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(54) **FE-NI-BASED ALLOY THIN PLATE**

(57) Provided are an Fe-Ni-based thin plate capable of having isotropic mechanical characteristics even if the plate is widened, and a method for producing the same. The Fe-Ni-based alloy thin plate and the method for producing the Fe-Ni-based alloy thin plate are characterized by the following: the thin plate is formed of, in terms of mass percentage, 35.0-43.0% of Ni + Co (Co is 0-6.0%), 0.5% or less of Si, 1.0% or less of Mn, with the remainder being Fe and impurities; a hot-rolled material is used as a material for cold rolling; first cold rolling is conducted

on the material for cold rolling, with a rolling reduction ratio of 85% or higher; after the first cold rolling, recrystallization sintering is conducted on such material under conditions where the temperature is 800°C or higher and the retention time is 0.1-1.2 minutes; after the recrystallization sintering, a final cold rolling is conducted on such material with a rolling reduction ratio of 40% or less to obtain a Fe-Ni-based alloy thin plate having a thickness of 0.25 mm or less; and no heat treatment is conducted after the final cold rolling.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a Fe-Ni-based alloy thin plate used for, for example, a lead frame or a metal mask.

BACKGROUND ART

10 **[0002]** For a Fe-Ni-based alloy thin plate used for a lead frame, a metal mask or the like, various investigations have been made for improving its properties. For example, JP 2003-253398 A discloses a method for producing a Fe-Ni-based alloy thin plate, including cold rolling and annealing, respectively at least one times, to produce a hot-rolled plate. In the method, a cold rolling is conducted before a last recrystallization annealing with a reduction ratio of not less than 90%. The last recrystallization annealing is conducted at not lower than 850°C, and a last rolling is conducted with a reduction ratio of not more than 30%, thereby etching accuracy is improved. JP 06-279946 A discloses a method of
15 producing shadow mask material, including at least one cold rolling with a reduction ratio of not less than 85% and annealing at not lower than 700°C, followed by sequentially cold rolling with a reduction ratio of not exceeding 85% and annealing at a temperature of not exceeding 850°C.

CITATION LIST

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[0003]

PATENT LITERATURE 1: JP 2003-253398 A

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PATENT LITERATURE 2: JP 06-279946 A

SUMMARY OF INVENTION

30 **[0004]** The Fe-Ni-based alloy thin plate is cut into a desired size for use according its application. However, the product has been required to have higher accuracy, and thus dimensional tolerance has been becoming severe increasingly, for a metal mask or the like. Therefore, such products that deviate from the dimensional tolerance after cut will increase. Although Patent Literatures 1 and 2 are useful for improving an etching properties, they do not describe suppress of a variation of thin plate properties after cut. Thus, there is a room for further investigation.

35 **[0005]** An object of the present invention is to provide an Fe-Ni-based alloy thin plate having a thickness of not more than 0.25 mm, and having little anisotropy of mechanical properties on a rolled surface and good shape processability. An object of the present invention is also to provide a method for producing the Fe-Ni-based alloy thin plate.

[0006] According to an aspect of the present invention, provided is a method for producing a Fe-Ni-based alloy thin plate, including:

40 preparing a hot-rolled material as a material to be cold-rolled, wherein the hot-rolled material includes, by mass, 35.0 to 43.0% of Ni+Co, wherein Co is 0 to 6.0%, not more than 0.5% of Si, not more than 1.0% of Mn, and the balance being Fe and impurities, and has a thickness of not less than 2 mm;
first-cold-rolling the hot-rolled material with a reduction ratio of not less than 85%;
then recrystallization-annealing the first-cold-roll material at a temperature of not lower than 800°C for a retention
45 time period of 0.1 to 1.2 minutes; and
then final cold rolling the annealed material with a reduction of not more than 40% to produce the Fe-Ni-based alloy thin plate having a thickness of not more than 0.25 mm,
wherein no heat treatment is conducted after the final cold rolling.

50 **[0007]** According to an another aspect of the present invention, provided is a Fe-Ni-based alloy thin plate including, by mass, 35.0 to 43.0% of Ni+Co, wherein Co is 0 to 6.0%, not more than 0.5% of Si, not more than 1.0% of Mn, and the balance being Fe and impurities, and having a thickness of not more than 0.25 mm,

55 wherein each difference of 0.2% yield stresses between a width direction, a longitudinal direction and a 45° direction of the thin plate is within 5% of an average of 0.2% yield stresses of the three directions, and
wherein each elongation in the three directions is 0.90 to 1.10 times an average elongation of the three directions.

