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(54) **Iron-nickel alloy sheet for shadow mask.**

(57) An alloy sheet for making a shadow mask consists essentially of 34 to 38wt.% Ni, 0.07wt.% or less Si, 0.001wt.% or less B, 0.003wt.% or less O, 0.002wt.% or less N, and the balance being Fe and inevitable impurities.

The alloy sheet has an average austenite grain size (Dav) of 10.5 to 15.0μm, a ratio of a maximum size to the minimum size of austenite grains (Dmax/Dmin) of 1 to 15, a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of

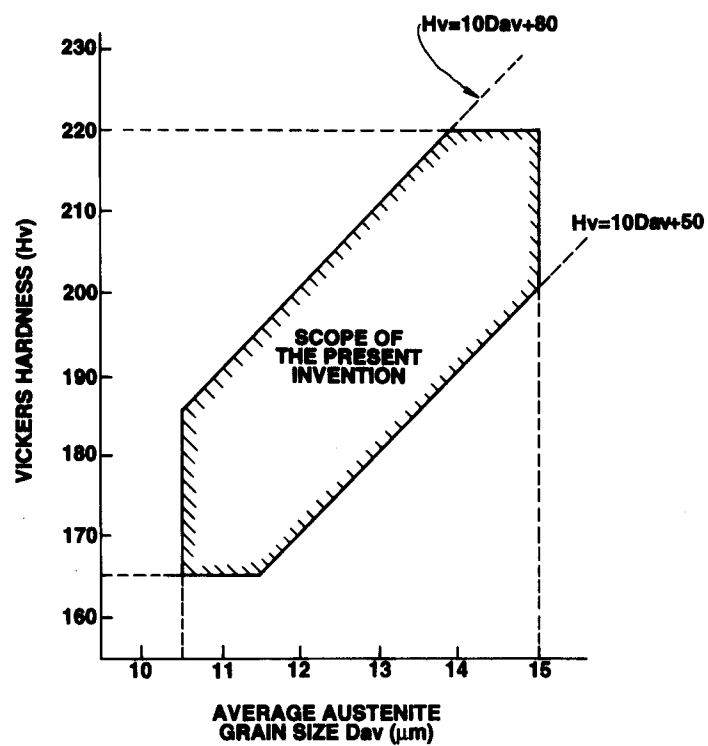
$$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50; \text{ and}$$

gathering degree of crystal planes on said alloy sheet surface of

14% or less for {111} plane,
5 to 75% for {100} plane,
5 to 40% for {110} plane,
20% or less for {311} plane,
20% or less for {331} plane,
20% or less for {210} plane, and
20% or less for {211} plane.

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FIG.1



Background of the InventionField of the Invention

5 The present invention relates to an alloy sheet for shadow mask having high press-formability.

Description of the Related Arts

10 Recent up-grading trend of color television toward high definition TV has employed Fe-Ni alloy containing 34 to 38wt.% Ni as the alloy for making a shadow mask to suppress color-phase shift. Compared with low carbon steel which has long been used as a shadow mask material, conventional Fe-Ni alloy has considerably lower thermal expansion coefficient. Accordingly, a shadow mask made of conventional Fe-Ni alloy raises no problem of color-phase shift coming from the thermal expansion of shadow mask even when an electron beam heats the shadow mask.

15 Common practice of making the alloy sheet for shadow mask includes the following steps. An alloy ingot is prepared by continuous casting process or ingot-making process. The alloy ingot is subjected to slabbing, hot-rolling, cold-rolling, and annealing to form an alloy sheet.

The alloy sheet for the shadow mask is then processed usually in the following steps to form shadow mask. (1) The alloy sheet is photo-etched to form passage-holes for the electron beam on the alloy sheet for shadow mask. The alloy sheet for shadow mask perforated by etching is hereinafter referred to as "flat mask". (2) The flat mask is subjected to annealing. (3) The annealed flat mask is pressed into a curved shape of cathode ray tube. (4) The press-formed flat mask is assembled to a shadow mask which is then subjected to blackening treatment.

25 Since the shadow mask material of conventional Fe-Ni alloy prepared by cold-rolling, recrystallization annealing, and finish-rolling has higher strength than conventional low carbon steel shadow mask material, it is softened by softening-annealing (annealing before pressing) at a temperature of 800°C or higher temperature for securing the good press-formability after perforation by etching. The softening at a high temperature of 800°C is, however, not favorable from the view point of work efficiency and also of economy. Accordingly, the industry waits for the development of materials which provide a strength as low as the material having been softened at the temperature of 800°C or higher even if they are subjected to softening at a low temperature.

30 Improvement of press-formability of an INVAR alloy for shadow mask was disclosed in the Japanese Unexamined Patent Publication No. 3-267320. This prior art provides a technology to reduce strength under a low temperature softening annealing at below 800°C, where an alloy is treated by cold-rolling, recrystallization annealing, and finish cold-rolling at the reduction ratio of 5 to 20wt%. The temperature of softening is below 800°C. The prior art produces a sheet having sufficiently low strength to give good press-formability with the 0.2wt% proof stress of 9.5kgf/mm² (less than 10kgf/mm²) at 200°C by the softening annealing at the temperature of less than 800°C.

40 However, the technology disclosed in the Japanese Unexamined Patent Publication No. 3-267320 only focuses on the average grain size and strength, and the disclosed process of induces considerable increase of degree of {100} plane and generates mixed grain structure. As a result, the shadow masks prepared by the prior art were found to gall the dies during press-forming and easily generate cracks at the edge of shadow masks. In addition, the material prepared by the prior art gave large plane anisotropy to induce blurted periphery of pierced hole of shadow mask after press-forming, which raised quality problems.

Summary of the Invention

The object of the present invention is to provide an alloy sheet for making a shadow mask which has a superior press-formability which offers a high screen quality without inducing color-phase shift.

50 To achieve the object, the present invention provides an alloy sheet for shadow mask consisting essentially of 34 to 38wt.% Ni, 0.07wt.% or less Si, 0.001wt.% or less B, 0.003wt.% or less O, 0.002wt.% or less N, and the balance being Fe and inevitable impurities;

said alloy sheet before annealing before press-forming having an average austenite grain size (Dav) of 10.5 to 15.0μm, a ratio of a maximum size to a minimum size of austenite grains (Dmax/Dmin) of 1 to 15, a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of

$$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50; \text{ and}$$

said alloy sheet having gathering degrees of crystal plane on the alloy sheet surface of

14% or less for {111} plane,

5 to 75% for {100} plane,

5 to 40% for {110} plane,

5 20% or less for {311} plane,

20% or less for {331} plane,

20% or less for {210} plane, and

20% or less for {211} plane.

Said alloy sheet may include 1wt.% or less Co.

10 Furthermore, the present invention provides an alloy sheet for making a shadow mask consisting essentially of 28 to 38wt.% Ni, 0.07wt.% or less Si, over 1wt.% to 7wt.% Co, 0.001wt.% or less B, 0.003wt.% or less O, 0.002wt.% or less N, and the balance being Fe and inevitable impurities;

said alloy sheet before annealing before press-forming having an average austenite grain size (Dav) of 10.5 to 15.0μm, a ratio of a maximum size to a minimum size of austenite grains (Dmax/Dmin) of 1 to 15, a
15 Vickers hardness (Hv) of 165 to 220 and satisfying a relation of

$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50$; and

said alloy sheet having gathering degrees of crystal planes on the alloy sheet surface of

20 14% or less for {111} plane,

5 to 75% for {100} plane,

5 to 40% for {110} plane,

20% or less for {311} plane,

20% or less for {331} plane,

25 20% or less for {210} plane, and

20% or less for {211} plane.

Still further, the present invention provides an alloy sheet for making a shadow mask consisting essentially of 34 to 38wt.% Ni, 0.01 to 3wt.% Cr, 0.2wt.% or less Si, 0.005wt.% or less B, 0.004wt.% or less O, 0.003wt.% or less N, 0.05wt.% or less Sb, and the balance being Fe and inevitable impurities;

30 said alloy sheet before annealing before press-forming having an average austenite grain size (Dav) of 10.5 to 15.0μm, a ratio of the maximum size to the minimum size of austenite grains (Dmax/Dmin) of 1 to 15, a Vickers hardness (Hv) of 165 to 220 and satisfying the relation of

$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50$;

35 said alloy sheet having degree of crystal plane on the alloy sheet surface of

14% or less for {111} plane,

5 to 75% for {100} plane,

5 to 40% for {110} plane,

40 20% or less for {311} plane,

20% or less for {331} plane,

20% or less for {210} plane, and

20% or less for {211} plane.

Said alloy sheet may include 1wt.% or less Co.

45 Furthermore, the present invention provides an alloy sheet for making a shadow mask consisting essentially of 28 to 38wt.% Ni, 0.01 to 3wt.% Cr, over 1wt.% to 7wt.% Co, 0.2wt.% or less Si, 0.005wt.% or less B, 0.004wt.% or less O, 0.003wt.% or less N, 0.05wt.% or less Sb, and the balance being Fe and inevitable impurities;

50 said alloy sheet before annealing before press-forming having an average austenite grain size (Dav) of 10.5 to 15.0μm, having the ratio of a maximum size to a minimum size of austenite grains, Dmax/Dmin, being 1 to 15, having Vickers hardness (Hv) of 165 to 220 and satisfying a relation of

$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50$; and

55 said alloy sheet having degrees of crystal planes on the alloy sheet surface of

14% or less for {111} plane,

5 to 75% for {100} plane,

5 to 40% for {110} plane,

20% or less for {311} plane,
 20% or less for {331} plane,
 20% or less for {210} plane, and
 20% or less for {211} plane.

5

Brief Description of the Drawings

Fig. 1 is a graph showing a effect of an average austenite grain size and a Vickers hardness on a press-formability according to the preferred embodiment 1;

10 Fig. 2 is a graph showing a relation between a degree of mixed grain for austenite grains and production of blurred periphery of pierced hole according to the preferred embodiment 1;

Fig. 3 is a graph showing a relation between a gathering degree of {100} plane and a degree of mixed grain of austenite grains according to the preferred embodiment 1;

15 Fig. 4 is a graph showing a effect of an average austenite grain size and Vickers hardness on a press-formability according to the preferred embodiment 2;

Fig. 5 is a graph showing a relation between a degree of mixed grain for austenite grains, and production of blurred periphery of pierced hole according to the preferred embodiment 2; and

Fig. 6 is a graph showing a relation between a gathering degree of {100} plane and a degree of mixed grain for austenite grains according to the preferred embodiment 2.

20

Description of the Preferred Embodiment

Preferred Embodiment 1

25 An alloy sheet consisting essentially of Fe, Ni, Si, B, O, and N, and an alloy sheet consisting essentially of Fe, Ni, Si, Co, B, O, and N of the present invention are described in the following.

The reason why the composition of the present invention is limited is described below.

