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(54) **Fe-Ni BASED ALLOY FOR SHADOW MASK HAVING EXCELLENT CORROSION RESISTANCE
AND SHADOW MASK MATERIAL**

(57) There is provided a Fe-Ni based alloy for shadow mask having high corrosion resistance, high rigidity and low thermal expansion and hardly generating rust even if being exposed in air in the course of circulation and transportation after the bright annealing as a middle step of the starting material production and a shadow mask material. A Fe-Ni based alloy for a shadow mask having an excellent corrosion resistance comprises

C≤0.01 wt%, Si: 0.01-0.1 wt%, Mn: 0.01-0.1 wt%, Ni: 35-37 wt%, Cr≤0.1 wt%, Nb: 0.01-1.0 wt%, S≤0.0020 wt%, Al≤0.005 wt% and the balance being Fe and inevitable impurity, and a shadow mask material is comprised of the alloy having a proof strength at 0.2% of not less than 300 N/mm² and a thermal expansion coefficient of not more than 1.0×10⁻⁶/°C.

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Description

TECHNICAL FIELD

[0001] This invention relates to a Fe-Ni based alloy for a shadow mask having an excellent corrosion resistance, which is used in a cathode tube for a color television or the like, and a shadow mask material, and more particularly to a Fe-Ni based alloy having an excellent corrosion resistance, a high stiffness and a low thermal expansion, which is less in the generation of rust even when being exposed to an atmosphere after the bright annealing at a production step of a starting material, and a shadow mask material using this alloy.

BACKGROUND ART

[0002] Heretofore, a low carbon aluminum killed steel sheet is used as a shadow mask material. This steel sheet is produced, for example, by subjecting a steel sheet after a middle cold rolling to a stress relief middle annealing in a continuous annealing furnace or a batch annealing furnace and then to a finish cold rolling and a temper rolling (including dull rolling).

[0003] In general, a material for a cathode tube or display of a high-quality color television, for example, a shadow mask for the cathode tube of the color television is sometimes heated to a temperature reaching to about 80°C because not more than 1/3 of electron beams pass through openings of the shadow mask and the remaining electron beams collide with the shadow mask. As a result, the shadow mask material is strained by thermal expansion and brings about the deterioration of color purity. For this end, as a material of the shadow mask material, it is advantageous to use a raw material having a small thermal expansion coefficient. In this connection, Fe-36 Ni based invar alloy being less in the influence of thermal expansion is recently used instead of the above aluminum killed steel sheet.

[0004] Among the Fe-Ni based alloy plates are used a low thermal expansion Fe-36 Ni based alloy plate reducing Mn as an alloying element (JP-A-5-186853), an alloy plate having a high strength by adding of Nb (Patent No. 3150831) and the like with the recent flattening and large-sizing of display face.

[0005] However, the low thermal expansion Fe-36 Ni based alloy having a reduced Mn and the high-strength Fe-36 Ni based alloy added with Nb are not exposed to corrosion environment in the cathode tube because the atmosphere is vacuum, but are exposed in air for a long time in the course of circulation and transportation after the bright annealing as a middle step in the production of the raw material, so that there is caused a case that rust is generated not to provide a product and there is left a problem in the rust prevention.

[0006] It is an object of the invention to provide a Fe-Ni based alloy for a high-rigidity, low-thermal expansion shadow mask material being less in the occurrence of rust even when it is exposed to an air over a long time for circulation and transportation after the bright annealing as a middle step in the production of the starting material as well as a shadow mask material.

DISCLOSURE OF THE INVENTION

[0007] As to the above object, the inventors have made various studies with respect to conditions of Fe-Ni based alloys hardly generating rust even when it is exposed to air after the bright annealing as a middle step in the production of the starting material and obtained the following knowledge. It has been found that the rust generated in the starting material (Fe-Ni based alloy) is apt to be easily caused after the bright annealing and also the rust is apt to be generated in low thermal expansion Fe-36 Ni alloy having a reduced Mn rather than the usual Fe-36 Ni alloy. As a result of further examination on this knowledge, it is discovered that in the low-Mn, Fe-Ni based alloy, the S concentration in the alloy ranging from its surface to a depth of 150 Å (surface layer portion) is considerably higher than that of a bulk portion (interior portion). As is generally known, as S is enriched in such a surface layer portion, S promotes the dissolution of a metal ion and induces the rust. Moreover, such a phenomenon may be solved when the surface layer portion of the alloy plate is removed mechanically and chemically, but it is difficult to conduct this treatment in a commercial scale.