[0008] According to the present invention, a Fe-Ni-based alloy thin plate with a thickness of not more than 0.25 mm

has little variation of mechanical properties between cutting directions, thereby good processability can be achieved.

DESCRIPTION OF EMBODIMENTS

5 **[0009]** Hereinafter, embodiments of the present invention will be explained. First, a method for producing a Fe-Ni-based alloy thin plate according to the present invention will be explained.

< Composition of hot-rolled material >

10 **[0010]** According to the present invention, there is provided a hot-rolled material having a composition including, by mass, 35.0 to 43.0% of Ni+Co wherein Co is 0 to 6.0%, not more than 0.5% of Si, not more than 1.0% of Mn, and the balance being Fe and impurities. The composition of the Fe-Ni-based alloy is determined for obtaining a desired thermal expansion coefficient.

15 [35.0 to 43.0% of Ni+Co, wherein Co is 0 to 6.0%]

[0011] As stated above, Ni and Co are elements for obtaining a desired thermal expansion coefficient. An austenite structure becomes unstable when the content of Ni+Co is less than 35.0%. However, when it exceeds 43.0%, a thermal expansion coefficient is increased so that a low thermal expansion is not satisfied. Thus, the content of Ni+Co is determined to be 35.0 to 43.0%. Co is not necessarily added. However, since Co has an effect of strengthening the Fe-Ni-based alloy, a part of Ni can be replaced by Co within a range up to 6.0% in the case of a thickness is small and an especially severe handling property is required.

[not more than 0.5% of Si, not more than 1.0% of Mn]

25 **[0012]** In general, Si and Mn are included in trace amounts in the Fe-Ni-based alloy for the purpose of deoxidation. However, since an excess addition thereof cause segregation, Si is limited up to 0.5%, and Mn is limited up to 1.0%. The lower limits of Si and Mn are not particularly defined. However, since they are added as deoxidation elements as mentioned above, at least 0.05% of each of Si and Mn remain in the alloy.

30 [the balance being Fe and Impurities]

[0013] Other than the above elements may be substantially Fe while impurities that are inevitably included in the alloy during the manufacturing thereof may be included. In particular, an impurity element to be limited is carbon (C). For example, the upper limit of carbon may be 0.05% for an application of etching.

35 **[0014]** Furthermore, a free-cutting element such as sulfur (S) may be included up to 0.020% in order to improve press punchability. An element improving hot processability such as boron (B) may be included up to 0.0050%.

< Hot-rolled material has a thickness of not less than 2 mm >

40 **[0015]** The hot-rolled material supplied for the method of the present invention has a thickness of not less than 2 mm. If the thickness is less than 2 mm, it may become impossible to conduct cold rolling with a reduction of not less than 85%. Furthermore, a special rolling equipment may be required to produce the material having a thickness of less than 2 mm. Thus, the thickness of the hot-rolled material is set to be not less than 2 mm.

45 **[0016]** The upper limit of the thickness is practically 5 mm. As the hot-rolled material has greater thickness, it is possible to increase a reduction ratio, but the pass number during the cold rolling process may be increased or it may become difficult to adjust a shape of the Fe-Ni-based alloy during the rolling.

[0017] Since an oxide layer is formed on a surface of the hot-rolled material, the thickness of the hot-rolled material includes that of the oxide layer.

50 < Material for cold rolling >

[0018] According to the present invention, the hot-rolled material is provided as a material for cold rolling. Since an oxide layer is formed on a surface of the hot-rolled material, the oxide layer is removed, for example, mechanically or chemically. Furthermore, in order to prevent defects such as cracks from an edge of the material during the cold rolling, edges may be cared. As such, a material for cold rolling is prepared.

55 **[0019]** Next, a cold rolling step will be explained in detail.

<First cold rolling>

[0020] According to the present invention, a reduction ratio in the first cold rolling, which is conducted before recrystallization annealing, is not less than 85%. Since the reduction ratio before the recrystallization annealing is great, crystal orientation of the alloy after the final rolling, described later, can be easily arranged in one direction, leading to minimize anisotropy of mechanical properties. Furthermore, since the number of cold rolling or the annealing steps can be decreased, a cost for the production can be also reduced. If the reduction ratio is less than 85%, the mechanical properties are deteriorated. Furthermore, the cost increases due to an increase in the number of times of the cold rolling with too low reduction ratio and the annealing. The reduction ratio is preferably not less than 87%, still more preferably not less than 90%. While the upper limit of reduction ratio is not particularly defined, it is practically 99%, since the rolling with the reduction ratio exceeding 99% leads to high cost due to excessive rolling time.

