a rolling machine, which is unrealistic.

The temperature of the plate during the cold-rolling is equal to or lower than

200°C.

In the heat-treating after the cold-rolling, the rolled plate is held at 350 to 550°C for 1 to 2 hours. When the temperature is lower than 350°C or the time is shorter than 1 hour, recrystallization becomes insufficient and the dispersion in the grain size increases.

- 5 When the temperature is higher than 550°C or the time is longer than 2 hours, crystal grain growth proceeds and the average grain size exceeds 30 μm .

[0036]

- After the rolled plate obtained as described above is straightened using a straightening press, a roller leveler, or the like, the rolled plate is finished to desired
10 dimensions through machining such as milling and electric discharge machining. The arithmetic average surface roughness (Ra) of the sputtering surface of the finally-obtained sputtering target is preferably 0.2 to 2 μm .

[0037]

- According to the Ag alloy sputtering target for forming a conductive film of the
15 present embodiment obtained as described above, it is possible to reduce the occurrence of abnormal electrical discharge and splash even when high power is applied during sputtering. Through the sputtering using the target, a conductive film having a high reflectance and excellent durability can be obtained. In addition, through the sputtering using the Ag alloy sputtering target for forming a conductive film, it is possible to obtain
20 a conductive film having an excellent corrosion resistance and heat resistance and having a lower electrical resistance. Particularly, the embodiment is effective in the case of a large target having dimensions of a width: 500 mm or more, a length: 500 mm or more, and a thickness: 6 mm or more.

EXAMPLES

[0038]

(Example 1)

Ag having a purity of 99.99 mass% or more and, as additive raw materials, In,
5 Sn, Sb, and Ga having a purity of 99.9 mass% or more were prepared. Then, they were
set into a high-frequency induction furnace equipped with a graphite crucible. The total
weight at the melting was set to approximately 1100 kg.

In the melting, first, Ag was melted. After Ag was fused, the additive raw
materials were added thereto so as to obtain the composition of the target shown in Table
10 1, and the molten alloy was sufficiently stirred using the stirring effect due to induction
heating. Then, it was cast in a mold made of cast iron.

The portions having shrinkage cavity of the ingot obtained through the
above-described casting were cut off. The surfaces of the ingot that had been in contact
with the mold were cut and removed. As a result, a cuboid ingot having approximate
15 dimensions of 640×640×180 (mm) was obtained as a robust portion.

[0039]

The ingot was heated to 650°C and was subjected to hot-rolling, which was
repeated multiple times with the rolling direction changed in the middle, until the
thickness of the plate reached 67 mm. In the hot-rolling, the conditions for the last three
20 passes (the rolling reduction per pass, the strain rate, and the temperature of the plate
after the pass) were set as shown in Table 1.

After the end of the hot-rolling, the rolled plate was cooled to 200°C or lower
under the conditions shown in Table 1.

After cooling, cold-rolling was carried out multiple times so that finally, a plate
25 having dimensions of 1700×2100×20 (mm) was obtained. In the cold-rolling the total

rolling reduction, the average value of the rolling reductions per pass throughout all the cold-rolling passes, and the average value of the strain rates throughout all the cold-rolling passes were set as shown in Table 1.

The cold-rolled plate material was heat-treated under the conditions

5 (temperature and time) shown in Table 1.

After the heat-treated plate were straightened using a roller leveler, the plate was machined to dimensions of 1600×2000×15 (mm). Thus, a target was obtained.