[0008] The inventors attempt to control the enrichment of S in the surface layer of the alloy plate. As a result of the inventors' studies, it has been found that the enrichment of S in the surface layer portion of the Fe-36 Ni alloy plate is zero in the Fe-Ni based alloy having a high Mn content but is conspicuous in the low thermal expansion type Fe-36 Ni alloy having a low Mn content, and that S is entrapped into Mn based inclusion of the Fe-Ni based alloy having the high Mn content, but the enriched amount of S decreases in inverse proportion to the Mn content in the low thermal expansion type Fe-36 Ni alloy having the low Mn content. That is, it has been confirmed that a great amount of S not entrapped into the Mn based inclusion is existent in the low thermal expansion Fe-36 Ni alloy having the low Mn content and such an S is enriched by diffusing near to the surface layer in the bright annealing.

[0009] On the other hand, the inventors have found that in order to prevent the occurrence of such a rust, it is required to control a ratio of Mn as an element producing the Mn inclusion to S, and made further studies. As a result, it has

been found that the rust hardly occurs when a relation between Mn and S satisfies $Mn/S \geq 25$. Also, it has been found that the rust is not particularly generated when the S concentration in a zone ranging from the surface of the alloy to 150 Å (surface layer portion) is not more than 20 times of that in the bulk portion (interior portion).

[0010] Furthermore, it has been found that the corrosion resistance of Fe-Ni alloy is largely dependent upon the crystal grain size. That is, it has been confirmed that the corrosion resistance after the bright annealing largely depends on the crystal grain size of the starting material and particularly the corrosion resistance of the material is improved as the crystal grain size becomes small (crystal grain number (ASTM) becomes large). This is considered due to the fact that as the crystal grain size becomes small, the area of the crystal grain boundary increases and the diffusion distance of S becomes long.

[0011] Moreover, it has been found that in order to suppress the occurrence of the rust, it is effective to control the non-metallic inclusion in addition to the above countermeasure. As acid-soluble MgO single inclusion or CaO single inclusion is produced, the corrosion resistance in the bedewing in air is deteriorated, and further in case of Nb-containing Fe-36 Ni alloy, the corrosion resistance is confirmed to be deteriorated when MgO single inclusion or CaO single inclusion is included in MnO-FeO-SiO₂-Nb₂O₅-MgO-Al₂O₃-CaO base composite oxide produced by controlling the formation of alumina based inclusion.

[0012] On the other hand, when an alloy plate has an inclusion composition not including the MgO single inclusion or CaO single inclusion, there is no problem in the corrosion resistance, so that it has been found that the non-metallic inclusion is effective to include one or more selected from silica (SiO₂), spinel (MgO · Al₂O₃) and niobium oxide (Nb₂O₅) in addition to MnO-FeO-SiO₂-Nb₂O₅-MgO-Al₂O₃-CaO base composite oxide.

[0013] The invention is based on the above knowledge and the gist and construction thereof are as follows.

[0014] That is, the invention is a Fe-Ni based alloy for a shadow mask having an excellent corrosion resistance comprising C ≤ 0.01 wt%, Si: 0.01-0.1 wt%, Mn: 0.01-0.1 wt%, Ni: 35-37 wt%, Cr ≤ 0.1 wt%, Nb: 0.01-1.0 wt%, S ≤ 0.0020 wt%, Al ≤ 0.005 wt% and the balance being Fe and inevitable impurity.

[0015] Moreover, the alloy of the invention is preferable to contain 0.005-1.0% in total of one or more selected from Ti, V, Zr, Ta, Hf and REM in addition to the above component composition.