<Recrystallization annealing>

[0021] According to the present invention, recrystallization annealing is conducted at a temperature of not lower than 800°C after the first cold rolling. In the step, strain of the work hardened thin plate due to the high reduction in the rolling is removed to soften the thin plate, thereby a desired thickness and mechanical properties can be obtained by the subsequent final cold rolling. If the annealing temperature is lower than 800°C, the material may not be softened sufficiently. While the upper limit of the annealing temperature is not particularly defined, it can be 1100°C since desired properties are not possibly obtained with too high temperature annealing.

[0022] According to the present invention, a retention time period of the annealing is adjusted to 0.1 to 1.2 minutes. By making the heating retention time period relatively short in the above temperature range, desired isotropic properties such as yield stress and elongation can be obtained without lowering productivity. If the annealing time is shorter than 0.1 minute, strain will not be sufficiently removed. If the annealing time exceeds 1.2 minutes, variations of mechanical properties may be caused or the cost may be increased due to the longer annealing time. It is preferable that the lower limit of annealing time period is 0.2 minute. Furthermore, the upper limit of annealing time period is preferably 0.9 minute and more preferably 0.6 minute for the purpose of further cost reduction.

[0023] The recrystallization annealing can be conducted by passing the first-cold-rolled material continuously through a heating furnace at a desired temperature. In the recrystallization annealing, for example, the first-cold-rolled material wound in a coil is drawn, is passed through the furnace, and then wound in a roll shape.

<Final cold rolling>

[0024] According to the method of the present invention, the recrystallization-annealed material is subjected to the final cold rolling with a reduction ratio of not more than 40%, thereby a Fe-Ni-based alloy thin plate has minimized anisotropy of mechanical properties. The rolling with a reduction ratio of more than 40% is not preferable since the anisotropy of mechanical properties tends to become larger due to excessive strain. While the lower limit of the reduction ratio is not particularly defined, the reduction ratio may be not less than 15%. If the reduction ratio is too low, it is difficult to adjust to a desired plate thickness. In order to make it easier to obtain the mechanical properties, it is preferable that a front tension in the final cold rolling is 200 to 500 MPa; a back tension is 100 to 200 MPa; and a rolling speed is 250 m/min. The lower limit of the front tension is more preferably 250 MPa, and the upper limit thereof is more preferably 400 MPa. The lower limit of the back tension is more preferably 120 MPa, and the upper limit thereof is more preferably 180 MPa. While the lower limit of the rolling speed is not particularly defined, approximately 100 m/minute is preferable in view of workability. In the method of the embodiment, the final cold rolling is preferable conducted with one pass in order to prevent cracks on a surface of the thin plate and obtain desired properties.

[0025] A thickness of the final-cold-rolled steel strip is not more than 0.1 mm. For example, this thickness can cope with pin multiplication when the Fe-Ni-based alloy thin plate is applied to a lead frame and can cope with high definition in etching processing when the thin plate is applied to a metal mask. The upper limit of the thickness is preferably 0.08 mm. While the lower limit is not particularly defined, it can be 0.02 mm since the plate tends to be deformed when the material is too thin. It is especially preferable that the Fe-Ni-based alloy thin plate has a broad width (for example, a width of 500 to 1200 mm).

<Omission of stress relief annealing>

[0026] According to the present invention, no heat treatment is conducted after the final cold rolling. The heat treatment is, for example, stress relief annealing conducted at a recrystallizing temperature or lower. By omitting the heat treatment, residual stress is not relieved so that a deformation of the thin plate and a variation of the mechanical properties can be suppressed. Even though the stress is not relieved, the product has little anisotropy in mechanical properties according

to the present invention. Thus, the heat treatment can be omitted. The omission of the heat treatment is economically advantageous due to energy saving.

[0027] Then, there will be explained the Fe-Ni-based alloy thin plate of the present invention, which can be produced by the method of the present invention.

<0.2% yield stress, elongation >

[0028] The Fe-Ni-based alloy thin plate of the present invention is characterized by

that each difference of 0.2% yield stresses between three directions: i.e. a width direction (a first direction of a surface of the thin plate, corresponding to a direction perpendicular to a rolling direction); a longitudinal direction (a second direction of the surface of the thin plate, perpendicular to the width direction and corresponding to the rolling direction), and a 45° direction (a third direction of the surface of the thin plate, having an angle 45° in relation to the width direction and the longitudinal direction) is not more than 5% of the average of the 0.2% yield stresses of the

three directions, and that each elongation in the three directions is 0.90 to 1.10 times the average elongation of the three directions.