A Fe-Ni alloy sheet for shadow mask is requested to have the upper limit of average thermal expansion coefficient of $2.0 \times (1/10^5)/^\circ\text{C}$ in the temperature range of 30 to 100°C for the prevention of color-phase shift. The thermal expansion coefficient depends on the Ni content of the alloy, and the Ni content which satisfies the above specified upper limit of the average thermal expansion coefficient is in a range of from 34 to 38wt.%. Accordingly, the Ni content is specified as 34 to 38wt.%. For further low average thermal expansion coefficient, the Ni content is preferably adjusted to 35 to 37wt.%, and most preferably to 35.5 to 36.5wt.%. Usually, Fe-Ni alloys include Co to some extent as an inevitable impurity, and the Co content of less than 1wt.% affects very little the characteristics of alloy while the above specified range of Ni content is acceptable. However, a Fe-Ni alloy which contains Co of over 1wt.% and to 7wt.% needs to limit the Ni content to be in the range of 28 to 38wt.% for satisfying the above described condition of average thermal expansion coefficient. Therefore, if the Co content is over 1wt.% to 7wt.%, then the Ni content is specified to be in a range of from 28 to 38wt.%. By adjusting the Co content to be 3 to 6wt.% and the Ni content to be 30 to 33wt.%, a superior characteristic giving lower average thermal expansion coefficient is obtained. If the Co content exceeds 7wt.%, the thermal expansion coefficient increases to give a superior characteristic, so the upper limit of Co content is specified as 7wt.%.

Oxygen is one of the inevitable impurities When oxygen content is increased, the non-metallic oxide inclusion increases in the alloy. The non-metallic inclusion suppresses the growth of crystal grains during the annealing before press-forming, particularly at the temperature of less than 800°C . If the content of O exceeds 0.0030wt.%, the growth of grains is inhibited, and the press-forming quality being aimed by the present invention can not be obtained. In this respect, the present invention specifies the upper limit of O content as 0.0030wt.%. The lower limit of O content is not specifically limited, but it is substantially selected as 0.0001wt.% from the economy of ingot-making process.

50 B improves the hot-workability of the alloy. Excess amount of B, however, induces the segregation of B at boundary of recrystallized grains formed during annealing before press-forming, which inhibits the free migration of grain boundaries and results in the suppression of grain growth and the dissatisfaction of necessary 0.2wt.% proof stress after the annealing before press-forming. In particular, under the annealing before press-forming at a relatively low temperature, which is specified in the present invention, the suppression against the grain growth is strong and the action does not uniformly affects on all grains. As a result, a severe mixed grain structure appears accompanied with irregular elongation of material during press-forming, which induces blurred periphery of pierced hole on shadow mask. Boron content above 0.0010wt.% significantly enhances the suppression of grain growth, and the press-formability aimed in the

present invention can not be obtained. Also the problem of blurred periphery of pierced hole arises. Consequently, the present invention specifies the upper limit of B content as 0.0010wt.%. From the above described viewpoint, more preferable B content is 0.0002wt.% or less.

Silicon is added as the deoxidizer element during ingot-making of the alloy. When the Si content exceeds 0.07wt.%, an oxide film of Si is formed on the surface of alloy at the annealing before press-forming. The oxide film degrades the fitness with dies during press-forming and results in the galling of dies by alloy sheet. Consequently, the upper limit of Si content is specified as 0.07wt.%. Further reduction of Si content improves the fitness of dies and alloy sheet. The lower limit of Si content is not necessarily specified but approximately 0.001wt.% is the virtual lower limit from the economy of ingot-making process.

Nitrogen is an element unavoidably entering into the alloy during ingot-making process. Nitrogen content of 0.0020wt.% or more induces the concentration of N on the surface of alloy during the annealing before press-forming and yields nitride. The nitride degrades the fitness of alloy with dies during the press-forming process and induces galling of dies by alloy sheet. Consequently, the N content is specified as less than 0.0020wt.%. Although the lower limit of N content is not necessarily defined, 0.0001wt.% is lower limit from the economy of ingot-making process.

Regarding the elements other than above described, preferable range of C is 0.0001 to 0.0040wt.%, that of Mn is 0.001 to 0.35wt.%, and that of Cr is 0.001 to 0.07wt.%.

According to the present invention, to improve the shape fix ability, to suppress crack generation on alloy sheet surface during press-forming, and to prevent generation of blurred periphery of pierced hole of prepared shadow mask, it is necessary to define, in addition to the composition above specified, the specific range for each of an average austenite grain size (D_{av}) before the annealing before press-forming, a ratio of maximum to minimum size of austenite grains, (D_{max}/D_{min}) and the Vickers hardness (Hv) and furthermore it is necessary to specify the relation between the Vickers hardness (Hv) and the average austenite grain size (D_{av}) to satisfy a specific correlation.

Fig. 1 shows the effect of average austenite grain size, D_{av} , and Vickers hardness, Hv, before the annealing before press-forming on the press-formability. In that case, the alloy was subjected to the annealing before press-forming at a temperature below 800°C followed by the press-forming. The employed alloy sheet included: 34 to 38wt.% Ni, 0.07wt.% or less Si, 0.001wt.% or less B, 0.003wt.% or less O, and below 0.002wt.% N. The gathering degree of plane of the alloy was as follows: 14% or less for {111} plane, 5 to 75% for {100} plane, 5 to 40% for {110} plane, 20% or less for {311} plane, 20% or less for {331} plane, 20% or less for {210} plane, and 20% or less for {211} plane. The alloy sheet had a ratio of a maximum size to a minimum size of austenite grains, D_{max}/D_{min} , in a range of from 1 to 15.

According to Fig. 1, the value of average austenite grain size, D_{av} , less than 10.5 μ m can not enhance the growth of grain in an alloy sheet during the annealing before press-forming under the temperature condition being aimed by the present invention, below 800°C, and increases spring back and results in a poor shape fix ability because of the insufficient growth of grains. On the other hand, the value of D_{av} above 15.0 μ m hinders the recrystallization during the annealing before press-forming and results in a poor shape fix ability owing to the insufficient recrystallization.

Vickers hardness, Hv, is mainly determined by the reduction ratio of cold-rolling. The value of Hv below 165 can not give sufficient strain to the alloy sheet, and gives only a weak driving force for recrystallization during the annealing before press-forming. The result is insufficient recrystallization, which leaves the alloy sheet at a rather rigid state even after the annealing before press-forming. As a result, the shape fix ability is poor. On the other hand, when excess strain is given to the alloy sheet to induce Hv above 220, the driving force for recrystallization during the annealing before press-forming becomes strong, which yields excess frequency of nuclei formation during recrystallization. Consequently, the grains become fine after the annealing before press-forming to degrade the shape fix ability.

Fig. 1 also indicates that an adequate recrystallization during the annealing before press-forming is realized by keeping the relation between Vickers hardness, Hv, and average austenite grain size D_{av} in a specific range. A large average austenite grain size, D_{av} , before the annealing before press-forming requests a large degree of strain for obtaining a sufficient driving force during the annealing before press-forming. Accordingly, the lower limit of Vickers hardness, Hv, is necessary to be defined depending on the corresponding average austenite grain size, D_{av} . On the other hand, since smaller average austenite grain size, D_{av} , has larger number of nucleation sites, the upper limit of Vickers hardness, Hv, is necessary to be defined depending on the corresponding average austenite grain size, D_{av} , to prevent the generation of fine grains after the annealing before press-forming. According to Fig. 1, even the Vickers hardness, Hv, is 165 or more, if the equation of $[Hv < 10 \times D_{av} + 50]$ is satisfied, then the driving force for the recrystallization during the annealing before press-forming is relatively too small, and sufficient recrystallization can not be attained. Therefore, the material remains rigid even after the annealing before press-forming and is poor in

the shape fix ability. Even when the Vickers hardness, Hv, is 220 or less, if the equation of $[Hv > 10 \times Dav + 80]$ is satisfied, then the driving force for the recrystallization during the annealing before press-forming is relatively too large, the grains become fine after the annealing before press-forming and the shape fix ability is poor.

5 Fig. 2 shows the relation between the ratio of the maximum size to the minimum size of austenite grains, D_{max}/D_{min} , and the blurred periphery of pierced hole. The employed alloy sheet consists essentially of: 34 to 38wt.% Ni, 0.07wt.% or less Si, 0.001wt.% or less B, 0.003wt.% or less O, and below 0.002wt.% N.

The Vickers hardness, Hv, and the average austenite grain size, Dav , satisfied the equation:

10

$$10 \times Dav + 80 \geq Hv \geq 10 \times Dav + 50$$

The degree of plane of the alloy was as follows: 14% or less for $\{111\}$ plane, 5 to 75% for $\{100\}$ plane, 5 to 40% for $\{110\}$ plane, 20% or less for $\{311\}$ plane, 20% or less for $\{331\}$ plane, 20% or less for $\{210\}$ plane, and 20% or less for $\{211\}$ plane.

15 According to Fig. 2, when the ratio of the maximum size to the minimum size of austenite grains, D_{max}/D_{min} , exceeds 15, the etched hole size becomes irregular and induces blurred periphery of pierced hole. Smaller D_{max}/D_{min} value is more favorable, and the lower limit of the D_{max}/D_{min} is specified as 1.

From the consideration given above, the present invention specifies the average austenite grain size, Dav , before the annealing before press-forming as in a range of from 10.5 to 15.0 μ m, the ratio of the maximum size to the minimum size of the austenite grains, D_{max}/D_{min} , (which ratio is hereinafter referred to simply as "degree of austenite mixed grain"), as in a range of from 1 to 15, and the Vickers hardness, Hv, as in a range of from 165 to 220, and also satisfies the following equation:

25 $10 \times Dav + 80 \geq Hv \geq 10 \times Dav + 50$

for enhancing the growth of grain during the annealing before press-forming, for improving the shape fix ability, and for suppressing the blurred periphery of pierced hole of prepared shadow mask.

For the prevention of crack generation during the press-forming and for the prevention of blurred periphery of pierced hole and partial color-phase shift on the prepared shadow mask, which are the objects of the present invention, it is important to limit the gathering degree of planes on the alloy sheet surface before annealing before press-forming, as well as the limitations specified above.

The inventors found that the control of the gathering degree of $\{211\}$ plane on the alloy sheet surface before annealing before press-forming effectively suppresses the crack generation during press-forming and that the control of the degree of $\{100\}$ plane and $\{110\}$ plane suppresses the blurred periphery of pierced hole on the prepared shadow mask and that the control of the degree of $\{111\}$ plane, $\{311\}$ plane, $\{331\}$ plane, and $\{210\}$ plane suppresses the partial color-phase shift on the prepared shadow mask.

In concrete terms, when the degree of $\{211\}$ plane exceeds 20%, the alloy sheet generates cracks during press-forming. When the degree of $\{111\}$ plane, $\{311\}$ plane, $\{331\}$ plane, and $\{210\}$ plane exceeds 14%, 20%, 20%, and 20%, respectively, the etched hole shape abnormally deforms during press-forming, which induces partial color-phase shift.

The control of the degree of $\{100\}$ plane and $\{110\}$ plane is necessary for limiting the degree of austenite mixed grain, D_{max}/D_{min} , in the range specified in the present invention. When the degree of $\{100\}$ plane exceeds 75% or when the degree of $\{110\}$ plane exceeds 40%, the degree of austenite mixed grain exceeds 15. In that case, the recrystallization during the annealing before press-forming does not proceed uniformly, and the grains after the annealing before press-forming become mixed grain state inducing blurred periphery of pierced hole on the prepared shadow mask. When the degree of $\{100\}$ plane is less than 5%, the degree of $\{110\}$ plane exceeds 40%. When the degree of $\{110\}$ plane is less than 5%, the degree of $\{100\}$ plane exceeds 75%. In both cases, the degree of austenite mixed grain exceeds 15 and induces blurred periphery of pierced hole on the prepared shadow mask. Fig. 3 shows the relation between the degree of $\{100\}$ plane and the degree of mixed grain. According to Fig. 3, the degree of austenite mixed grain can be controlled in a range of 1 to 15 by controlling the degree of $\{100\}$ plane in a range of 5 to 75%. The degree of mixed grain is further reduced by controlling the degree of $\{100\}$ plane in a further limited range of 8 to 46% for more effective suppression of blurred periphery of pierced hole.

