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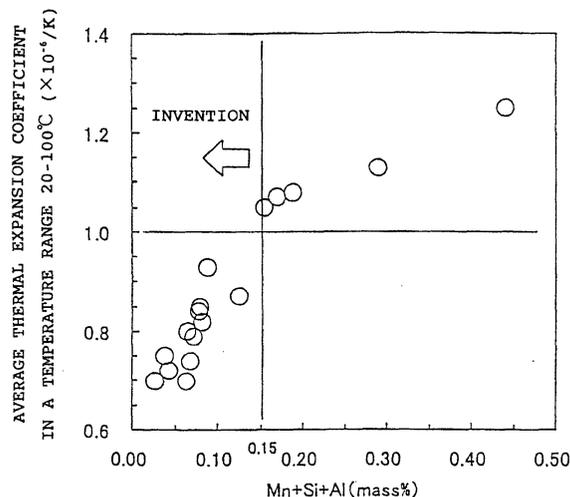
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(54) **THIN ALLOY SHEET OF LOW THERMAL EXPANSION AND SHADOW MASK USING THE SAME**

(57) The invention provides a low thermal expansion alloy sheet consisting essentially of: 35.0 to 37.0% Ni, 0.01 to 0.09% Mn, 0.01 to 0.04% Si, 0.01 to 0.04% Al, by mass, and balance of Fe. The value of (Mn/S) is from 20 to 300, and the amount of (Mn + Si + Al) is 0.15% or less. The average thermal expansion coefficient is 1.0

x 10⁻⁶/K or less in a temperature range from 20°C to 100°C. The low thermal expansion alloy sheet does not induce cracks, fractures, or flaws during manufacturing process, and assures excellent etching property and dimensional accuracy during manufacturing process of shadow masks.

FIG. 1



Description**TECHNICAL FIELD**

5 **[0001]** The present invention relates to a low thermal expansion alloy sheet, specifically to a low thermal expansion alloy sheet used for shadow mask in cathode-ray tube and the like, having excellent manufacturability and etching property, and having average thermal expansion coefficient of $1.0 \times 10^{-6}/K$ or less in a temperature range from 20°C to 100°C, and relates to a shadow mask using the same.

BACKGROUND ART

10 **[0002]** Owing to the extremely low thermal expansion coefficient at around room temperature, Fe-Ni alloys containing about 36% of Ni are used in a wide field such as precision equipments, bimetals, and shadow masks in cathode-ray tubes of computers and TVs, and the like, which do not allow dimensional variations under varied temperature conditions.

15 **[0003]** Many of the alloys have average thermal expansion coefficient of around 1.2×10^{-6} to $2.0 \times 10^{-6}/K$ in a temperature range from room temperature to 100°C. However, much lower thermal expansion coefficient is required in recent years to the materials of shadow masks in cathode-ray tubes, where shadow masks face severe requirement of increased brightness and increased image quality.

20 **[0004]** To cope with the requirement, for example, Japanese Patent No. 2694864 provides a low thermal expansion Fe-Ni alloy as a shadow mask material, containing 34% or more Ni, 0.1% or less Mn, and less than 0.009% C, and balance of Fe and inevitable impurities, giving average thermal expansion coefficient of less than $1 \times 10^{-6}/K$ in a temperature range from around room temperature to 100°C.

25 **[0005]** However, when a sheet of the low thermal expansion Fe-Ni alloy disclosed in the Japanese Patent No. 2694864 is manufactured, there occur problems such as generation of cracks, fractures, or flaws at rolling processes such as slabbing, hot-rolling, and cold-rolling, and failing in stably attaining the target low thermal expansion coefficient. Furthermore, during manufacturing the shadow masks, problems of etching, dimensional accuracy, and the like also occur.

DISCLOSURE OF THE INVENTION

30 **[0006]** An object of the present invention is to provide a low thermal expansion alloy sheet which does not induce cracks, fractures, or flaws during manufacturing process, provides stably average thermal expansion coefficient of $1.0 \times 10^{-6}/K$ or less in a temperature range from 20°C to 100°C, and assures excellent etching property and dimensional accuracy during the manufacturing process of shadow masks.