[0040]

(Examples 2 to 21 and Comparative Examples 1 to 11)

10 Similar to Example 1, melting, casting, hot-rolling, cooling, cold-rolling, and heat-treating were carried out under conditions shown in Table 1 regarding the composition of the target, the conditions of the last three hot-rolling passes in the finishing hot-rolling (the rolling reduction per pass, the strain rate, and the temperature of the plate after the pass), the cooling rate after the hot-rolling, the cold-rolling conditions
 15 (the total rolling reduction of the cold-rolling, the average value of the rolling reductions per pass throughout all the cold-rolling passes, and the average value of the strain rates throughout all the cold-rolling passes), and the heat-treating conditions after the cold-rolling (temperature and time). Then, targets of Examples 2 to 21 and Comparative Examples 1 to 11 were produced through straightening and machining. In
 20 Table 1, values of the cooling rates were shown regarding targets that were cooled using a water shower, while “no water-cooling” means that targets were simply left to stand in the air.

[0041]

[Table 1-1]

	Composition of target (mass%)					Conditions for finishing hot-rolling								
						Third last rolling pass			Second last rolling pass			Last rolling pass		
	In	Sn	Sb	Ga	Ag	Strain rate (/sec)	Rolling reduction (%)	Temperature after pass (°C)	Strain rate (/sec)	Rolling reduction (%)	Temperature after pass (°C)	Strain rate (/sec)	Rolling reduction (%)	Temperature after pass (°C)
Example 1	0.6	0	0	0	Balance	2.3	15	570	3.3	23	540	3.8	24	510
Example 2	0.7	0	0	0	Balance	2.3	17	550	2.9	21	520	3.1	20	500
Example 3	0.5	0	0	0	Balance	3.7	31	600	4.4	31	580	5.4	31	550
Example 4	0.7	0	0	0	Balance	2.7	17	440	4.0	27	420	4.9	29	400
Example 5	0.9	0	0	0	Balance	3.8	29	680	4.5	29	650	6.0	34	630
Example 6	0.6	0	0	0	Balance	3.3	26	540	4.3	30	520	5.4	32	500
Example 7	0.8	0	0	0	Balance	2.6	16	550	3.8	25	520	5.3	33	500
Example 8	0.7	0	0	0	Balance	1.9	17	490	3.1	32	470	3.4	28	450
Example 9	0.5	0	0	0	Balance	3.1	21	610	4.2	29	580	5.3	31	550
Example 10	0.9	0	0	0	Balance	2.6	20	550	3.7	29	530	4.5	29	510
Example 11	0.2	0	0	0	Balance	3.7	20	590	4.3	22	550	5.4	26	520
Example 12	1.5	0	0	0	Balance	3.7	20	580	4.3	22	540	5.4	26	510
Example 13	0	1.0	0	0	Balance	3.7	20	560	4.3	22	530	5.4	26	500
Example 14	0.6	0.6	0	0	Balance	3.7	20	570	4.3	22	540	5.4	26	500
Example 15	0.7	0	0.5	0	Balance	3.7	20	560	4.3	22	530	5.4	26	500
Example 16	0.4	0	0	1.5	Balance	3.7	20	590	4.3	22	560	5.4	26	530
Example 17	0	0.5	1.1	0	Balance	3.7	20	600	4.3	22	560	5.4	26	520
Example 18	0	1.5	0	0.5	Balance	3.7	20	550	4.3	22	530	5.4	26	500
Example 19	0.3	0.3	2.3	0	Balance	3.7	20	560	4.3	22	530	5.4	26	500
Example 20	0.6	0.4	0	2.2	Balance	3.7	20	580	4.3	22	550	5.4	26	520
Example 21	0.4	0.4	0.5	0.3	Balance	3.7	20	580	4.3	22	540	5.4	26	510
Comparative Example 1	0.6	0	0	0	Balance	1.9	17	540	2.1	18	520	2.3	18	500
Comparative Example 2	0.9	0	0	0	Balance	2.3	15	380	3.9	30	360	4.1	25	350
Comparative Example 3	0.5	0	0	0	Balance	2.6	18	730	3.2	20	700	3.6	21	670
Comparative Example 4	0.7	0	0	0	Balance	2.3	15	650	3.1	22	630	3.6	22	600
Comparative Example 5	0.6	0	0	0	Balance	2.0	16	500	2.7	23	470	3.2	24	450
Comparative Example 6	0.8	0	0	0	Balance	2.4	16	630	3.8	28	610	4.5	29	580
Comparative Example 7	0.5	0	0	0	Balance	2.7	17	630	3.9	26	610	4.8	29	580
Comparative Example 8	0.7	0	0	0	Balance	3.1	20	630	3.6	21	610	4.3	23	580
Comparative Example 9	0	0	0	0	Balance	2.3	15	630	3.9	30	610	4.8	31	580
Comparative Example 10	2.0	0	0	0	Balance	3.7	20	560	4.3	22	530	5.4	26	500
Comparative Example 11	1.0	0.8	0	0	Balance	3.7	20	590	4.3	22	530	5.4	26	500