[0029] The 0.2% yield stress is a parameter relating to processability such as plastic deformation, and the elongation is a parameter relating to a product shape after processing. By controlling them in the above range, the thin plate of the present invention has minimized variation in strength and shape between cutting directions. For example, a variation in cutting condition is minimized when the thin plate is cut in various directions, leading to good workability. If each difference of 0.2% yield stresses between three directions exceeds 5% of the average of the three directions, the anisotropy becomes larger. Thus, shape differences according to the cutting directions become larger, leading to increase of a possibility of occurrence of a thin plate that does not fulfill desired properties depending on the cutting direction. Preferably, each difference of the 0.2% yield stresses in the three directions is not more than 3% of the average 0.2% yield stresses of the three directions. Although it is most desirable that each difference of the 0.2% yield stresses and the elongation in the three directions is 0% (i.e. the properties in three directions are same), it is difficult to make them 0%. Thus, the lower limit of the each difference of the 0.2% yield stresses can be set to e.g. 0.1%. Furthermore, it is preferable to make the average of the 0.2% yield stresses in the three directions not more than 580 MPa since the anisotropy can be further suppressed. The average elongation is made not more than 2% to suppress the deformation of the product shape after cutting.

<Crystal orientation>

[0030] The Fe-Ni-based alloy thin plate of the present invention has an integration degree of (200) plane of not less than 90%. This feature can further enhance the tendency to minimize the anisotropy of mechanical properties in the Fe-Ni-based alloy thin plate. Besides the above case, when producing, for example, a lead frame or the like by press process, the product can be pressed regardless of directions. More preferably, the integration degree of (200) plane is not less than 95%. The integration degree of (200) plane in the embodiment can be calculated by the formula:

$$I(200) / \{I(111) + I(200) + I(220) + I(311)\}$$

where I(111), I(200), I(220) and I(311) are X-ray diffraction integral intensities of, respectively, (111), (200), (220) and (311) of the rolled surface of the Fe-Ni-based alloy thin plate, measured with use of e.g. an X-ray diffraction (XRD) method.

EXAMPLES

[0031] A hot-rolled material having 3.0 mm thickness was produced through vacuum melting, thermally homogenizing heat treatment, hot press and hot-rolling. A chemical composition of the hot-rolled material is shown in the Table 1.

[0032] An oxide layer on a surface of the hot-rolled material was removed by chemical polishing and machine polishing, and cracks generated during the hot-rolling at the both sides of the material in a width direction were cut by a trim processing. Thus, 1.55 mm thick material for cold rolling was produced. The material had a width of 860 mm.

[0033] Next, the material was divided into samples of Example according to the invention and Comparative Example. They were subjected to steps shown in the Table 2 to produce Fe-Ni-based alloy thin plates. For Example according to the invention, first cold rolling, recrystallization annealing, and final cold rolling were conducted. For Comparative Example 1, intermediate rolling (1), recrystallization annealing, intermediate rolling (2), recrystallization annealing, and final cold rolling were conducted. In Comparative Example 2, the steps were the same as Example according to the invention,

although a reduction ratio in the final cold rolling was greater.

[0034] In the first cold rolling (1) of Example according to the invention and Comparative Example 2, and in the intermediate rolling (1) and (2) of Comparative Example 1, the material for cold rolling was cold-rolled through 10 passes and with a reduction ratio shown in the Table 2. Thereafter, for both Example according to the invention and Comparative Examples, the recrystallization annealing was conducted at 900°C for retention time period of 0.36 minute. Then, the final cold rolling was conducted under conditions of a front tension being 320 MPa, a back tension being 140 MPa and a rolling speed at 200 m/min. In Comparative Example 1, the recrystallization annealing was conducted two times. Furthermore, in Comparative Example 3, the same steps as Example according to the invention were conducted until the final cold rolling, but stress relief annealing was conducted at a temperature of 600°C after the final cold rolling. The stress relief annealing after the final cold rolling was not conducted in Example according to the invention and Comparative Examples 1 and 2.

[TABLE 1]

(mass%)					
C	Si	Mn	Ni	Co	balance
0.01	0.1	0.5	40.7	0.4	Fe and inevitable impurities

[TABLE 2]

No	Cold rolling step	Reduction ratio (%) of first cold rolling (intermediate rolling)	Reduction ratio (%) of final cold rolling	Final thickness (mm)	Remarks
1	first cold rolling→Recrystallization annealing →final cold rolling	92	36	0.08	Example according to the invention
11	Intermediate rolling①→Recrystallization annealing→Intermediate rolling②→Recrystallization annealing→final cold rolling	①60 ②80	20	0.1	Comparative Example 1
12	first cold rolling→Recrystallization annealing →final cold rolling	92	52	0.06	Comparative Example 2
13	first cold rolling→Recrystallization annealing→final cold rolling →Stress relief annealing	92	36	0.08	Comparative Example 3
* The cold rolling step are conducted after production of the material for cold rolling.					