35 **[0007]** The object is attained by a low thermal expansion alloy sheet consisting essentially of: 35.0 to 37.0% Ni, 0.01 to 0.09% Mn, 0.01 to 0.04% Si, 0.01 to 0.04% Al, by mass, and balance of Fe; the value of (Mn/S) being 20 to 300, and the amount of (Mn + Si + Al) being 0.15% or less; having average thermal expansion coefficient of $1.0 \times 10^{-6}/K$ or less in a temperature range from 20°C to 100°C.

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BRIEF DESCRIPTION OF THE DRAWINGS

45 **[0008]** Fig. 1 is a graph showing the relationship between the amount of (Mn + Si + Al) and the average thermal expansion coefficient in a temperature range from 20°C to 100°C.

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EMBODIMENTS OF THE INVENTION

50 **[0009]** The inventors of the present invention studied the low thermal expansion alloy sheet which would not induce cracks, fracture, or flaws during manufacturing process, provide stably average thermal expansion coefficient of $1.0 \times 10^{-6}/K$ or less in a temperature range of from 20°C to 100°C, and assure excellent etching property and dimensional accuracy during the manufacturing process of shadow masks. As a result, the following-described findings were obtained.

55 1) For reducing the thermal expansion coefficient, reduction in the content of Mn, Si, and Al is effective. However, excessive reduction in quantity of these strong sulfide-forming elements and oxygen-removing elements increases solute S and oxide inclusions, thus inducing generation of cracks and fractures during hot-rolling, cracks and flaws during cold-rolling, and problems of etching.

2) If the content of these elements is not controlled in a certain range, the quantity of inclusions varies, which

variations give influence on the microstructure formation, thus failing in attaining the thermal expansion coefficient of $1.0 \times 10^{-6}/K$ or less.

3) Furthermore, by controlling the amount of (Mn + Si + Al) to 0.15% or less, the thermal expansion coefficient of $1.0 \times 10^{-6}/K$ or less can be stably attained.

[0010] The present invention was carried out on the basis of above-given findings. The detail of the present invention is described below.

Ni:

[0011] Nickel is an essential element to attain low thermal expansion coefficient. To obtain $1.0 \times 10^{-6}/K$ or less of average thermal expansion coefficient in a temperature range from 20°C to 100°C, the content of Ni is specified to a range of 35.0 to 37.0%.

Mn, Si, Al:

[0012] To prevent the generation of fractures, cracks, and flaws during hot-rolling and cold-rolling, and to attain $1.0 \times 10^{-6}/K$ or less of thermal expansion coefficient, and to prevent the problem of etching and the dimensional accuracy of shadow mask, each of Mn, Si, and Al has to be added by at least 0.01%. However, excess addition of these elements may result in degradation of etching property by forming fine oxides in the surface of the sheet during the heat treatment in manufacturing process, may result in hindrance of formation of dense blackened film on the shadow mask aiming at the prevention of electron beam scattering and at the increase in heat radiation performance, and further may result in increase in the thermal expansion coefficient. Consequently, the content of Mn, Si, and Al is required to control to not higher than 0.09%, 0.04%, and 0.04%, respectively. As shown in Fig. 1, to attain $1.0 \times 10^{-6}/K$ or less of thermal expansion coefficient stably, the amount of (Mn + Si + Al) has to be controlled to not higher than 0.15%.

[0013] Manganese is a strong sulfide-forming element, and has a function to improve the hot-workability by fixing S, which induces grain boundary embrittlement during hot-working, as a sulfide, thus preventing generation of cracks and fractures during slabbing, forging, hot-rolling and the like. To attain the effect, the value of (Mn/S) has to be kept to 20 or more. If the value of (Mn/S) exceeds 300, the content of Mn becomes excessive to induce the above-described problems even when the content of Mn is not higher than 0.09%. Therefore, the value of (Mn/S) is required to 300 or less.

O:

[0014] Oxygen forms oxides to become a cause of crack generation during hot-rolling, flaw generation during cold-rolling, and problems of etching. Also oxygen hinders the grain growth during heat treatment to give an influence on the microstructure formation, which may result in failing in stably assuring the low thermal expansion coefficient. Accordingly, the content of O is preferably controlled to 0.005% or less.

S:

[0015] Sulfur induces grain boundary embrittlement during hot-working, thus causing generation of cracks and fractures during slabbing, forging, and hot-rolling. Furthermore, if S which could not be fixed by Mn or the like increased, the hot-workability and the etching property significantly degrade at portions having strong segregation. Consequently, the content of S is preferably controlled to 0.002% or less.