[Table 1-2]

	Cooling rate after hot-rolling (°C/min)	Conditions for cold-rolling			Conditions for heat-treating after cold-rolling
		Total rolling reduction (%)	Average of strain rates throughout all passes (/sec)	Average of rolling reductions throughout all passes (%)	
Example 1	300	70	4.8	18	480°C, 1 hour
Example 2	300	69	3.8	15	500°C, 1 hour
Example 3	300	57	4.5	13	480°C, 1 hour
Example 4	300	51	4.6	16	450°C, 1 hour
Example 5	300	56	5.2	15	480°C, 1 hour
Example 6	300	55	3.9	11	500°C, 1 hour
Example 7	300	45	3.7	11	510°C, 1 hour
Example 8	300	60	3.4	17	480°C, 1 hour
Example 9	300	78	7.0	22	390°C, 1 hour
Example 10	300	68	4.5	15	540°C, 1 hour
Example 11	300	54	5.2	14	480°C, 1 hour
Example 12	300	54	5.2	14	480°C, 1 hour
Example 13	300	54	5.2	14	480°C, 1 hour
Example 14	300	54	5.2	14	480°C, 1 hour
Example 15	300	54	5.2	14	480°C, 1 hour
Example 16	300	54	5.2	14	480°C, 1 hour
Example 17	300	54	5.2	14	480°C, 1 hour
Example 18	300	54	5.2	14	480°C, 1 hour
Example 19	300	54	5.2	14	480°C, 1 hour
Example 20	300	54	5.2	14	480°C, 1 hour
Example 21	300	54	5.2	14	480°C, 1 hour
Comparative Example 1	300	65	3.1	16	500°C, 1 hour
Comparative Example 2	300	68	5.2	20	460°C, 1 hour
Comparative Example 3	300	63	4.6	18	520°C, 1 hour
Comparative Example 4	No water-cooling	72	4.9	19	510°C, 1 hour
Comparative Example 5	300	55	2.4	9	520°C, 1 hour
Comparative Example 6	300	38	3.3	11	540°C, 1 hour
Comparative Example 7	300	60	4.9	17	340°C, 1 hour
Comparative Example 8	300	58	5.5	19	590°C, 1 hour
Comparative Example 9	300	65	4.6	16	490°C, 1 hour
Comparative Example 10	300	54	5.8	18	480°C, 1 hour
Comparative Example 11	300	54	5.8	18	480°C, 1 hour

[0042]

For the obtained targets, warpage after machining, the average grain size, and the dispersion therein were measured. In addition, each target was mounted on the sputtering apparatus, and the number of abnormal electrical discharges was measured during the sputtering using the targets. For conductive films obtained through the above-described sputtering, the surface roughness, the reflectance, the chloride resistance, and the specific resistance were measured.

(1) Warpage after machining

For the Ag alloy sputtering targets after machining, the amount of warpage per meter in length was measured, and the results were described in Table 2.