[0035] Test pieces for respective measurements were taken from the final-cold-rolled thin plates and subjected to respective tests. The results thereof are collectively shown in Table 3. 0.2% yield stress and elongation were measured according to a method pursuant to JIS Z 2241, with JIS No. 13 B test pieces. Example according to the invention and Comparative Example 1 were measured of an integration degree of (200) plane on the surface of the thin plate with use of an X-ray diffraction apparatus. This integration degree of (200) plane was obtained by measuring integrated intensities $I(111)$, $I(200)$, $I(220)$ and $I(311)$ and calculating it with the formula:

$$I(200) / \{I(111) + I(200) + I(220) + I(311)\}.$$

As a result, the integration degree of (200) plane of Example according to the invention was 98%, and that of Comparative Example 1 was 68%. Thus, it was confirmed that the Fe-Ni-based alloy thin plate of Example according to the invention had a very high integration degree of (200) plane.

[TABLE 3]

No.	Direction	0.2% yield stress (MPa)	5% of average value of 0.2% yield stress (MPa)	Difference of 0.2% yield stress (MPa)			Elongation (%)	ratio of elongation to average	Remarks
				Difference between width direction and longitudinal direction	Difference between width direction and 45° direction	Difference between longitudinal direction and 45° direction			
1	Width direction	552	27.8	7	4	2	1.3	1.00	Example according to the invention
	Longitudinal direction	559					1.3	1.00	
	45° direction	557					1.2	0.92	
	Average	556					1.3	-	
11	Width direction	579	29.7	48	4	52	4.4	0.98	Comparative Example 1
	Longitudinal direction	627					5.1	1.13	
	45° direction	575					4	0.89	
	Average	594					4.5	-	
12	Width direction	573	29.1	4	22	18	0.5	0.83	Comparative Example 2
	Longitudinal direction	577					0.8	1.33	
	45° direction	595					0.4	0.67	
	Average	582					0.6	-	
13	Width direction	525	26.7	19	5	14	4	1.74	Comparative Example 3
	Longitudinal direction	544					2.3	1.00	
	45° direction	530					0.6	0.26	
	Average	533					2.3	-	

[0036] As the above, each difference of 0.2% yield stresses between the width direction, the longitudinal direction and the 45° direction was 7 MPa at a maximum and approximately 1.3% of the average value in the Fe-Ni-based alloy thin plate of the present invention. The elongations of the three directions were also approximately 0.92 to 1 times the average value, and it was confirmed that the thin plate of the present invention had a good property with very little anisotropy. In the Fe-Ni-based alloy thin plate of Comparative Example 1, on the other hand, each difference of 0.2% yield stress between the width direction, the longitudinal direction and the 45° direction was 52 MPa at a maximum and approximately 8.8% of the average value. The elongations of the three directions were also approximately 0.89 to 1.13 times the average value, and it was confirmed to have a larger anisotropy of mechanical properties than the thin plate of Example according to the invention. In the Fe-Ni-based alloy thin plate of Comparative Example 2, each difference of 0.2% yield stress between the width direction, the longitudinal direction and the 45° direction was 22 MPa at a maximum and approximately 3.8% of the average value, which was within the preferable range. However, the elongations of the three directions were approximately 0.67 to 1.33 times the average value, and it was confirmed to have a larger anisotropy of elongation than the thin plate of Example according to the invention. In the Fe-Ni-based alloy thin plate of Comparative Example preferable range, but elongations of the three directions varied largely.

Claims

1. AFe-Ni-based alloy thin plate comprising, by mass,

35.0 to 43.0% of Ni+Co, wherein Co is 0 to 6.0%,
 more than 0% and not more than 0.5% of Si,
 more than 0% and not more than 1.0% of Mn,
 optionally not more than 0.05% of C,
 optionally not more than 0.020% of S,
 optionally not more than 0.0050% of B, and
 the balance being Fe and impurities, and having a thickness of not more than 0.1 mm,
 wherein each difference of 0.2% yield stresses between a width direction, a longitudinal direction and a 45°
 direction of the thin plate is within 5% of an average of 0.2% yield stresses of the three directions, and
 wherein each elongation in the three directions is 0.90 to 1.10 times an average elongation of the three directions,
 the average elongation being not more than 2%, and the integration degree of the (200) plane is not less than 90%.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2003253398 A [0002] [0003]
- JP 6279946 A [0002] [0003]