[0016] The low thermal expansion alloy sheet according to the present invention can be manufactured by ordinary process of smelting, refining, casting, hot-rolling, cold-rolling, and annealing. For example, an alloy having the above-given composition is prepared by smelting, which is then processed by continuous casting method or ingot-making method to prepare a slab having thickness of 100 to 400 mm. In this case, it is preferable that the cast ingot or the slab is subjected to a sufficient homogenization heat treatment at 1050°C or higher, or to a casting treatment to reduce the segregation. Then, the cast ingot or the slab is hot-rolled at 800°C or higher to prepare a sheet having thickness of 2 to 4 mm, followed by one or more cycles of cold-rolling and annealing to obtain a final product.

Example

[0017] The Fe-Ni alloys Nos. 1-21 having the compositions given in Table 1 were prepared by smelting, which were then subjected to slabbing and hot-rolling to form hot-rolled sheets. After pickled, the hot-rolled sheets were subjected to cold-rolling, annealing, and, if necessary, tension leveler treatment and stress relief annealing, to obtain sheets having thickness of 0.1 mm and of 0.2 mm. In the estimation of the manufacturability, ○ denotes the case when the

sheet was manufactured without problem, and × denotes the case when the sheet was manufactured with generating fractures and flaws. After applying heat treatment to thus obtained sheets at 850°C for 15 minutes, an optical interferometer was applied to determine the average thermal expansion coefficient in a temperature range from 20°C to 100°C. For every alloy, the measurement was done for ten samples thereof to determine the maximum value. × denotes the alloy which gave the difference between the maximum value and the minimum value exceeding $0.5 \times 10^{-6}/K$ and was judged to be not stable enough for manufacturing. The resist film having many circular holes with the hole opening of 90 μm was prepared on the surface of each of the sheet sample. A ferric chloride solution having the concentration of 40% or more and the temperature of 40°C or higher was sprayed onto the surface of the resist film with the spraying pressure of 30 to 50 MPa to etch the sheet to form holes having the diameter of 100 to 200 μm. For 100 holes of each sheet sample, the presence/absence of abnormal hole shape and the dimensional accuracy to the average diameter, namely the dispersion of hole diameter, were investigated. ○ denotes the alloy sheets which gave high roundness and dimensional accuracy of within ±3%, and × denotes the alloy sheets which gave poor roundness and dimensional accuracy of more than ±3%.

[0018] The result is given in Table 2.

[0019] The alloys Nos. 1-10 of the Examples according to the present invention showed excellent manufacturability without generating crack and fracture during hot-rolling and cold-rolling. Furthermore, these alloys showed excellent etching property and extremely low thermal expansion coefficient.

[0020] On the contrary, the alloys Nos. 11-21 of the Comparative Examples showed poor results in at least one characteristic among those tested here. That is, the alloy No. 11 failed to attain low thermal expansion coefficient because the amount of (Mn + Si + Al) was outside the range of the present invention. The alloy No. 12 failed to attain low thermal expansion coefficient because the content of Mn and Si, the amount of (Mn + Si + Al), and the value of (Mn/S) were outside the range of the present invention. The alloy No. 13 generated cracks and fractures during hot-rolling, thus giving poor manufacturability, because the content of Mn and the value of (Mn/S) were outside the range of the present invention. The alloy No. 14 failed to attain low thermal expansion coefficient because the content of Mn and the amount of (Mn + Si + Al) were outside the range of the present invention. The alloy No. 15 failed to attain low thermal expansion coefficient because the content of Si and the amount of (Mn + Si + Al) were outside the range of the present invention. The alloy No. 16 generated cracks and fractures during hot-rolling, thus giving poor manufacturability, because the content of Si and Al was outside the range of the present invention. The alloy No. 17 generated flaws during cold-rolling to give poor manufacturability, because the content of Si and Al was outside the range of the present invention. The alloy No. 18 generated flaws during cold-rolling to give poor manufacturability, because the content of Al was outside the range of the present invention. The alloys Nos. 17 and 18 also gave large dispersion in thermal expansion coefficient and in the size of the etched holes. The alloy No. 19 failed to attain low thermal expansion coefficient and also failed to give good etching property, because the content of Al was outside the range of the present invention. The alloy No. 20 failed to attain low thermal expansion coefficient because the content of Ni was outside the range of the present invention. The alloy No. 21 failed to attain low thermal expansion coefficient because the content of Ni and Si was outside the range of the present invention.