[0016] Also, the alloy of the invention is preferable to be an alloy wherein a relation of Mn and S satisfies $Mn/S \geq 25$.

[0017] Furthermore, it is preferable that a maximum value of S concentration in a region ranging from a surface of the alloy to 150 Å is not more than 20 times of a bulk.

[0018] In the alloy of the invention, it is also preferable that a crystal grain size is not less than No. 9 of ASTM grain size number.

[0019] Further, the alloy of the invention is preferable to contain one or more selected from silica (SiO₂), spinel (MgO · Al₂O₃) and niobium oxide (Nb₂O₅) in addition to MnO-FeO-SiO₂-Nb₂O₅-MgO-Al₂O₃-CaO base composite oxide.

[0020] Also, the invention proposes a shadow mask material having a high corrosion resistance, a high rigidity and a low thermal expansion comprised of the above Ni-Fe based alloy and having a proof strength at 0.2% of not less than 300 N/mm² and a thermal expansion coefficient of not more than $1.0 \times 10^{-6}/^{\circ}\text{C}$.

BEST MODE FOR CARRYING OUT THE INVENTION

[0021] The reason why the composition of the Fe-Ni based alloy according to the invention is limited to the above range will be described below.

C ≤ 0.01 wt%

[0022] C is an element contributing to strengthen the material through solid solution and work hardening action. When the content thereof exceeds 0.01 wt%, a great amount of carbide is precipitated to deteriorate the etching property, press formability, graphitizing property and low thermal expansion property. Therefore, the C content is limited to not more than 0.01 wt%. Preferably, it is not more than 0.005 wt%.

Si: 0.01-0.1 wt%

[0023] Although it is required to add not less than 0.01 wt% of Si as a deoxidizing material in the refining of the alloy, if the addition amount thereof exceeds 0.1 wt%, the thermal expansion is increased, so that the amount is limited to a range of 0.01-0.1 wt%. Preferably, it is 0.02-0.05 wt%.

Mn: 0.01-0.1 wt%

[0024] Mn is useful as a solid-soluting element and further is required to add in an amount of not less than 0.01 wt% as a deoxidizing material in the refining of the alloy. However, when the addition amount exceeds 0.1 wt%, the thermal

expansion is increased, so that the amount is limited to a range of 0.01-0.1 wt%. Preferably, it is 0.01-0.05 wt%.

[0025] Also, Mn is added to produce Mn inclusion, which fixes S diffused in the bright annealing, so that a constant amount of Mn inclusion is required. Therefore, it is necessary that the relation of Mn and S is controlled to satisfy $Mn/S \geq 25$ in view of the corrosion resistance.

Ni: 35-37 wt%

[0026] Ni is an element largely exerting upon the thermal expansion property of the Fe-Ni alloy. When the Ni content is 36 wt%, the thermal expansion is minimum, so that Ni is limited to 35-37 wt%.

Cr $\leq$ 0.1 wt%

[0027] Cr is an element considerably improving the corrosion resistance. When the content exceeds 0.1 wt%, the thermal expansion coefficient becomes high and also the graphitizing property is deteriorated, so that it is limited to not more than 0.1 wt%.

Nb: 0.01-1.0 wt%

[0028] Nb increases the proof strength at 0.2% when being added to the alloy. Also, it has an effect that the crystal grain size is remarkably fined to increase the area of the crystal boundary and to prolong the diffusion distance of S to control the enrichment of S on the surface. Also, not only the toughness, etching property and press formability but also the graphitizing property are improved.

[0029] In order to obtain the above effect, and particularly provide the corrosion resistance and the proof strength at 0.2%, therefore, Nb is required to be added in an amount of at least 0.01 wt%. Preferably, it is added in an amount of not less than 0.10 wt%. However, when the amount exceeds 1.0 wt%, the toughness, press formability and low thermal expansion property rather lower, so that it is limited to 0.01-1.0 wt%.