From the consideration given above, the present invention specifies the gathering degree of each plane on the alloy sheet before annealing before press-forming as listed below:

Gathering degree of $\{111\}$ plane : 14% or less

Gathering degree of $\{100\}$ plane : 5 to 75%

Gathering degree of {110} plane : 5 to 40%

Gathering degree of {311} plane : 20% or less

Gathering degree of {331} plane : 20% or less

Gathering degree of {210} plane : 20% or less

5 Gathering degree of {211} plane : 20% or less

The value of the gathering degree given above is the relative rate of each plane to the total gathering degree of planes, {111}, {100}, {110}, {311}, {331}, {210}, and {211}.

The gathering degree of respective plane is determined from the X-ray diffraction intensity on each X-ray diffraction plane, (111), (200), (220), (311), (331), (420), and (422). For example, the degree of (111) plane is determined by dividing the relative X-ray diffraction intensity ratio of (111) plane by the sum of relative X-ray intensity ratio on each diffraction plane, (111), (200), (220), (311), (331), (420), and (422). The degree of other planes, (100), (110), (311), (331), (210), and (211) can be determined by the same procedure. The relative X-ray diffraction intensity ratio is the ratio of the X-ray diffraction intensity measured on each diffraction plane to the theoretical X-ray intensity on the diffraction plane. For instance, the relative X-ray diffraction intensity ratio of (111) plane is the X-ray diffraction intensity of (111) diffraction plane divided by the theoretical X-ray diffraction intensity of (111) diffraction plane.

The degree of each plane, {100}, {110}, {210}, and {211} is determined from the relative X-ray diffraction intensity ratio of (200), (220), (420), and (422) plane, each of which has the same orientation with corresponding plane, divided by the sum of relative X-ray diffraction intensity ratio of the seven diffraction planes, (111) through (422).

The degree of each plane, {111}, {100}, {110}, {311}, {331}, {210}, and {211}, before the annealing before press-forming, which is specified by the present invention, is normally obtained by selecting adequate condition of treatment after the hot-rolling step.

For example, when an alloy sheet of the present invention is produced by hot-rolling a slab prepared by slabbing or continuous casting followed by a sequence of annealing of hot-rolled sheet, cold-rolling, recrystallization annealing, cold-rolling, recrystallization annealing, cold-rolling, recrystallization annealing, finish cold rolling, and stress relief annealing, an effective condition to obtain the degree of plane defined above is the control of the annealing temperature during the annealing of hot-rolled sheet at an adequate level in a range of from 910 to 990 °C and furthermore the selection of optimum condition of cold-rolling, recrystallization annealing, finish cold-rolling, and stress relief annealing. Also for the average austenite grain size, D_{av} , the degree of austenite mixed grain, D_{max}/D_{min} , and the Vickers hardness, Hv, specified by the present invention, the optimization is achieved by controlling the conditions of cold-rolling, recrystallization annealing, finish cold-rolling, and stress relief annealing.

To obtain a degree of planes specified by the present invention, the uniform heat treatment of a slab after blooming or after continuous casting is not preferable. For instance, when the homogenization is carried out at 1200 °C or higher temperature and for 10 hours or longer period, the degree of one or more of the planes {111}, {100}, {110}, {311}, {331}, {210}, and {211} dissatisfies the specification of the present invention. Therefore, such a homogenization treatment should be avoided.

Other means may be employed to satisfy the degree of planes specified by the present invention. Quenching to solidify and agglomeration controlling through the control of recrystallization during hot working are some of the examples of applicable means.

The alloy sheet of the present invention may be subjected to the annealing before press-forming before the photo-etching step. If the annealing before press-forming is performed at a relatively low temperature which is a condition of the present invention, the quality of photo-etching is not degraded. In a conventional material, if the photo-etching is applied after the annealing before press-forming at a relatively low temperature specified by the present invention, the quality of the photo-etching is degraded, so the annealing before press-forming is substantially not applicable before the photo-etching. On the contrary, the materials of the present invention accept the photo-etching after the annealing before press-forming without degrading the etching performance.

Example 1

The inventors prepared the alloys of No. 1 through No. 23 having the composition listed on Table 1 and Table 2 by ladle refining, and cast the alloys of No. 1 through No. 13 and No. 18 through No. 23 to form ingots. After they are subjected to slabbing, scarfing, and hot-rolling at 1100 °C for 3 hours, the hot-rolled sheets were obtained. The alloys of No. 14 through No. 17 were cast directly into sheets which were then hot-rolled at the reduction ratio of 30% in the temperature range of from 1000 to 1300 °C followed by coiling at 750 °C to obtain the hot-rolled sheets. From these hot-rolled sheets, the alloy sheets of materials

No. 1 through No. 34 listed on Table 3 through Table 6 were prepared.

In Table 3 and Table 4, Dmax represents the maximum austenite grain size in alloy sheet, and Dmin represents the minimum austenite grain size in the alloy sheet.

In Table 5 and Table 6, the criteria for evaluation of the shape fix ability, the fitness of dies and alloy sheet, and the blurted periphery of pierced hole are the following.

Regarding the shape fix ability, "◎" mark indicates "very good", "○" indicates "good", and "X" indicates "rather poor".

As for the fitness to dies and alloy sheet, "○" mark indicates "good without ironing mark", "△" indicates "rather poor with a few ironing marks", and "X" indicates "poor with lots of ironing marks".

For the blurred periphery of pierced hole, "◎" mark indicates "definitely none", "○" indicates "none", "△" indicates "found some", and "X" indicates "generated".

Materials No. 1 through No. 21 and No. 27 through No. 30 were the alloy sheets having the thickness of 0.25mm and were produced from the hot-rolled sheets of alloys No. 1 through No. 21 by the treatment of annealing of hot-rolled sheet in the temperature range of 910 to 990 °C, cold-rolling, recrystallization annealing in the temperature range of 860 to 940 °C for 125sec., cold-rolling, recrystallization annealing in the temperature range of 860 to 940 °C for 125sec., finish cold-rolling at the reduction ratio of 15%, and stress relief annealing at 530 °C for 30sec.

Materials No. 22 and No. 26 were the alloy sheets having the thickness of 0.25mm and were produced from the hot-rolled sheets of alloys No. 22 and No. 2 by the treatment of cold-rolling at the reduction ratio of 92.5%, recrystallization annealing at 850 °C for 1min., finish cold-rolling at the reduction ratio of 15%, and stress relief annealing at 530 °C for 3sec.

Material No. 24 was the alloy sheet having the thickness of 0.25mm and was produced from the hot-rolled sheet of alloy No. 1 by the treatment of annealing of hot-rolled sheet at 950 °C, cold-rolling at the reduction ratio of 74%, recrystallization annealing at 950 °C for 180sec., cold-rolling at the reduction ratio of 40%, recrystallization at 950 °C for 180sec., finish cold-rolling at the reduction ratio of 15%, and stress relief annealing at 530 °C for 30sec.

Material No. 25 was the alloy sheet having the thickness of 0.25mm and was produced from the hot-rolled sheet of alloy No. 1 by the treatment of annealing of hot-rolled sheet at 950 °C, cold-rolling, recrystallization annealing at 800 °C for 30 sec., cold-rolling, recrystallization annealing at 800 °C for 30sec., finish cold-rolling, and stress relief annealing at 530 °C for 30sec.

Material No. 23 was the alloy sheet having the thickness of 0.25mm and was produced from the hot-rolled sheet of alloy No. 23 by the treatment of annealing of hot-rolled sheet at 970 °C, cold-rolling, recrystallization annealing at 800 °C for 30sec., cold-rolling, recrystallization annealing at 800 °C for 30sec., finish cold-rolling, and stress relief annealing at 530 °C for 30sec.

Materials No. 31 through No. 34 were the alloy sheets having the thickness of 0.25mm and were produced from the hot-rolled sheets of alloys No. 3, No. 4, and No. 7 by the treatment of cold-rolling, recrystallization annealing in the temperature range of 860 to 940 °C for 125sec., cold-rolling, recrystallization annealing in the temperature range of 860 to 940 °C for 125sec., finish cold-rolling, and stress relief annealing at 530 °C for 30sec.

All those produced hot-rolled sheets showed sufficient recrystallization after annealing.

Alloy sheets of material No. 1 through No. 12 and No. 15 through No. 34 prepared by the treatment described above were etched and formed into flat masks. The flat masks were treated by the annealing before press-forming at 770 °C for 45min., followed by press-forming. The press-formability was tested during the procedure. Partial color-phase shift was measured after blackening the press-formed shadow masks, assembling them into cathode ray tube, and irradiating electron beam on the surface thereof. Alloy sheets of material No. 13 and No. 14 were subjected to the annealing before press-forming at 795 °C for 3min., which were then etched and formed into flat masks. Those flat masks were press-formed to determine the press-formability. Those alloys were also checked for the partial color-phase shift using the same procedure as before.

Table 3 and Table 4 give the average austenite grain size, Dav, before the annealing before press-forming, the degree of austenite mixed grains, Dmax/Dmin, the Vickers hardness, Hv, $[10 \times D_{av} + 80 - Hv]$ and $[Hv - 10 \times D_{av} - 50]$. Table 5 and Table 6 give the degree of each plane on the sheet surface before the annealing before press-forming, the press-formability, and the partial color-phase shift.

According to Table 3 through Table 6, materials No. 1 through No. 13 satisfied the conditions specified in the present invention, which conditions include the degree of planes, {111}, {100}, {110}, {311}, {331}, {210}, and {211}, the average austenite grain size, Dav, the degree of austenite mixed grain, Dmax/Dmin, the Vickers hardness, Hv, and the condition of $[10 \times D_{av} + 80 \geq Hv \geq 10 \times D_{av} + 50]$. All of those materials gave an excellent press-formability without giving partial color-phase shift. Materials No. 14

through No. 17 which contained Co and which are the examples of the present invention also showed excellent characteristics. Materials No. 13 and No. 14 were subjected to the annealing before press-forming before the etching, and they were found to have proper performance as the shadow mask even they were treated by the described production process.

On the contrary, materials No. 18 and No. 20 are comparative examples each containing the amount of Si and N larger than the specified level of the present invention, respectively, and they raised the problem of fitness to dies during press-forming step. Material No. 19 is a comparative example containing the amount of O larger than the specified level of the present invention, and it gave the average austenite grain size, D_{av} , before the annealing before press-forming less than $10.5\mu\text{m}$. Therefore, the material No. 19 gave a poor shape fix ability at the press-forming, and generated cracks on the alloy sheet. Furthermore, the degree of austenite mixed grain of the material No. 19 exceeded the specified level of the present invention, so the blurred periphery of pierced hole also occurred.