Table 1

Alloy No.	Compositions (mass%)						Mn/S	Mn+Si+Al (mass%)	Remark
	Ni	Mn	Si	Al	O	S			
1	36.3	0.028	0.020	0.020	0.0030	0.0007	40	0.07	Example
2	36.1	0.080	0.026	0.019	0.0012	0.0016	50	0.13	Example
3	35.9	0.012	0.014	0.017	0.0034	0.0002	60	0.04	Example
4	36.1	0.025	0.010	0.028	0.0009	0.0007	36	0.06	Example
5	36.0	0.018	0.040	0.020	0.0019	0.0007	26	0.08	Example
6	36.0	0.044	0.010	0.011	0.0046	0.0020	22	0.07	Example
7	36.1	0.049	0.020	0.020	0.0015	0.0002	245	0.09	Example
8	36.5	0.015	0.013	0.010	0.0017	0.0003	50	0.04	Example
9	36.0	0.030	0.040	0.012	0.0030	0.0007	43	0.08	Example
10	36.2	0.040	0.020	0.020	0.0010	0.0007	57	0.08	Example

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Table 1 (continued)

Alloy No.	Compositions (mass%)						Mn/S	Mn+Si+Al (mass%)	Remark
	Ni	Mn	Si	Al	O	S			
11	36.1	0.090	0.040	0.039	0.0022	0.0009	100	0.17	Comparative example
12	35.8	0.380	0.050	0.010	0.0030	0.0012	317	0.44	Comparative example
13	36.0	0.004	0.010	0.013	0.0050	0.0014	3	0.03	Comparative example
14	35.7	0.240	0.035	0.015	0.0020	0.0015	160	0.29	Comparative example
15	35.8	0.090	0.084	0.014	0.0010	0.0009	100	0.19	Comparative example
16	36.1	0.054	0.009	0.009	0.0049	0.0027	20	0.07	Comparative example
17	35.6	0.051	0.004	0.009	0.0074	0.0010	51	0.06	Comparative example
18	36.0	0.042	0.031	0.004	0.0069	0.0009	47	0.08	Comparative example
19	36.4	0.039	0.035	0.080	0.0007	0.0009	43	0.15	Comparative example
20	37.5	0.019	0.010	0.010	0.0030	0.0006	32	0.04	Comparative example
21	34.3	0.050	0.044	0.008	0.0019	0.0007	71	0.10	Comparative example

Table 2

Alloy No.	Manufacturability	Average thermal expansion coefficient (20°C to 100°C) ($\times 10^{-6}$ / K)	Etching property	Remark
1	○	0.74	○	Example
2	○	0.87	○	Example
3	○	0.72	○	Example
4	○	0.70	○	Example
5	○	0.84	○	Example
6	○	0.80	○	Example
7	○	0.93	○	Example
8	○	0.75	○	Example
9	○	0.82	○	Example
10	○	0.85	○	Example
11	○	1.07	○	Comparative example
12	○	1.25	○	Comparative example