S $\leq$ 0.0020 wt%

[0030] S is an element characterizing the alloy according to the invention and is an element largely affecting the corrosion resistance. When the content of S exceeds 0.0020 wt%, S diffuses near to the neighborhood of the surface of the raw material after the bright annealing and hence the S concentration in a region from the surface of the raw material to a depth of 150Å (surface layer portion) considerably rises to a bulk to thereby deteriorate the corrosion resistance. For this end, the S content is limited to not more than 0.0020 wt%, and is preferably not more than 0.0010 wt%.

[0031] However, it is required to satisfy $Mn/S \geq 25$ in view of the relation of Mn and S.

Al $\leq$ 0.005 wt%

[0032] Al is a relatively active element, so that if it is included in a great amount, oxidation is preferentially caused on the surface of the steel sheet to obstruct the graphitizing property. Further, Al based oxide is increased to obstruct the etching property. Particularly, when it exceeds 0.005 wt%, the low thermal expansion property lowers, so that it is limited to 0.005 wt%.

Ti, V, Zr, Ta, Hf and REM

[0033] Ti, V, Zr, Ta, Hf and REM are elements contributing to finely divide crystal grains by bonding to C and N to form carbide and nitride and contribute to corrosion resistance by bonding to S to form sulfide. When one or more selected from Ti, V, Zr, Ta, Hf and REM is less than 0.005 wt% alone or in total, the above effect is insufficient. While when it exceeds 1.0 wt%, the solid soluted amount of the element becomes too large and the low thermal expansion property lowers, so that the amount is limited to 0.005-1.0 wt%.

Mn/S $\geq$ 25

[0034] In the Fe-Ni alloy according to the invention, Mn and S are required to adjust so as to satisfy a relation of the following equation:

Mn/S $\geq$ 25.

[0035] That is, it is important that S content badly affecting the corrosion resistance is controlled with Mn by adjusting the Mn content in accordance with the S content. when the ratio Mn/S is less than 25, the S content including in Mn based inclusion is less and hence S diffuses near to the surface layer and is enriched in the bright annealing and rust is apt to be caused. A preferable upper limit is about 70.

[0036] In the Fe-Ni alloy according to the invention, the S concentration in a region ranging from the surface of the alloy sheet to 150Å is made to not more than about 20 times. Because, if the degree of S enriched in the surface layer exceeds 20 times the S concentration of a bulk (base), the dissolution of the metal ion is promoted and the rust is induced. Moreover, the S concentration is preferably not more than 18 times.

Crystal grain size

[0037] In the invention, it is effective to make the crystal grain size to not less than No. 9 as an ASTM grain size number in addition to the above composition planning. According to the inventors' studies, it has been confirmed that the corrosion resistance after the bright annealing largely depends upon the crystal grain size of the starting material, and particularly the corrosion resistance of the material is improved as the crystal grain size becomes small (the grain size number becomes large). Also, since the proof strength at 0.2% largely depends upon the crystal grain size, it is desirable that the crystal grain size is not less than ASTM No. 9 in order to obtain excellent corrosion resistance and rigidity.

Non-metallic inclusion

[0038] In addition to the above composition planning and the crystal grain size adjustment, the control of the non-metallic inclusion is further conducted in the invention. That is, the non-metallic inclusion included in the alloy of the invention is required to be a non-metallic inclusion further containing one or more selected from SiO₂, MgO · Al₂O₃ and Nb₂O₅ in addition to MnO-FeO-SiO₂-Nb₂O₅-MgO-Al₂O₃-CaO base composite oxide. According to the inventors' studies, it has been confirmed that if acid-soluble MgO single inclusion or CaO single inclusion is produced, the corrosion resistance in the dewing in air is deteriorated. Further, it has been confirmed that in Nb-containing Fe-36 Ni alloy, when MgO single inclusion or CaO single inclusion is contained in the MnO-FeO-SiO₂-Nb₂O₅-MgO-Al₂O₃-CaO base composite oxide produced in the control of the alumina inclusion formation, the corrosion resistance is also deteriorated. On the other hand, the inclusion composition containing no MgO single inclusion and CaO single inclusion does not cause problems in the corrosion resistance, so that the inclusion is rendered into the above composition.