(2) Average grain size and dispersion therein

The grain sizes of the Ag alloy crystal grains were measured as described in the embodiment. Specimens were equally taken from 16 positions in the each targets produced as described above. The average grain size was measured on a surface seen from the sputtering surface of each specimen. Then, the dispersion between the average grain size of Ag alloy crystal grains as the average value of average grains in each specimen, and the average grain size of Ag alloy crystal grains was calculated.

[0043]

(3) Number of occurrence of abnormal electrical discharge during sputtering

A round plate having a diameter of 152.4 mm and a thickness of 6 mm was cut out from an arbitrary portion in the each target produced as described above. The plate was soldered to a copper backing plate. The soldered target was used as a target for evaluating splash during sputtering, and the number of abnormal electrical discharges during sputtering was measured.

In this case, the soldered target was mounted on an ordinary magnetron

sputtering apparatus, and the air was exhausted to 1×10^{-4} Pa. Then, sputtering was carried out under conditions of an Ar gas pressure of 0.5 Pa, an applied power of DC1000 W, and a distance between target and substrate of 60 mm. The number of abnormal electrical discharges was measured during sputtering for 30 minutes using the target at initial use. In addition, the number of occurrence of abnormal electrical discharge was measured during sputtering for 30 minutes using the target consumed by intermittent sputtering for 20 hours in which fake sputtering for four hours and the exchange of adhesion shield plates were repeated. The number of occurrence of abnormal electrical discharge was measured using the arc count function of a DC power supply (model No.: RPDG-50A) manufactured by MKS Instruments Inc.

[0044]

(4) Evaluation of basic properties of conductive film

(4-1) Surface roughness of film

Sputtering was carried out under the same conditions as described above using each target for evaluation so as to form a film having thickness of 100 nm on a glass substrate having dimensions of 20×20 (mm). Thereby, an Ag alloy film was obtained.

Furthermore, in order for the evaluation of heat resistance, heat-treating was carried out on the Ag alloy film at 250°C for 10 minutes, and then the average surface roughness (Ra) of the Ag alloy film was measured using an atomic force microscope.

(4-2) Reflectance

The absolute reflectance at a wavelength of 550 nm of an Ag alloy film was measured using a spectrophotometer, the Ag alloy film formed on a glass substrate having dimensions of 30×30 (mm) in the same manner as described above.

Furthermore, in order for the evaluation of corrosion resistance, the absolute

reflectance at a wavelength of 550 nm of an Ag alloy film formed in the same manner as described above was measured using a spectrophotometer, after holding the Ag alloy film in a constant temperature and humidity chamber at a temperature of 80°C and a humidity of 85% for 100 hours.

5 (4-3) Chloride resistance

In order to evaluate the effect of the addition of Ga, an aqueous solution containing 5 weight% of NaCl was sprayed onto the film surface of an Ag alloy film formed in the same manner as described above using a target to which Ga is added (Examples 16, 18, 20, and 21). The aqueous solution was sprayed from a location
10 which was 20 cm above from the film surface and 10 cm away from the end of the substrate in a direction parallel to the film surface so that the NaCl aqueous solution sprayed onto the film fell freely as much as possible and attached to the film. After the aqueous solution was sprayed every minute five times in total, the film was washed and rinsed with pure water three times and was dried by injecting dry air so as to blow
15 moisture away.

After the above-described spraying of the saline water, the film surface of the Ag alloy film was visually observed and the state of the surface was evaluated. Regarding the evaluation standards for chloride resistance, the state of the surface was evaluated into two steps by evaluating a surface on which white turbid or spots were not or partially
20 observed as favorable with an “O” and a surface on which white turbid or spots were observed throughout as poor with an “X”. Since the evaluation was not carried out on targets to which Ga was not added, the targets have a “-” sign in the table.

(4-4) Specific resistance of film

The specific resistance of an Ag alloy film formed in the same manner as
25 described above was measured.

The respective evaluation results thereof are described in Table 2.