Materials No. 21 and No. 22 are comparative examples including the amount of B above the specified range of the present invention, and both gave the average austenite grain size, D_{av} , less than $10.5\mu\text{m}$. Consequently, they were inferior in the shape fix ability at press-forming and they induced cracks on the alloy sheets. In addition, their degree of austenite mixed grain also exceeded the specified range of the present invention so that the blurred periphery of pierced hole occurred. In particular, the material No. 22 was produced by cold-rolling at the reduction ratio of 92.5%, recrystallization annealing at 850°C for 1min., and finish cold-rolling at the reduction ratio of 15% without applying the annealing of hot-rolled sheet, following the technology which was disclosed by the Japanese Unexamined Patent Publication No. 3-267320. The material No. 22 gave the degree of $\{110\}$ plane and $\{100\}$ plane outside of the range specified by the present invention. Particularly, the degree of austenite mixed grain became a high level.

Material No. 26 was prepared with the same procedure as applied to material No. 22, and the material No. 26 is a comparative example which gave the degree of $\{100\}$ plane and $\{110\}$ plane outside of the range specified by the present invention. The material No. 26 gave a large degree of austenite mixed grain so that the blurred periphery of pierced hole occurred. As described above, even if an alloy satisfies the composition condition of the present invention, it can not provide an excellent press-formability unless it satisfies the condition of the present invention on the degree of planes and the degree of austenite mixed grain.

Materials No. 24 and No. 25 were produced under the condition of recrystallization annealing after the cold-rolling, at 950°C for 180sec. and at 800°C for 30sec., respectively. Material No. 24 is a comparative example which gave the average austenite grain size, D_{av} , above the specified range of the present invention, and material No. 25 is a comparative example which gave the average austenite grain size, D_{av} , below the specified range of the present invention. Both materials were inferior in the shape fix ability.

Materials No. 31 through No. 34 were prepared employing the same processes after the cold-rolling step as in the case of No. 1 through No. 21 without using annealing of hot-rolled sheet. Among them, the material No. 31 is a Comparative example giving the degree of $\{110\}$ plane outside of the specified range of the present invention, which material gave the degree of austenite mixed grain above the specified range of the present invention, and the blurred periphery of pierced hole occurred. Material No. 33 is a Comparative example giving the degree of $\{211\}$ plane above the specified range of the present invention, which induced cracks on the alloy sheet. Material No. 32 is a Comparative example giving the degree of $\{111\}$ plane and $\{311\}$ plane outside of the specified range of the present invention. Material No. 34 is a Comparative example giving the degree of $\{311\}$ plane and $\{210\}$ plane above the specified range of the present invention. Those comparative examples induced partial color phase shift.

Materials No. 27, No. 28, No. 29, and No. 30 are Comparative examples giving Vickers hardness, Hv, above the specified range of the present invention, Vickers hardness, Hv, below the specified range of the present invention, $10 \times D_{av} + 80 < \text{Hv}$, and $\text{Hv} < 10 \times D_{av} + 50$, respectively. All of them showed poor shape fix ability.

As described above, the Fe-Ni alloy sheet and Fe-Ni-Co alloy sheet for shadow mask having excellent press-formability and screen quality being aimed by the present invention are obtained by satisfying the conditions of composition, degree of planes before the annealing before press-forming, average austenite grain size, D_{av} , degree of austenite mixed grain, $D_{\text{max}}/D_{\text{min}}$, Vickers hardness, Hv, and the condition of $10 \times D_{av} + 80 \geq \text{Hv} \geq 10 \times D_{av} + 50$, which conditions are specified by the present invention.

As described above in detail, Fe-Ni alloy sheet and Fe-Ni-Co alloy sheet for shadow mask of the present invention provide excellent press-formability even they are subjected to the annealing before press-forming at a relatively low temperature, below 800°C . The excellent press-formability includes good shape fix ability, good fitness to dies, and less occurrence of cracks on the alloy sheet during press-forming. Excellent screen quality is also secured without partial color-phase shift. Furthermore, the alloy sheet of the

present invention provides a necessary etching performance and press-formability even when it is subjected to the annealing before press-forming before the etching. Therefore, a preliminary annealing on the alloy sheet eliminates the annealing before press-forming at the cathode ray tube manufacturer. This process optimization gives the users of alloy sheets a great economical advantage.

Table 1

Alloy No.	Chemical composition (wt.% excluding H)										
	N i	S i	O	N	B	C	M n	C r	H (ppm)	C o	
1	35.9	0.005	0.0010	0.0008	0.00005	0.0013	0.25	0.01	1.0	—	
2	36.1	0.02	0.0013	0.0010	0.0001	0.0011	0.26	0.02	0.2	—	
3	36.0	0.03	0.0014	0.0011	0.0001	0.0015	0.04	0.02	0.8	0.001	
4	36.5	0.05	0.0020	0.0015	0.0005	0.0040	0.35	0.02	1.0	0.020	
5	35.3	0.01	0.0015	0.0010	0.0002	0.0023	0.25	0.05	0.9	—	
6	35.7	0.01	0.0012	0.0009	0.0001	0.0020	0.27	0.01	0.9	0.500	
7	36.0	0.02	0.0008	0.0007	0.0002	0.0009	0.11	0.03	0.7	—	
8	36.2	0.05	0.0005	0.0005	0.0001	0.0007	0.05	0.02	0.9	0.500	
9	36.2	0.001	0.0002	0.0002	0.0001	0.0005	0.005	0.01	0.6	0.004	
10	35.5	0.04	0.0018	0.0011	0.0001	0.0032	0.01	0.01	0.6	—	
11	35.8	0.03	0.0016	0.0012	0.0002	0.0030	0.20	0.02	0.3	—	
12	35.0	0.05	0.0019	0.0015	0.0004	0.0039	0.15	0.03	0.2	0.750	

Table 2

Alloy No.	Chemical composition (wt.% excluding H)									
	N i	S i	O	N	B	C	M n	C r	H (ppm)	C o
13	36.0	0.01	0.0017	0.0012	0.0001	0.0037	0.05	0.04	0.5	0.050
14	31.9	0.05	0.0021	0.0015	0.0001	0.0018	0.13	0.02	0.4	5.300
15	31.0	0.03	0.0014	0.0019	0.0001	0.0020	0.30	0.04	0.7	5.953
16	30.0	0.02	0.0017	0.0016	0.0002	0.0023	0.24	0.04	0.8	4.101
17	29.5	0.01	0.0016	0.0008	0.0010	0.0045	0.35	0.03	0.8	6.521
18	35.6	0.08	0.0020	0.0014	0.0002	0.0021	0.28	0.03	1.1	—
19	36.2	0.05	0.0035	0.0012	0.0001	0.0017	0.31	0.04	1.1	—
20	36.3	0.04	0.0018	0.0020	0.0002	0.0019	0.25	0.03	1.3	0.020
21	36.0	0.04	0.0017	0.0015	0.0011	0.0025	0.28	0.04	1.2	0.010
22	35.8	0.05	0.0023	0.0016	0.0021	0.0032	0.27	0.04	1.3	—
23	34.2	0.02	0.0020	0.0007	0.0005	0.0017	0.31	0.05	0.8	2.534

Table 3

Material No.	Alloy No.	Average grain size D_{av} (μm)	D_{max}/D_{min}	Vickers hardness before annealing before press-forming (Hv)	$10 \times D_{av} + 80$ — Hv	Hv — $10 \times D_{av}$ — 50	Type of example
1	1	11.8	5.0	181	Positive	Positive	Present invention
2	2	11.7	15.0	180	Positive	Positive	Present invention
3	3	11.8	6.5	175	Positive	Positive	Present invention
4	4	12.6	12.5	206	0	Positive	Present invention
5	5	12.5	8.0	175	Positive	Positive	Present invention
6	6	12.5	11.0	190	Positive	Positive	Present invention
7	7	11.1	5.4	191	0	Positive	Present invention
8	8	13.7	15.0	188	Positive	Positive	Present invention
9	9	11.5	12.0	166	Positive	Positive	Present invention
10	10	10.5	9.0	185	0	Positive	Present invention
11	11	10.6	10.1	165	Positive	Positive	Present invention
12	12	14.0	11.8	219	Positive	Positive	Present invention
13	13	15.0	9.8	220	Positive	Positive	Present invention
14	14	12.5	5.5	179	Positive	Positive	Present invention
15	15	12.7	7.0	180	Positive	Positive	Present invention
16	16	12.4	6.2	175	Positive	Positive	Present invention
17	17	13.0	6.8	200	Positive	Positive	Present invention

Table 4

Material No.	Alloy No.	Average grain size D_{av} (μm)	D_{max}/D_{min}	Vickers hardness before annealing before pressing forming (Hv)	$10 \times D_{av} + 80 - H_v$	$H_v - 10 \times D_{av} - 50$	Type of example
18	18	10.8	14.0	185	Positive	Positive	Comparative example
19	19	8.5	19.5	175	Negative	Positive	Comparative example
20	20	10.5	15.0	173	Positive	Positive	Comparative example
21	21	9.0	18.5	180	Negative	Positive	Comparative example
22	22	10.0	20.0	183	Negative	0	Comparative example
23	23	10.0	10.0	160	Positive	Positive	Comparative example
24	1	15.5	14.0	205	Positive	Positive	Comparative example
25	1	9.5	14.5	170	Positive	Positive	Comparative example
26	2	10.5	22.0	180	Positive	Positive	Comparative example
27	5	11.0	14.0	225	Negative	Positive	Comparative example
28	2	10.8	13.5	163	Positive	Positive	Comparative example
29	6	11.9	15.0	200	Negative	Positive	Comparative example
30	6	13.3	12.0	175	Positive	Negative	Comparative example
31	4	10.9	16.7	170	Positive	Positive	Comparative example
32	3	11.5	6.0	185	Positive	Positive	Comparative example
33	4	10.8	6.0	167	Positive	Positive	Comparative example
34	7	11.2	13.0	190	Positive	Positive	Comparative example

Table 5

Material No.	Alloy No.	Gathering degree of crystal plane before annealing before press-forming (%)						Press-formability				Partial color shift	Type of example
		(111)	(100)	(110)	(311)	(331)	(210)	(211)	Shape fix ability	Fitness to die	Cracking on the alloy sheet	Blurred periphery of pierced hole	
1	1	9	16	24	14	12	13	12	◎	○	None	◎	Present invention
2	2	2	72	8	3	8	4	3	◎	○	None	○	Present invention
3	3	6	27	30	11	7	11	8	◎	○	None	◎	Present invention
4	4	3	62	15	6	8	4	2	○	○	None	○	Present invention
5	5	7	36	23	12	8	10	4	○	○	None	○	Present invention
6	6	6	51	17	7	9	5	5	◎	○	None	○	Present invention
7	7	10	21	29	10	10	10	10	○	○	None	◎	Present invention
8	8	4	5	37	17	12	13	12	○	○	None	○	Present invention
9	9	4	55	15	7	8	6	5	○	○	None	○	Present invention
10	10	6	41	22	9	10	7	5	○	○	None	◎	Present invention
11	11	10	8	31	15	11	12	13	○	○	None	◎	Present invention
12	12	9	7	35	16	12	10	11	○	○	None	○	Present invention
13	13	7	45	18	8	9	6	5	○	○	None	◎	Present invention
14	14	9	22	30	10	9	9	11	◎	○	None	◎	Present invention
15	15	8	28	25	9	10	10	10	◎	○	None	◎	Present invention
16	16	7	23	32	12	9	8	9	◎	○	None	◎	Present invention
17	17	5	31	35	7	8	8	6	◎	○	None	◎	Present invention