EXAMPLE

[0039] The action and effect of the alloys according to the invention will be concretely described with reference to the examples, but the invention is not limited to only the examples mentioned below.

[0040] A material to be tested is produced by adjusting the components of the alloy so as to have a component composition shown in the following Table 1, and the test material is melted in an air induction furnace to prepare an ingot. Then, the ingot is subjected to a hot forging work at a temperature of 1000-1150°C, hot rolled at a rolling reduction of not less than 80% and then subjected to a solid-soluting heat treatment at 900°C for 60 seconds in an atmosphere of 30% H₂ + N₂ having a dew point of -40°C. Thereafter, it is gradually cooled to obtain a Fe-Ni alloy having a thickness of 0.12 mm.

[0041] The thermal expansion coefficient shown in the table is measured in a range of from room temperature to 300°C and is determined by an average thermal expansion coefficient at 30-100°C, and the proof strength at 0.2% is measured by a tension test. Also, a maximum value of S enriched amount in a region ranging from the surface of the sheet to 150 Å is carried out by sputtering at an interval of 50 Å through an OJ electron spectroscopic apparatus and conducting an elementary analysis every time to calculating an atomic concentration of S to show a ratio to bulk (the bulk in this examples is a value chemically reviewing of the starting material as a whole). The corrosion resistance is evaluated by a rust generating area ratio at a corrosion state after the exposure in an outdoor air exposure test. Moreover, when the rust generating area ratio is not less than 0.5%, rust is generated by exposing to air for a long period of time after the bright annealing as a middle step of the starting material production, and hence such a starting material is unsuitable. These results are shown in Table 2.

[0042] As seen from Table 2, it can be said that the alloys adaptable in the invention have sufficient properties such as corrosion resistance, rigidity and low thermal expansion property. That is, the test materials according to the invention have a high rigidity as the proof strength at 0.2% is not less than 300 N/mm², and are low thermal expansion as the

thermal expansion coefficient is not more than $1.0 \times 10^{-6}/^{\circ}\text{C}$. Also, they have an excellent corrosion resistance as the rust generating area ratio after the exposure test in air is not more than 0.5%. On the contrary, the comparative materials 19, 20 are poor in the corrosion resistance because the S amount in the bulk is large. Also, the comparative materials 21, 22 are poor in the corrosion resistance because the form of the inclusion contains MgO single body or CaO single body. The comparative material 23 is poor in the corrosion resistance and rigidity because the crystal grain size is large. The comparative material 24 is poor in the corrosion resistance because the maximum value of the S enriched amount in the region from the sheet surface to 150 Å is not less than 20. Moreover, the Fe-Ni based alloy according to the invention can be produced as a material for shadow mask without generating the rust after the bright annealing. Particularly, the starting material for shadow mask having a high rigidity and a low thermal expansion can be produced, in which the proof strength at 0.2% is not less than 300 N/mm² and the thermal expansion coefficient is not more than $1.0 \times 10^{-6}/^{\circ}\text{C}$ as a quality of the material before the formation of the mask.

[Table 1]