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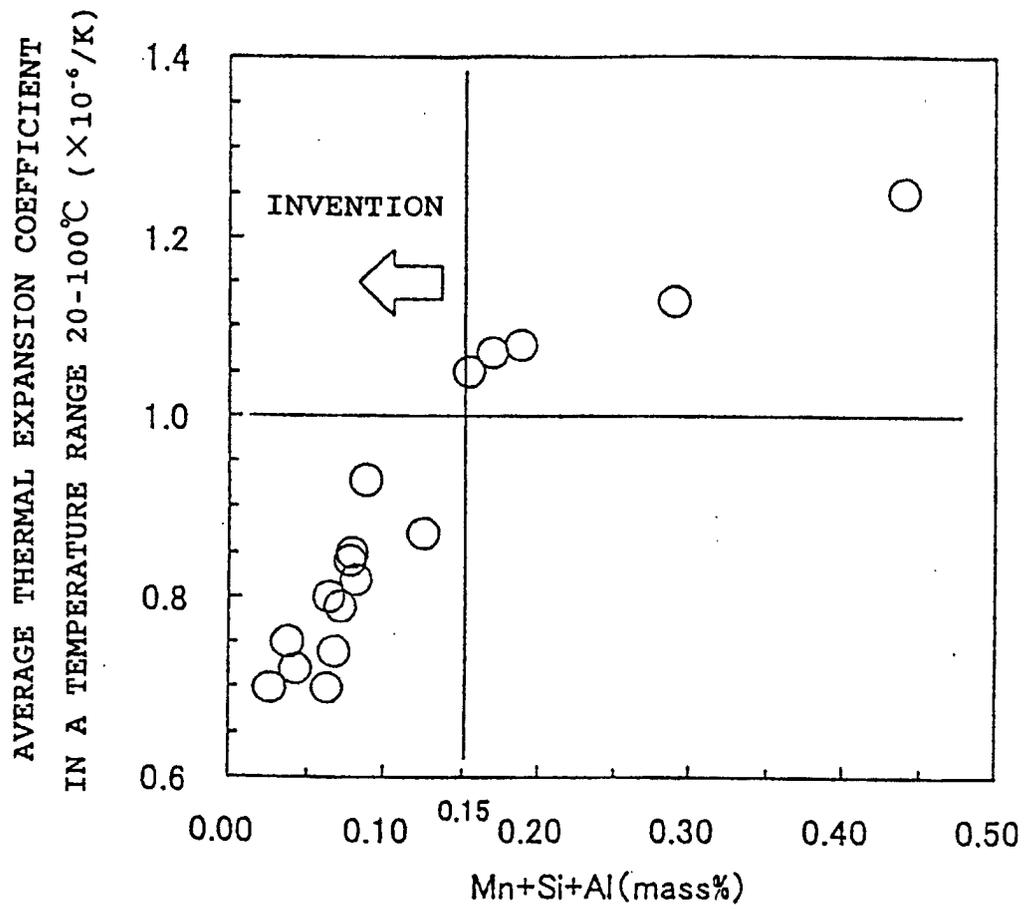
Table 2 (continued)

Alloy No.	Manufacturability	Average thermal expansion coefficient (20°C to 100°C) (x10 ⁻⁶ / K)	Etching property	Remark
13	X (Cracks and fracture were generated during hot-rolling)	0.70	○	Comparative example
14	○	1.13	○	Comparative example
15	○	1.08	○	Comparative example
16	X (Cracks and fracture were generated during hot-rolling)	0.79	○	Comparative example
17	X (Flaws were generated during hot-rolling)	×	×	Comparative example
18	X (Flaws were generated during hot-rolling)	×	×	Comparative example
19	○	1.05	×	Comparative example
20	○	1.72	○	Comparative example
21	○	1.61	○	Comparative example

Claims

1. A low thermal expansion alloy sheet consisting essentially of: 35.0 to 37.0% Ni, 0.01 to 0.09% Mn, 0.01 to 0.04% Si, 0.01 to 0.04% Al, by mass, and balance of Fe; the value of (Mn/S) being 20 to 300, and the amount of (Mn + Si + Al) being 0.15% or less; having average thermal expansion coefficient of $1.0 \times 10^{-6}/K$ or less in a temperature range from 20°C to 100°C.
2. The low thermal expansion alloy sheet as in claim 1 further containing 0.005% or less O, by mass.
3. The low thermal expansion alloy sheet as in claim 1 further containing 0.002% or less S, by mass.
4. The low thermal expansion alloy sheet as in claim 2 further containing 0.002% or less S, by mass.
5. A shadow mask manufactured of the low thermal expansion alloy sheet of any one of claims 1-4.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/06785

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C38/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C22C38/00-38/08		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 4402684 A1 (Krupp VDM GmbH), 01 December, 1994 (01.12.94), & JP 7-3401 A	1-5
A	JP 9-176797 A (Nippon Mining & Metals Co., Ltd.), 08 July, 1997 (08.07.97), (Family: none)	1-5
P,A	JP 2001-192775 A (Nisshin Steel Co., Ltd.), 17 July, 2001 (17.07.01), (Family: none)	1-5
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		<input type="checkbox"/> See patent family annex.
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Date of the actual completion of the international search 02 October, 2002 (02.10.02)		Date of mailing of the international search report 15 October, 2002 (15.10.02)
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