Table 6

Material No.	Alloy No.	Gathering degree of crystal plane before annealing before press-forming (%)						Press-formability				Partial color phase shift	Type of example
		{111}	{100}	{110}	{311}	{210}	{211}	Shape fix ability	Fitness to die	Cracking on the alloy sheet	Blurred periphery of pierced hole		
18	18	2	65	12	6	8	5	2	○	None	○	None	Comparative example
19	19	2	90	3	1	2	1	1	×	Yes	×	Impossible to evaluate	Comparative example
20	20	3	73	6	4	7	4	3	○	None	○	None	Comparative example
21	21	2	85	4	2	4	2	1	×	Yes	×	Impossible to evaluate	Comparative example
22	22	1	93	0	1	3	1	1	×	Yes	×	Impossible to evaluate	Comparative example
23	23	9	45	25	8	4	5	4	×	Yes	⊙	Impossible to evaluate	Comparative example
24	1	3	70	10	2	9	4	2	×	None	○	Impossible to evaluate	Comparative example
25	1	3	73	6	3	7	4	4	×	None	○	Impossible to evaluate	Comparative example
26	2	0	97	3	0	0	0	0	○	None	×	Impossible to evaluate	Comparative example
27	5	2	71	9	4	7	5	2	×	None	○	Impossible to evaluate	Comparative example
28	2	1	65	10	7	9	7	1	×	None	○	Impossible to evaluate	Comparative example
29	6	12	5	40	10	11	11	11	×	None	○	Impossible to evaluate	Comparative example
30	6	11	7	37	13	9	10	13	×	None	○	Impossible to evaluate	Comparative example
31	4	13	3	45	9	9	11	10	○	None	△	Impossible to evaluate	Comparative example
32	3	16	15	7	22	15	13	12	○	None	○	Yes	Comparative example
33	4	8	24	32	4	3	3	26	○	Yes	○	None	Comparative example
34	7	14	6	15	11	21	23	10	○	None	○	Yes	Comparative example

Preferred Embodiment 2

An alloy sheet consisting essentially of Fe, Ni, Cr, Si, B, O, N, and Sb, and an alloy sheet consisting essentially of Fe, Ni, Cr, Co, Si, B, O, N, and Sb of the present invention are described in the following.

The reason why the composition of the present invention is limited is described below.

A Fe-Ni alloy sheet for shadow mask is requested to have the upper limit of average thermal expansion coefficient of $3.0 \times (1/10^6)/^{\circ}\text{C}$ in the temperature range of 30 to 100°C for the prevention of color-phase shift. The thermal expansion coefficient depends on the Ni content of the alloy, and the Ni content which satisfies the above specified upper limit of the average thermal expansion coefficient is in a range of from 34 to 38wt.%. Accordingly, the Ni content is specified as 34 to 38wt.%. For further low average thermal expansion coefficient, the Ni content is preferably adjusted to 35 to 37wt.%, and most preferably to 35.5 to 36.5wt.%. In ordinary cases, Fe-Ni alloys contain Co to some extent as an inevitable impurity, and the Co content of 1wt.% or less affects very little on the characteristics of alloy while the above specified range of Ni content is acceptable.

However, a Fe-Ni alloy which contains Co over 1wt.% to 7wt.% needs to limit the Ni content to be in a range from 28 to 38wt.% for satisfying the above described condition of average thermal expansion coefficient. Therefore, if the Co content is over 1wt.% to 7wt.%, then the Ni content is specified to be in a range of from 28 to 38wt.%. By adjusting the Co content to be in a range of 3 to 6wt.% and the Ni content to a range of from 30 to 33wt.%, a superior characteristic giving lower average thermal expansion coefficient is obtained. If the Co content exceeds 7wt.%, the thermal expansion coefficient degrades, so the upper limit of Co content is specified as 7wt.%.

Chromium improves the corrosion resistance of alloy, but degrades (increase) thermal expansion coefficient. When the alloy is adjusted to have a gathering degree of planes, grain size, and hardness to satisfy the condition of the present invention, which condition is described below, an effect of improving corrosion resistance is obtained when the alloy has Co content of 0.01wt.% or more. On the other hand, when the Cr content exceeds 3wt.%, the alloy can not provide the average thermal expansion coefficient specified by the present invention. Chromium content of less than 0.01% gives no effect of improvement in corrosion resistance. Therefore, the upper limit and the lower limit of Cr content are specified as 3.0wt.% and 0.01wt.%, respectively.

Oxygen is one of the inevitable impurities. Increased content of O increases the non-metallic oxide inclusion in the alloy, which inclusion suppresses the growth of crystal grains during the annealing before press-forming. Particularly at the temperature less than 800°C , the O inclusion suppresses the grain growth. If the content of O exceeds 0.004wt.%, the growth of grains is significantly interfered, and the press-forming quality being aimed by the present invention can not be obtained. In this respect, the present invention specifies the upper limit of O content as 0.004wt.%. The lower limit of O content is not specifically limited, but it is substantially selected as 0.0001wt.% from the economy of ingot-making process.

B improves the hot-working performance of the alloy. Excess amount of B, however, induces the segregation of B at boundary of recrystallized grains formed during annealing before press-forming, which inhibits the free migration of grain boundaries and results in the suppression of grain growth and the dissatisfaction of necessary 0.2wt.% proof stress after the annealing before press-forming. In particular, under the annealing before press-forming at a relatively low temperature, which is specified in the present invention, the suppression against the grain growth is strong and the action does not uniformly affects on all grains. As a result, a severe mixed grain structure appears accompanied with irregular elongation of material during press-forming, which induces blurred periphery of pierced hole on shadow mask. Boron content above 0.005wt.% significantly enhances the suppression of grain growth, and the press-formability being aimed in the present invention can not be obtained. Also the problem of blurred periphery of pierced hole arises. Consequently, the present invention specifies the upper limit of B content as 0.005wt.%. From the above described viewpoint, more preferable B content is 0.001wt.% or less.

Silicon is added as the deoxidizer element during ingot-making of the alloy. When the Si content exceeds 0.2wt.%, an oxide film of Si is formed on the surface of alloy at the annealing before press-forming. The oxide film degrades the fitness with dies during press-forming and results in the galling of dies by alloy sheet. Consequently, the upper limit of Si content is specified as 0.2wt.%. Further reduction of Si content improves the fitness of dies and alloy sheet. The lower limit of Si content is not necessarily specified but approximately 0.001wt.% is the virtual lower limit from the economy of ingot-making process.

Nitrogen is an element unavoidably enters into the alloy during ingot-making process. Nitrogen content of 0.003wt.% or more induces the concentration of N on the surface of alloy during the annealing before press-forming and yields nitride. The nitride degrades the fitness of alloy with dies during the press-forming process and induces galling of dies by alloy sheet. Consequently, the N content is specified as 0.003wt.% or less. Although the lower limit of N content is not necessarily defined, approximately 0.0001wt.% is the virtual lower limit from the economy of ingot-making process.

Antimony is an element of unavoidable inclusion, and the Sb content more than 0.05wt.% interferes the growth of the alloy grains of the present invention, which inhibits to obtain a grain size being aimed in the

present invention. Consequently, the upper limit of Sb content is specified as 0.05wt.%.

Regarding the elements other than above described, preferable range of C is 0.0001 to 0.010wt.% and that of Mn is 0.001 to 0.5wt.%.

According to the present invention, to improve the shape fix ability, to suppress crack generation on alloy sheet surface during press-forming, and to prevent generation of blurred periphery of pierced hole of prepared shadow mask, it is necessary to define, in addition to the composition above specified, the specific range for each of the average austenite grain size, D_{av} , before the annealing before press-forming, the ratio of maximum size to minimum size of austenite grains, D_{max}/D_{min} , and the Vickers hardness, H_v , and furthermore it is necessary to limit the relation between the Vickers hardness, H_v , and the average austenite grain size, D_{av} , to satisfy a specific correlation.

Fig. 4 shows the effect of average austenite grain size, D_{av} , and Vickers hardness, H_v , before the annealing before press-forming on the press-formability. In that case, the alloy sheet had the composition specified in the present invention and had the values of the ratio of the maximum size to the minimum size of austenite grains, D_{max}/D_{min} , before annealing before press-forming and of the degree of each plane in the range specified in the present invention, and the alloy sheet was subjected to the annealing before press-forming at a temperature below 800 °C followed by the press-forming. According to Fig. 4, the value of D_{av} below 10.5 μ m can not enhance the growth of grain in alloy sheet during the annealing before press-forming under the temperature condition being aimed by the present invention, below 800 °C, and increases spring back and results in a poor shape fix ability because of the insufficient growth of grains. On the other hand, the value of D_{av} above 15.0 μ m hinders the recrystallization during the annealing before press-forming and results in a poor shape fix ability owing to the insufficient recrystallization.

Vickers hardness, H_v , is mainly determined by the reduction ratio of cold-rolling. The value of H_v below 165 can not give sufficient strain to the alloy sheet, and gives only a weak driving force for recrystallization during the annealing before press-forming. The result is insufficient recrystallization, which leaves the alloy sheet at a rather rigid state even after the annealing before press-forming. As a result, the shape fix ability is poor. On the other hand, when excess strain is given to the alloy sheet to induce H_v above 220, the driving force for recrystallization during the annealing before press-forming becomes strong, which yields excess frequency of nuclei formation during recrystallization. Consequently, the grains become fine after the annealing before press-forming to degrade the shape fix ability.

Fig. 4 also indicates that an adequate recrystallization during the annealing before press-forming is realized by keeping the relation between Vickers hardness, H_v , and average austenite grain size D_{av} . A large average austenite grain size, D_{av} , before the annealing before press-forming requests a large degree of strain for obtaining a sufficient driving force during the annealing before press-forming step. Accordingly, the lower limit of Vickers hardness, H_v , is necessary to be defined depending on the corresponding average austenite grain size, D_{av} . On the other hand, since smaller average austenite grain size, D_{av} , has larger number of nucleation sites, the upper limit of Vickers hardness, H_v , is necessary to be defined depending on the corresponding average austenite grain size, D_{av} , to prevent the generation of fine grains after the annealing before press-forming. According to Fig. 4, even the Vickers hardness, H_v , is 165 or more, if the equation of $[H_v < 10 \times D_{av} + 50]$ is satisfied, then the driving force for the recrystallization during the annealing before press-forming is relatively too small, and sufficient recrystallization can not be obtained. Therefore, the material remains rigid even after the annealing before press-forming and is poor in the shape fix ability. Even when the Vickers hardness, H_v , is 220 or less value, if the equation of $[H_v > 10 \times D_{av} + 80]$ is satisfied, then the driving force for the recrystallization during the annealing before press-forming is relatively too large, and the grains become fine after the annealing before press-forming and shape fix ability is poor.