Alloy Number	Chemical components											Form of inclusion	
	C	Si	Mn	Ni	Cr	Nb	S	Al	others	Mn/S			
Invention alloys	1	0.003	0.03	0.01	35.89	0.01	0.17	0.0003	0.002	—	33	1	
	2	0.004	0.04	0.03	35.96	0.02	0.18	0.0008	0.001	—	38	1	
	3	0.003	0.03	0.05	36.01	0.01	0.22	0.0010	0.003	—	50	1	
	4	0.003	0.04	0.03	35.97	0.05	0.21	0.0012	0.002	—	25	1	
	5	0.003	0.08	0.08	35.89	0.03	0.20	0.0012	0.004		67	1	
	6	0.004	0.05	0.05	35.97	0.04	0.02	0.0015	0.003		33	1	
	7	0.005	0.02	0.03	35.95	0.05	0.50	0.0010	0.001		30	1	
	8	0.003	0.03	0.04	36.02	0.01	0.95	0.0013	0.004		31	1	
	9	0.004	0.03	0.03	36.03	0.01	0.19	0.0012	0.003	Ti 0.05	25	1	
	10	0.003	0.05	0.05	36.20	0.05	0.15	0.0018	0.002	V 0.07	28	1	
	11	0.002	0.06	0.02	36.15	0.04	0.18	0.0008	0.003	Ti 0.03 V 0.01	25	1	
	12	0.003	0.02	0.03	36.25	0.03	0.16	0.0011	0.004	Ta 0.05	27	1	
	13	0.003	0.03	0.04	36.33	0.02	0.21	0.0015	0.001	Zr 0.08	27	1	
	14	0.004	0.03	0.05	35.98	0.05	0.18	0.0010	0.003	Ta 0.03 Zr 0.07	50	1	
	15	0.005	0.03	0.02	36.62	0.06	0.20	0.0008	0.002	Hf 0.05	25	1	
	16	0.003	0.04	0.03	35.99	0.01	0.21	0.0012	0.003	REM 0.05	25	1	
	17	0.003	0.04	0.03	35.95	0.08	0.19	0.0012	0.002	—	25	2	
	18	0.004	0.03	0.03	36.26	0.03	0.21	0.0011	0.002	—	27	3	
	19	0.004	0.02	0.02	36.00	0.02	0.10	0.0022	0.004	—	9	1	
Comparative alloys	20	0.004	0.03	0.03	36.07	0.04	0.21	0.0030	0.003	—	10	1	
	21	0.004	0.05	0.04	35.85	0.05	0.18	0.0016	0.002	—	25	4	
	22	0.003	0.08	0.06	36.05	0.01	0.20	0.0020	0.002	—	30	5	
	23	0.003	0.03	0.05	35.97	0.04	0.02	0.0015	0.003	—	33	1	
	24	0.003	0.02	0.05	35.96	0.01	0.22	0.0020	0.002	—	25	1	

Form of inclusion 1: MnO-FeO-SiO₂-Nb₂O₅-MgO-Al₂O₃-CaO composite systemForm of inclusion 2: MgO-Al₂O₃-Nb₂O₅ systemForm of inclusion 3: SiO₂-Nb₂O₅ systemForm of inclusion 4: SiO₂-MgO system + MgO single bodyForm of inclusion 5: Al₂O₃-CaO system + CaO single body

[Table 2]

Alloy Number	Proof strength at 0.2% (N/mm ²)	Thermal expansion coefficient ($\times 10^{-6}/^{\circ}\text{C}$)	Crystal grain size No.	S amount of bulk (A)	Maximum value of S concentration in a region from surface layer to 150 μm (B)	Relative ratio (B/A)	Rust generating area ratio after air exposing test (%)
Invention alloys	1 315	0.81	11	0.0003	0.0050	16.8	0.26
	2 316	0.84	10	0.0008	0.0013	16.1	0.24
	3 320	0.88	11	0.0010	0.0152	15.2	0.25
	4 318	0.89	10	0.0012	0.0218	18.2	0.30
	5 319	0.88	11	0.0012	0.0160	13.3	0.24
	6 305	0.83	9	0.0015	0.0260	17.3	0.26
	7 340	0.92	10	0.0010	0.0170	17.0	0.27
	8 351	0.95	10	0.0013	0.0224	17.2	0.29
	9 321	0.88	11	0.0012	0.0223	18.6	0.31
	10 318	0.85	10	0.0018	0.0311	17.3	0.32
	11 316	0.87	11	0.0008	0.0146	18.3	0.31
	12 322	0.85	11	0.0011	0.0193	17.5	0.30
	13 319	0.89	11	0.0015	0.0252	16.8	0.30
	14 317	0.87	11	0.0010	0.0153	15.3	0.27
	15 335	0.93	11	0.0008	0.0145	18.1	0.30
	16 309	0.86	11	0.0012	0.0226	18.8	0.32
	17 312	0.88	11	0.0012	0.0223	18.6	0.33
	18 319	0.89	11	0.0011	0.0187	17.0	0.30
Comparative alloys	19 319	0.85	10	0.0022	0.1118	50.8	0.97
	20 315	0.88	11	0.0030	0.1458	48.6	0.92
	21 316	0.83	10	0.0025	0.0770	30.8	0.60
	22 319	0.85	11	0.0035	0.0990	25.7	0.52
	23 290	0.80	7	0.0015	0.0260	17.3	0.51
	24 320	0.88	11	0.0020	0.0430	21.5	0.50