[0045]

[Table 2]

	Average grain size (μm)	Dispersion in grain size (%)	Warpage after machining (mm)	Number of abnormal electrical discharges		Absolute reflectance of film (%)	Specific resistance of film ($\mu\Omega\cdot\text{cm}$)	Absolute reflectance after maintaining film at constant temperature and humidity (%)	Evaluation of chloride resistance of film	Surface roughness after heat-treating of film (nm)
				At initial use (times)	After consumption (times)					
Example 1	21	23	0.7	0	0	96.7	4.3	96.4	-	0.8
Example 2	28	26	0.6	1	1	96.5	4.3	96.3	-	0.9
Example 3	18	26	0.5	0	0	96.8	4.2	96.5	-	0.9
Example 4	17	28	0.8	1	2	96.6	4.3	96.4	-	0.8
Example 5	25	23	0.7	0	0	96.4	4.4	96.1	-	0.8
Example 6	27	27	0.5	0	1	96.7	4.2	96.5	-	0.8
Example 7	27	23	0.6	0	0	96.6	4.4	96.3	-	0.9
Example 8	24	27	0.7	0	0	96.7	4.3	96.4	-	0.9
Example 9	3.3	29	0.9	2	4	96.7	4.1	96.5	-	0.8
Example 10	29	19	0.5	1	0	96.3	4.4	96.1	-	0.8
Example 11	28	27	1.3	1	2	97	3.7	96.4	-	1.4
Example 12	19	26	0.6	0	1	95.6	5.8	95	-	0.7
Example 13	21	25	0.8	0	0	95.8	5.2	95.2	-	0.8
Example 14	22	24	0.6	0	0	95.7	5.5	95.1	-	0.7
Example 15	17	24	0.7	0	0	96.5	4.9	96.3	-	0.6
Example 16	16	26	0.6	0	1	94.8	5.8	93.3	O	0.6
Example 17	17	24	0.7	0	0	96	5.7	95.5	-	0.5
Example 18	20	24	0.8	0	0	95.9	6	95.1	O	0.6
Example 19	16	27	0.7	0	1	94.8	7.2	92.8	-	0.5
Example 20	17	27	0.6	1	0	94	7.2	90.2	O	0.5
Example 21	18	26	0.7	0	0	95.3	5.9	94.2	O	0.6
Comparative Example 1	36	38	0.8	7	27	96.7	4.3	96.3	-	0.9
Comparative Example 2	25	53	0.9	9	40	96.4	4.4	96	-	0.8
Comparative Example 3	40	26	0.5	3	21	96.7	4.1	96.5	-	0.9
Comparative Example 4	32	27	0.8	1	15	96.6	4.2	96.4	-	0.8
Comparative Example 5	35	42	0.6	8	33	96.6	4.2	96.3	-	0.9
Comparative Example 6	44	27	0.7	3	20	96.4	4.3	96.1	-	0.8
Comparative Example 7	41	60	1	10	45	96.7	4.1	96.5	-	0.9
Comparative Example 8	35	26	0.5	3	16	96.5	4.3	96.3	-	0.8
Comparative Example 9	36	28	3.1	2	18	97.6	3.2	87.4	-	2.5
Comparative Example 10	22	25	0.9	0	0	92.2	7.8	89.1	-	0.6
Comparative Example 11	20	27	0.8	0	0	92	7.6	88.9	-	0.8

[0046]

In the target materials of the examples, the average grain sizes of the Ag alloy crystal grains were in a range of 1 μm to less than 30 μm and the dispersion in the grain size of the Ag alloy crystal grains was 30% or less of the average grain size of the Ag alloy crystal grains. Warpage after machining was small and the number of occurrence of abnormal electrical discharge during sputtering was also small both at the initial phase of the use and after the consumption of the target. In addition, in the targets to which Sb and Ga were added, the average grain size tended to decrease and the number of occurrence of abnormal electrical discharge was also as small as one or less.