Fig. 5 shows the effect of the ratio of the maximum size to the minimum size of austenite grains, D_{max}/D_{min} , before the annealing before press-forming on the blurred periphery of pierced hole of prepared shadow mask. In that case, the alloy sheet had the composition specified in the present invention and had the values of the average austenite grain size, D_{av} , before annealing before press-forming, the Vickers hardness, H_v , and the degree of each plane within the range specified in the present invention, and the alloy sheet was subjected to the annealing before press-forming at a temperature less than 800 °C followed by the press-forming. According to Fig. 5, when the ratio of the maximum size to the minimum size of austenite grains, D_{max}/D_{min} , exceeds 15, the etched hole size becomes irregular and induces blurred periphery of pierced hole. Smaller D_{max}/D_{min} value is more favorable, and the lower limit of the D_{max}/D_{min} is specified as 1.

From the consideration given above, the present invention specifies the average austenite grain size, D_{av} , before the annealing before press-forming as in a range of from 10.5 to 15.0 μ m, the ratio of the maximum size to the minimum size of the austenite grains, D_{max}/D_{min} , (which ratio is hereinafter referred

to simply as "degree of austenite mixed grain"), as in a range of from 1 to 15, and the Vickers hardness, Hv, as in a range of from 165 to 220, and also specifies the following equation:

$$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50$$

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for enhancing the growth of grain during the annealing before press-forming, for improving the shape fixability, and for suppressing the blurred periphery of pierced hole of prepared shadow mask.

For the prevention of crack generation during the press-forming and for the prevention of blurred periphery of pierced hole and partial color-phase shift on the prepared shadow mask, which are the objects of the present invention, it is important to limit the degree of planes on the alloy sheet surface before annealing before press-forming, as well as the limitations specified above.

The inventors found that the control of the degree of {211} plane on the alloy sheet surface before annealing before press-forming effectively suppresses the crack generation during press-forming and that the control of the degree of {100} plane and {110} plane suppresses the blurred periphery of pierced hole on the prepared shadow mask and that the control of the degree of {111} plane, {311} plane, {331} plane, and {210} plane suppresses the partial color-phase shift on the prepared shadow mask.

In concrete terms, when the degree of {211} plane exceeds 20%, the alloy sheet generates cracks during press-forming.

When the degree of {111} plane, {311} plane, {331} plane, and {210} plane exceeds 14%, 20%, 20%, and 20%, respectively, the etched hole shape abnormally deforms during press-forming, which induces partial color-phase shift.

The control of the degree of {100} plane and {110} plane is necessary for limiting the degree of austenite mixed grain, D_{max}/D_{min} , within the range specified in the present invention. When the degree of {100} plane exceeds 75% or when the degree of {110} plane exceeds 40%, the degree of austenite mixed grain exceeds 15. In that case, the recrystallization during the annealing before press-forming does not proceed uniformly, and the grains after the annealing before press-forming become mixed grain state inducing blurred periphery of pierced hole on the prepared shadow mask. When the degree of {100} plane is less than 5%, the degree of {110} plane exceeds 40%. When the degree of {110} plane is less than 5%, the degree of {100} plane exceeds 75%. In both cases, the degree of austenite mixed grain, D_{max}/D_{min} , exceeds 15 and induces blurred periphery of pierced hole on the prepared shadow mask.

Fig. 6 shows the relation between the degree of {100} plane and the degree of austenite mixed grain, D_{max}/D_{min} . According to Fig. 6, the degree of austenite mixed grain can be controlled within a range of 1 to 15 by controlling the degree of {100} plane within a range of 5 to 75%. The degree of mixed grain is further reduced by controlling the degree of {100} plane within a further limited range of 8 to 46% for more effective suppression of blurred periphery of pierced hole.

From the consideration given above, the present invention specifies the degree of each plane on the alloy sheet before annealing before press-forming as listed below:

Degree of {111} plane : 14% or less
 Degree of {100} plane : 5 to 75%
 Degree of {110} plane : 5 to 40%
 Degree of {311} plane : 20% or less
 Degree of {331} plane : 20% or less
 Degree of {210} plane : 20% or less
 Degree of {211} plane : 20% or less

The value of the degree given above is the relative rate of each plane to the total degree of planes, {111}, {100}, {110}, {311}, {331}, {210}, and {211}.

The degree of each plane is determined from the degree of each plane divided by the sum of the degree of planes, {111}, {100}, {110}, {311}, {331}, {210}, and {211}, and expressed by percentage.

The degree of each plane, {111}, {100}, {110}, {311}, {331}, {210}, and {211}, before the annealing before press-forming, which is specified by the present invention, is normally obtained by selecting adequate condition of treatment after the hot-rolling step.

For example, when an alloy sheet of the present invention is produced by hot-rolling a slab which was prepared by slabbing or continuous casting followed by a sequence of annealing of hot-rolled sheet, primary cold-rolling, recrystallization annealing, secondary cold-rolling, recrystallization annealing, finish cold rolling, and stress relief annealing, an effective condition to obtain the degree of plane defined above is the control of the annealing temperature during the annealing of hot-rolled sheet step at an adequate level in a range of from 910 to 990 °C and furthermore the selection of optimum condition of cold-rolling, recrystallization annealing, finish cold-rolling, and stress relief annealing.

To obtain the degree of planes specified by the present invention, the uniform heat treatment of a slab after blooming or after continuous casting is not preferable. For instance, when the uniform heat treatment is carried out at 1200 °C or higher temperature and for 10 hours or longer period, the degree of one or more of the planes {111}, {100}, {110}, {311}, {331}, {210}, and {211} dissatisfies the specification of the present invention. Therefore, such a uniform heat treatment should be avoided.

Other means may be employed to satisfy the degree of planes specified by the present invention. Quenching to solidify and texture controlling through the control of recrystallization during hot working are some of the examples of applicable means.

The alloy sheet of the present invention may be subjected to the annealing before press-forming before the photo-etching step. If the annealing before press-forming is performed at a relatively low temperature which is a condition of the present invention, the quality of photo-etching is not degraded. In a conventional material, if the photo-etching is applied after the annealing before press-forming at a relatively low temperature specified by the present invention, the quality of the photo-etching is degraded, so the annealing before press-forming is virtually not applicable before the photo-etching. On the contrary, the materials of the present invention accept the photo-etching after the annealing before press-forming without degrading the etching performance.

Example 2

The inventors prepared the alloys of No. 1 through No. 23 having the composition listed on Table 7 by ladle refining. The alloys No. 1 through No. 13 were further treated by continuous casting to obtain the continuous cast slabs, and the alloys No. 18 through No. 23 were treated by molding to obtain ingots, which ingots were then treated by adjusting and slabbing to prepare the slabs. Those slabs were subjected to surface treatment and were charged into a furnace to be heated at 1100 °C for 3 hours followed by hot-rolling to obtain the hot-rolled sheets.

Alloys No. 14 through No. 17 were cast directly into cast sheets which were then hot-rolled in the temperature range of 1000 to 1300 °C at the reduction ratio of 30% and were coiled at 750 °C to obtain the hot-rolled sheets.

Table 7

Alloy No.	Chemical composition 1)										
	Ni	Si	O	N	B	C	Mn	Cr	H(ppm)	Co	Sb
1	35.8	0.005	0.0020	0.0008	0.00005	0.0012	0.27	0.01	1.1	—	0.01
2	36.2	0.04	0.0018	0.0012	0.0001	0.0011	0.25	0.03	0.2	—	0.02
3	36.4	0.03	0.0015	0.0014	0.0001	0.0017	0.05	0.50	0.9	0.001	0.02
4	36.6	0.05	0.0022	0.0015	0.0005	0.0040	0.35	0.02	1.0	0.023	0.01
5	35.5	0.01	0.0019	0.0010	0.0002	0.0024	0.28	1.02	1.0	—	0.01
6	35.6	0.02	0.0014	0.0008	0.0001	0.0020	0.27	1.50	0.9	0.505	0.02
7	36.0	0.02	0.0009	0.0007	0.0002	0.0010	0.12	0.03	0.7	—	0.02
8	36.2	0.05	0.0006	0.0006	0.0001	0.0006	0.05	0.03	0.8	0.500	0.01
9	36.0	0.001	0.0001	0.0002	0.0001	0.0005	0.005	0.04	0.6	0.005	0.005
10	35.6	0.01	0.0017	0.0014	0.0001	0.0032	0.02	2.00	0.7	—	0.01
11	35.7	0.07	0.0016	0.0012	0.0002	0.0030	0.22	0.07	0.3	—	0.02
12	35.2	0.06	0.0018	0.0016	0.0004	0.0049	0.17	0.03	0.5	0.751	0.02
13	36.0	0.01	0.0016	0.0018	0.0001	0.0037	0.08	0.05	0.8	0.050	0.02
14	31.8	0.15	0.0024	0.0014	0.0001	0.0088	0.50	2.80	0.4	0.320	0.02
15	31.1	0.18	0.0024	0.0019	0.0001	0.0020	0.32	0.04	0.8	5.950	0.03
16	30.2	0.17	0.0037	0.0017	0.0002	0.0021	0.40	0.06	0.8	4.100	0.04
17	29.6	0.01	0.0016	0.0020	0.0010	0.0055	0.50	2.95	0.9	6.520	0.05
18	35.7	0.21	0.0022	0.0016	0.0005	0.0024	0.28	0.03	1.1	—	0.02
19	36.2	0.05	0.0045	0.0013	0.0001	0.0027	0.32	0.04	1.1	—	0.02
20	36.1	0.03	0.0018	0.0035	0.0002	0.0019	0.28	<0.01	1.3	0.020	0.02
21	36.1	0.02	0.0018	0.0015	0.0055	0.0025	0.30	0.05	1.2	0.012	0.02
22	35.8	0.09	0.0028	0.0016	0.0021	0.0042	0.28	0.04	1.3	—	0.03
23	34.1	0.08	0.0023	0.0008	0.0005	0.0027	0.32	0.06	0.9	2.530	0.06

1) Unit of chemical composition is wt.% except for H

From these hot-rolled sheets of alloys No. 1 through No. 23, the alloy sheets of No. 1 through No. 34 listed on Table 8 and Table 9 were prepared.

In Table 8 and Table 9, D_{max} represents the maximum austenite grain size in alloy sheet, and D_{min} represents the minimum austenite grain size in the alloy sheet.