INDUSTRIAL APPLICABILITY

[0043] As mentioned above, according to the invention, there can be provided Fe-Ni based alloys for shadow mask having high corrosion resistance, high rigidity and low thermal expansion and hardly generating rust even if being exposed in air in the course of circulation and transportation after the bright annealing as a middle step of the starting material production. Therefore, the shadow mask material in a cathode tube for a color television or display can be surely produced in a high yield.

Claims

1. A Fe-Ni based alloy for a shadow mask having an excellent corrosion resistance comprising C $\leq$ 0.01 wt%, Si: 0.01-0.1 wt%, Mn: 0.01-0.1 wt%, Ni: 35-37 wt%, Cr $\leq$ 0.1 wt%, Nb: 0.01-1.0 wt%, S $\leq$ 0.0020 wt%, Al $\leq$ 0.005 wt% and the balance being Fe and inevitable impurity.
2. A Fe-Ni based alloy for a shadow mask according to claim 1, wherein a relation of Mn and S is rendered into Mn/S $\geq$ 25.
3. A Fe-Ni based alloy for a shadow mask according to claim 1 or 2, wherein the alloy contains 0.005-1.0% in total of one or more selected from Ti, V, Zr, Ta, Hf and REM in addition to the above component composition.
4. A Fe-Ni based alloy for a shadow mask according to any one of claims 1 to 3, wherein a maximum value of S concentration in a region ranging from a surface of the alloy to 150Å is not more than 20 times of a bulk.
5. A Fe-Ni based alloy for a shadow mask according to any one of claims 1 to 4, wherein a crystal grain size is not less than No. 9 of ASTM grain size number.
6. A Fe-Ni based alloy for a shadow mask having an excellent corrosion resistance according to any one of claims 1 to 5 wherein the alloy contains a non-metallic inclusion comprising one or more selected from silica (SiO₂), spinel (MgO · Al₂O₃) and niobium oxide (Nb₂O₅) in addition to MnO-FeO-SiO₂-Nb₂O₅-MgO-Al₂O₃-CaO base composite oxide.
7. A shadow mask material having a high corrosion resistance, a high rigidity and a low thermal expansion comprised of a Ni-Fe based alloy as claimed in any one of claims 1 to 6 and having a proof strength at 0.2% of not less than 300 N/mm² and a thermal expansion coefficient of not more than 1.0 $\times$ 10⁻⁶/°C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/10718

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C38/00, 38/48, 38/50, H01J29/07		
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 C22C38/00-60, H01J29/07		
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 1994-2003 Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2001-181796 A (Hitachi Metals, Ltd.), 03 July, 2001 (03.07.01), (Family: none)	1-3, 5-7 4
Y A	JP 7-102345 A (Nippon Yakin Kogyo Co., Ltd.), 18 April, 1995 (18.04.95), Table 3 (Family: none)	1-3, 5-7 4
Y	JP 2001-40454 A (Nippon Yakin Kogyo Co., Ltd.), 13 February, 2001 (13.02.01), Table 4 (Family: none)	5
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 20 January, 2003 (20.01.03)		Date of mailing of the international search report 04 February, 2003 (04.02.03)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5916380 A (Nippon Mining & Metals Co., Ltd.), 29 June, 1999 (29.06.99), & JP 9-87808 A & KR 202318 B1 & TW 346507 A	6
Y	JP 5-186853 A (Nippon Yakin Kogyo Co., Ltd.), 27 July, 1993 (27.07.93), Table 1 (Family: none)	7

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