In addition, in the conductive films obtained using the target materials of the examples, the reflectance and the specific resistance were excellent, and the surface roughness Ra was as small as 1.4 nm or less.

In addition, it is found that the conductive films obtained using the targets to which Ga was added was excellent in terms of chloride resistance and was suitable for a conductive film for a touch panel and the like.

[0047]

The present invention is not limited to the above-described embodiment, and various modifications can be made without departing from the spirits of the present invention.

INDUSTRIAL APPLICABILITY

[0048]

According to the Ag alloy sputtering target for forming a conductive film of the present invention and an Ag alloy sputtering target for forming a conductive film produced using the producing method of the present invention, it is possible to further

reduce arc discharge and splash even when high power is applied during sputtering. As a result, it is possible to form a conductive film having a high reflectance and excellent durability.

CLAIMS

1. An Ag alloy sputtering target for forming a conductive film, comprising:

0.1 to 1.5 mass% in total of one or more of In and Sn which can be solid-solved

5 in Ag; and

the balance including Ag and inevitable impurities,

wherein an average grain size of crystal grains in an alloy is 1 μm or more and less than 30 μm , and a dispersion in a grain size of the crystal grains is 30% or less of the average grain size.

10

2. An Ag alloy sputtering target for forming a conductive film, comprising:

0.1 to 1.5 mass% in total of one or more of In and Sn which can be solid-solved

in Ag;

0.1 to 2.5 mass% in total of one or more of Sb and Ga which can be solid-solved

15 in Ag; and

the balance including Ag and inevitable impurities,

wherein an average grain size of crystal grains in an alloy is 1 μm or more and less than 30 μm , and a dispersion in a grain size of the crystal grains is 30% or less of the average grain size.

20

3. A method of producing an Ag alloy sputtering target for forming a conductive film by subjecting a melted and cast ingot to: a hot-rolling step; a cooling step; a cold-rolling step; a heat-treating step; and a machining step in this order, the ingot comprising: 0.1 to 1.5 mass% in total of one or more of In and Sn; and the balance

including Ag and inevitable impurities,

wherein the hot-rolling step includes one or more passes of finishing hot-rolling in which a rolling reduction per pass is 20 to 35%, a strain rate is 3 to 10/sec, and a temperature after the pass is 400 to 650°C,

5 in the cooling step, the ingot is quenched to 200°C or lower at a cooling rate of 100 to 1000°C/min,

the cold-rolling step is carried out so that a plate having a target thickness is obtained at an average value of the rolling reductions per pass throughout all cold-rolling passes of 10 to 30%, an average value of the strain rates throughout all the cold-rolling
10 passes of 3 to 10/sec, and a total rolling reduction of 40 to 80%, and

in the heat-treating step, the ingot is held at 350 to 550°C for 1 to 2 hours.

4. A method of producing an Ag alloy sputtering target for forming a conductive film by subjecting a melted and cast ingot to: a hot-rolling step; a cooling
15 step; a cold-rolling step; a heat-treating step; and a machining step in this order, the ingot comprising: 0.1 to 1.5 mass% in total of one or more of In and Sn; 0.1 to 2.5 mass% in total of one or more of Sb and Ga; and the balance including Ag and inevitable impurities,

wherein the hot-rolling step includes one or more passes of finishing hot-rolling
20 in which a rolling reduction per pass is 20 to 35%, a strain rate is 3 to 10/sec, and a temperature after the pass is 400 to 650°C,

in the cooling step, the ingot is quenched to 200°C or lower at a cooling rate of 100 to 1000°C/min,

the cold-rolling step is carried out so that a plate having a target thickness is

obtained at an average value of the rolling reductions per pass throughout all cold-rolling passes of 10 to 30%, an average value of the strain rates throughout all the cold-rolling passes of 3 to 10/sec, and a total rolling reduction of 40 to 80%, and

in the heat-treating step, the ingot is held at 350 to 550°C for 1 to 2 hours.