Table 8

Material No.	Alloy No.	Average grain size Dav (μm)	Dmax/Dmin	Vickers hardness before annealing before press-forming (Hv)	$10 \times \text{Dav} + 80 - \text{Hv}$	Hv-10 \times Dav -50	Type of example
1	1	11.7	5.1	180	Positive	Positive	Present invention
2	2	11.7	15.0	181	Positive	Positive	Present invention
3	3	11.9	6.4	176	Positive	Positive	Present invention
4	4	12.5	13.0	205	0	Positive	Present invention
5	5	12.5	8.2	174	Positive	Positive	Present invention
6	6	12.4	11.1	190	0	Positive	Present invention
7	7	11.2	11.5	191	Positive	Positive	Present invention
8	8	13.7	15.0	187	Positive	Positive	Present invention
9	9	11.5	11.9	165	0	Positive	Present invention
10	10	10.6	9.1	186	0	Positive	Present invention
11	11	10.8	10.2	165	Positive	Positive	Present invention
12	12	14.0	11.8	218	Positive	Positive	Present invention
13	13	15.0	9.7	220	Positive	Positive	Present invention
14	14	12.6	5.5	178	Positive	Positive	Present invention
15	15	12.7	7.1	180	Positive	Positive	Present invention
16	16	12.5	6.3	176	Positive	Positive	Present invention
17	17	13.0	6.7	201	Positive	Positive	Present invention

Table 9

Material No.	Alloy No.	Average grain size Dav (μm)	Dmax/Dmin	Vickers hardness before annealing before press-forming (Hv)	10×Dav+80-Hv	Hv-10×Dav-50	Type of example
18	18	10.6	14.2	185	Positive	Positive	Comparative example
19	19	8.9	19.6	176	Negative	Positive	Comparative example
20	20	10.5	14.9	173	Positive	Positive	Comparative example
21	21	9.0	18.6	180	Negative	Positive	Comparative example
22	22	10.0	20.2	182	Negative	0	Comparative example
23	23	10.0	10.0	161	Positive	Positive	Comparative example
24	24	15.6	14.0	206	Positive	Positive	Comparative example
25	1	9.5	14.6	170	Positive	Positive	Comparative example
26	2	10.5	22.0	180	Positive	Positive	Comparative example
27	5	11.0	14.1	226	Negative	Positive	Comparative example
28	2	10.9	13.5	163	Positive	Positive	Comparative example
29	6	11.9	15.0	200	Negative	Positive	Comparative example
30	9	13.3	12.0	176	Positive	Negative	Comparative example
31	4	10.8	16.8	170	Positive	Positive	Comparative example
32	3	11.5	6.3	186	Positive	Positive	Comparative example
33	4	10.9	6.0	167	Positive	Positive	Comparative example
34	7	11.1	13.0	190	Positive	Positive	Comparative example

The alloy sheets of materials No. 1 through No. 21 and No. 27 through No. 30 prepared from the hot-rolled alloy sheets No. 1 through No. 21 had the thickness of 0.13mm and were produced by the process (1) given below.

(1) annealing of hot-rolled sheet in the temperature range of 910 to 990 °C - primary cold-rolling - recrystallization annealing in the temperature range of 860 to 940 °C for 125sec. - secondary cold-rolling - recrystallization annealing in the temperature range of 860 to 940 °C for 125sec. - finish cold-rolling at the reduction ratio of 15% - stress relief annealing at 530 °C for 30sec.

The alloy sheets of materials No. 22 and No. 26 prepared from the hot-rolled sheets of alloys No. 22 and No. 26 had the thickness of 0.13mm and were produced by the process (2) given below.

(2) primary cold-rolling at the reduction ratio of 92.5% - recrystallization annealing at 850 °C for 60sec. - finish cold-rolling at the reduction ratio of 15% - stress relief annealing at 530 °C for 30sec.

The alloy sheet of material No. 23 prepared from the hot-rolled sheet of alloy No. 23 had the thickness of 0.13mm and was produced by the process (3) given below.

(3) annealing of hot-rolled sheet at 970 °C - primary cold-rolling - recrystallization annealing at 860 °C for 30sec. - secondary cold-rolling - recrystallization annealing at 860 °C for 30sec. - finish cold-rolling - stress relief annealing at 530 °C for 30sec.

The alloy sheet of material No. 24 prepared from the hot-rolled sheet of alloy No. 1 had the thickness of 0.13mm and was produced by the process (4) given below.

(4) annealing of hot-rolled sheet at 950 °C - primary cold-rolling at the reduction ratio of 74% - recrystallization annealing at 950 °C for 180sec. - secondary cold-rolling at the reduction ratio of 40% - recrystallization at 950 °C for 180sec. - finish cold-rolling at the reduction ratio of 15% - stress relief annealing at 530 °C for 30sec.

The alloy sheets of materials No. 25 prepared from the hot-rolled sheet of alloy No. 1 had the thickness of 0.13mm and was produced by the process (5) given below.

(5) annealing of hot-rolled sheet at 950 °C - primary cold-rolling - recrystallization annealing at 800 °C for 30sec. - secondary cold-rolling - recrystallization annealing at 800 °C for 30sec. - finish cold-rolling - stress relief annealing at 530 °C for 30sec.

The alloy sheets of materials No. 31 and No. 33 prepared from the hot-rolled sheet of alloy No. 4, and the alloy sheet of material No. 32 prepared from the hot-rolled sheet of alloy No. 3, and the alloy sheet of material No. 34 prepared from the hot-rolled sheet of alloy No. 7 had the thickness of 0.13mm and were produced by the process (6) given below.

(6) primary cold-rolling - recrystallization annealing in the temperature range of 860 to 940 °C for 125sec. - secondary cold-rolling - recrystallization annealing in the temperature range of 860 to 940 °C for 125sec. - finish cold-rolling - stress relief annealing at 530 °C for 30sec.

All those produced hot-rolled sheets showed sufficient recrystallization after annealing.

The alloy sheets of materials No. 1 through No. 12 and No. 15 through No. 34 prepared by the treatment described above were etched and formed into flat masks (shadow masks before the press-forming). The flat masks were treated by the annealing before press-forming at 770 °C for 45min., followed by press-forming. The press-formability was tested during the procedure. Partial color-phase shift was measured after blackening the press-formed shadow masks, assembling them into cathode ray tubes, and irradiating electron beam on the surface thereof. The alloy sheets of materials No. 13 and No. 14 were subjected to the annealing before press-forming at 795 °C for 3min., which were then etched and formed into flat masks. Those flat masks were press-formed to determine the press-formability. Those alloys were also checked for the partial color-phase shift using the same procedure as before.

Table 8 and Table 9 give the average austenite grain size, D_{av} , before annealing before press-forming, the degree of austenite mixed grain, D_{max}/D_{min} , the Vickers hardness, Hv, and identification of the sign of $[10 \times D_{av} + 80 - Hv]$ and $[Hv - 10 \times D_{av} - 50]$. Table 10 and Table 11 give the degree of each plane on the sheet surface before the annealing before press-forming, the press-formability, the partial color-phase shift, and the corrosion resistance.

In Table 10 and Table 11, the criteria for evaluation of the shape fix ability, the fitness of dies and alloy sheet, and the blurred periphery of pierced hole are the following.

Regarding the shape fix ability, "◎" mark indicates "very good", "○" indicates "good", and "X" indicates "rather poor".

As for the fitness of dies and alloy sheet, "○" mark indicates "good without ironing mark", "△" indicates "rather poor with a few ironing marks", and "X" indicates "poor with lots of ironing marks".

For the blurred periphery of pierced hole, "◎" mark indicates "definitely none", "○" indicates "none", "△" indicates "found some", and "X" indicates "generated".

The spot rust frequency is the number of spot corruptions per 1cm² of the alloy surface, determined by the salt water spray test for 50 hours in accordance with JIS Z 2371.

Table 10

Material No.	Alloy No.	Gathering degree of the crystal plane on the alloy sheet before annealing before press-forming							Press-formability				Partial color phase shift	Corrosion resistance	Type of examples
		{111}	{100}	{110}	{311}	{331}	{210}	{211}	Shape fix ability	Fitness to die	Cracking on the alloy sheet	Blurred periphery of pierced hole		Generation of spot rust	
1	1	9	17	23	14	12	13	12	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
2	2	2	75	8	2	7	3	3	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
3	3	5	27	30	12	7	11	8	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	3	Present invention
4	4	3	64	14	6	7	4	2	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
5	5	7	35	23	13	8	10	4	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	2	Present invention
6	6	6	50	16	7	9	5	5	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	2	Present invention
7	7	9	20	28	10	10	11	10	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
8	8	4	5	37	17	12	13	12	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
9	9	4	53	15	8	9	6	5	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
10	10	6	43	21	9	9	7	5	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	1	Present invention
11	11	11	8	30	15	11	12	13	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	4	Present invention
12	12	10	7	34	16	12	10	11	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
13	13	7	46	17	8	9	6	5	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	1	Present invention
14	14	9	24	29	10	9	9	10	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	0	Present invention
15	15	7	29	24	10	10	10	10	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	5	Present invention
16	16	7	24	32	11	9	8	9	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	4	Present invention
17	17	5	30	35	8	8	8	6	◎◎◎◎◎	○○○○○○○○	None	◎◎	None	0	Present invention

Table 11

Material No.	Alloy No.	Gathering degree of the crystal plane on the alloy sheet before annealing before press-forming							Press-formability			Partial color phase shift	Corrosion resistance	Type of examples
		{111}	{100}	{110}	{311}	{331}	{210}	{211}	Shape fix ability	Fitness to die	Cracking on the alloy sheet	Blurred periphery of pierced hole		
18	18	2	64	12	7	8	5	2	○	×	None	○	6	Comparative example
19	19	1	90	3	2	2	1	1	×	○	Yes	×	6	Comparative example
20	20	3	74	5	4	7	4	3	○	×	None	○	11	Comparative example
21	21	2	86	3	2	4	2	1	×	×	Yes	×	6	Comparative example
22	22	1	93	0	1	3	1	1	×	○	Yes	×	6	Comparative example
23	23	9	46	24	8	4	5	4	×	○	Yes	⊙	5	Comparative example
24	1	3	7	10	2	9	4	2	×	○	None	○	5	Comparative example
25	1	3	7	7	3	8	5	4	×	○	None	○	5	Comparative example
26	2	0	97	3	0	0	0	0	○	○	None	×	5	Comparative example
27	5	1	74	8	4	6	5	2	×	○	None	○	2	Comparative example
28	2	1	66	9	7	9	7	1	×	○	None	○	5	Comparative example
29	6	12	5	40	10	11	11	11	×	○	None	○	2	Comparative example
30	6	11	8	37	13	9	10	13	×	○	None	○	2	Comparative example
31	4	13	3	45	9	9	11	10	×	○	None	○	3	Comparative example
32	3	16	16	6	22	15	13	12	○	○	None	△	5	Comparative example
33	4	8	25	32	3	3	3	26	○	○	Yes	○	3	Comparative example
34	7	14	7	14	11	21	23	10	○	○	None	○	5	Comparative example

According to Table 8 through Table 10, Fe-Ni alloy sheets of materials No. 1 through No. 13 satisfied the conditions specified by the present invention, which conditions include the degree of planes, {111}, {100}, {110}, {311}, {331}, {210}, and {211}, the average austenite grain size, D_{av} , the degree of austenite mixed grain, D_{max}/D_{min} , the Vickers hardness, H_v , and the condition of $[10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50]$. All of those Fe-Ni alloy sheets gave an excellent press-formability without giving

partial color-phase shift.

Also the Fe-Ni-Co alloy sheets of materials No. 14 through No. 17 satisfied the conditions specified by the present invention. All of those Fe-Ni-Co alloy sheets gave an excellent press-formability without giving partial color-phase shift.

Alloy sheets of materials No. 13 and No. 14 were subjected to annealing before press-forming before the etching. Even under the processing, those alloy sheets obtained the optimum functions as the shadow mask.

All of those alloy sheets of materials No. 1 through No. 17 clearly had superior characteristics to those of the Comparative materials which will be described below.

The alloy sheet of Comparative material No. 18 contained Si larger than the upper limit of the present invention, 0.2wt.%. The alloy sheet of Comparative material No. 20 contained N more than the upper limit of the present invention, 0.003wt.%. Both alloy sheets raised a problem of fitness with dies during press-forming.

The alloy sheet of Comparative material No. 19 contained O more than the upper limit of the present invention, 0.004wt.%. The alloy sheet of Comparative material No. 23 contained Sb more than the upper limit of the present invention, 0.05wt.%. Both alloy sheets gave the average austenite grain size, D_{av} , before the annealing before press-forming less than the lower limit of the present invention, $10.5\mu\text{m}$, gave a poor shape fix ability at press-forming, and generated cracks on the sheet surface.

The alloy sheet of Comparative material No. 19 also gave the degree of austenite mixed grain, D_{max}/D_{min} , more than the upper limit of the present invention, 15, so it induced blurred periphery of pierced hole.

The alloy sheet of Comparative material No. 20 contained Co less than the lower limit of the present invention, 0.001wt.%, so the corrosion resistance was significantly inferior to the Examples of the present invention.

The alloy sheet of Comparative material No. 21 contained B more than the upper limit of the present invention, 0.005wt.%, so the average austenite grain size, D_{av} , before the annealing before press-forming was less than the lower limit of the present invention, $10.5\mu\text{m}$, and the shape fix ability was poor, and generated cracks on the sheet surface. The alloy sheet of material No. 21 had the degree of austenite mixed grain, D_{max}/D_{min} , more than the upper limit of the present invention, 15, so the blurred periphery of pierced hole occurred.

The alloy sheet of Comparative material No. 22 was produced by the process (7) given below without employing hot-rolled annealing. The process employed is the same as disclosed in the Japanese Patent Unexamined Publication No. 3-267320 which was described before.

(7) primary cold-rolling at the reduction ratio of 92.5% - recrystallization annealing at 850°C for 60sec. - finish cold-rolling at the reduction ratio of 15% - stress relief annealing at 530°C for 30sec.

The alloy sheet of Comparative material No. 22 gave the degree of $\{100\}$ plane above the upper limit of the present invention, 75%, and gave the degree of $\{110\}$ plane below the lower limit of the present invention, 5%, and further gave the degree of austenite mixed grain, D_{max}/D_{min} , above the upper limit of the present invention, 15.

The alloy sheet of Comparative material No. 24 was subjected to recrystallization annealing at 950°C for 180sec. after the primary cold-rolling and the secondary cold-rolling. The alloy sheet of Comparative material No. 25 was subjected to recrystallization annealing at 800°C for 30sec. after the primary cold-rolling and the secondary cold-rolling. The alloy sheet of material No. 24 gave the average austenite grain size, D_{av} , before the annealing before press-forming more than the upper limit of the present invention, $15\mu\text{m}$, and the alloy sheet of material No. 25 gave the value less than the lower limit of this invention, $10.5\mu\text{m}$. Both alloy sheets showed poor shape fix ability at press-forming.

The alloy sheet of Comparative material No. 26 was produced by the process employed for the preparation of the alloy sheet of No. 22. The alloy sheet gave the degree of $\{100\}$ plane more than the upper limit of the present invention, 75%, gave the degree of $\{110\}$ plane less than the lower limit of the present invention, 5%, and gave the degree of austenite mixed grain, D_{max}/D_{min} , more than the upper limit of the present invention, 15. As a result, the alloy sheet generated blurred periphery of pierced hole. Consequently, even an alloy sheet which satisfies the specification of composition of the present invention, it can not give an excellent press-formability if it does not satisfy the conditions of the present invention on the degree of each plane and on the degree of austenite mixed grain, D_{max}/D_{min} .

The alloy sheet of Comparative material No. 27 gave the Vickers hardness, H_v , more than the upper limit of the present invention, 220. The alloy sheet of Comparative material No. 28 gave the Vickers hardness, H_v , less than the lower limit of the present invention, 165. The alloy sheet of Comparative material No. 29 gave the Vickers hardness, H_v , more than the value of $(10 \times D_{av} + 80)$ specified by the

present invention. The alloy sheet of Comparative material No. 30 gave the Vickers hardness, Hv, less than the value of $(10 \times D_{av} + 50)$ specified by the present invention. As a result, all of these alloy sheets gave poor shape fix ability.

The alloy sheets of Comparative materials No. 31 through No. 34 were produced by the process which was employed to prepare the alloy sheets of materials No. 1 through No. 21 without applying annealing of hot-rolled sheet. The alloy sheet of material No. 31 gave the degree of $\{110\}$ plane more than the upper limit of the present invention, 40%, and gave the degree of austenite mixed grain, D_{max}/D_{min} , more than the upper limit of the present invention, 15, so the sheet generated blurred periphery of pierced hole. The alloy sheet of material No. 32 gave the degree of $\{111\}$ plane more than the upper limit of the present invention, 14%, and gave the degree of $\{311\}$ plane more than the upper limit of the present invention, 20%, so the sheet induced partial color-phase shift. The alloy sheet of material No. 33 gave the degree of $\{211\}$ plane more than the upper limit of the present invention, 20%, so the sheet generated cracks on the sheet surface. The alloy sheet of material No. 34 gave the degree of $\{331\}$ plane and $\{210\}$ plane more than the upper limit of the present invention, 20%, so the sheet induced partial color-phase shift.

As described in detail above, an alloy sheet for shadow mask having excellent press-formability and screen quality is obtained by producing an alloy sheet which satisfies the conditions specified in the present invention, which conditions include the composition of the alloy, the gathering degree of each plane of the alloy sheet before annealing before press-forming, the average austenite grain size, D_{av} , before the annealing before press-forming, the degree of austenite mixed grain, D_{max}/D_{min} , the Vickers hardness, Hv, and the relation of $[10 \times D_{av} + 80 \geq Hv \geq 10 \times D_{av} + 50]$.

The present invention provides an alloy sheet for shadow mask which has excellent shape fix ability during press-forming, shows good fitness with dies, suppresses crack generation on the material, induces no blurred periphery of pierced hole, is free from color-phase shift, and has corrosion resistance.

The above described alloy sheets of the present invention offer favorable etching quality and press-formability even they are subjected to the annealing before press-forming before the etching. Accordingly, the present invention provides an additional advantage for the manufacturer of cathode ray tubes to eliminate the annealing before press-forming if the supplier of the alloy sheets carries out the annealing before press-forming in advance.

Claims

1. An alloy sheet consisting essentially of 34 to 38wt.% Ni, 0.07wt.% or less Si, 0.001wt.% or less B, 0.003wt.% or less O, 0.002wt.% or less N, and the balance being Fe and inevitable impurities;

said alloy sheet before annealing before press-forming having an average austenite grain size (D_{av}) of 10.5 to 15.0 μ m, a ratio of a maximum size to the minimum size of austenite grains (D_{max}/D_{min}) of 1 to 15, a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of

$$10 \times D_{av} + 80 \geq Hv \geq 10 \times D_{av} + 50; \text{ and}$$

said alloy sheet having gathering degree of crystal planes on said alloy sheet surface of

14% or less for $\{111\}$ plane,

5 to 75% for $\{100\}$ plane,

5 to 40% for $\{110\}$ plane,

20% or less for $\{311\}$ plane,

20% or less for $\{331\}$ plane,

20% or less for $\{210\}$ plane, and

20% or less for $\{211\}$ plane.

2. The alloy sheet of Claim 1, wherein said Ni content is 35 to 37wt.%.
3. The alloy sheet of Claim 2, wherein said Ni content is 35.5 to 36.5wt.%.
4. The alloy sheet of Claim 1, wherein said O content is 0.0001 to 0.003wt.%.
5. The alloy sheet of Claim 1, wherein said B content is 0.0002wt.% or less.
6. The alloy sheet of Claim 1, wherein said Si content is 0.001 to 0.07wt.%.

7. The alloy sheet of Claim 1, wherein said N content is 0.0001 to 0.002wt.%.
8. The alloy sheet of Claim 1, wherein said ratio of the maximum size to the minimum size of austenite grains (D_{\max}/D_{\min}) is 1 to 10.
- 5 9. The alloy sheet of Claim 1, wherein said gathering degree of {100} plane is 8 to 46.
- 10 10. An alloy sheet consisting essentially of 34 to 38wt.% Ni, 0.07wt.% or less Si, 1wt.% or less Co, 0.001wt.% or less B, 0.003wt.% or less O, 0.002wt.% or less N, and the balance being Fe and inevitable impurities;
said alloy sheet before annealing before press-forming having an average austenite grain size (D_{av}) of 10.5 to 15.0 μm , a ratio of a maximum size to a minimum size of austenite grains (D_{\max}/D_{\min}) of 1 to 5, a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of
15 $10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50$; and
said alloy sheet having gathering degree of crystal plane on said alloy sheet surface of
14% or less for {111} plane,
5 to 75% for {100} plane,
20 5 to 40% for {110} plane,
20% or less for {311} plane,
20% or less for {331} plane,
20% or less for {210} plane, and
20% or less for {211} plane.
- 25 11. The alloy sheet of Claim 10, wherein said Ni content is 35 to 37wt.%.
12. The alloy sheet of Claim 11, wherein said Ni content is 35.5 to 36.5wt.%.
- 30 13. The alloy sheet of Claim 10, wherein said O content is 0.0001 to 0.003wt.%.
14. The alloy sheet of Claim 10, wherein said B content is 0.0002wt.% or less.
15. The alloy sheet of Claim 10, wherein said Si content is 0.001 to 0.07wt.%.
- 35 16. The alloy sheet of Claim 10, wherein said N content is 0.0001 to 0.002wt.%.
17. The alloy sheet of Claim 10, wherein said ratio of the maximum size to the minimum size of austenite grains (D_{\max}/D_{\min}) is 1 to 10.
- 40 18. The alloy sheet of Claim 10, wherein said degree of {100} plane is 8 to 46.
- 45 19. An alloy sheet consisting essentially of 28 to 38wt.% Ni, 0.07wt.% or less Si, over 1wt.% to 7wt.% Co, 0.001wt.% or less B, 0.003wt.% or less O, 0.002wt.% or less N, and the balance being Fe and inevitable impurities;
said alloy sheet before annealing before press-forming having an average austenite grain size (D_{av}) of 10.5 to 15.0 μm , a ratio of a maximum size to a minimum size of austenite grains (D_{\max}/D_{\min}) of 1 to 15, and a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of
50 $10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50$; and
said alloy sheet having gathering degrees of crystal planes on said alloy sheet surface of
14% or less for {111} plane,
5 to 75% for {100} plane,
55 5 to 40% for {110} plane,
20% or less for {311} plane,
20% or less for {331} plane,
20% or less for {210} plane, and

20% or less for {211} plane.

20. The alloy sheet of Claim 19, wherein said Ni content is 30 to 33wt.% and said Co content is 3 to 6wt.%.

21. The alloy sheet of Claim 19, wherein said O content is 0.0001 to 0.003wt.%.

22. The alloy sheet of Claim 19, wherein said B content is 0.0002wt.% or less.

23. The alloy sheet of Claim 19, wherein said Si content is 0.001 to 0.07wt.%.

24. The alloy sheet of Claim 19, wherein said N content is 0.0001 to 0.002wt.%.

25. The alloy sheet of Claim 19, wherein said ratio of the maximum size to the minimum size of austenite grains, D_{max}/D_{min} , is 1 to 10.

26. The alloy sheet of Claim 19, wherein the gathering degree of {100} plane is 8 to 46.

27. An alloy sheet consisting essentially of 34 to 38wt.% Ni, 0.01 to 3wt.% Cr, 0.2wt.% or less Si, 0.005wt.% or less B, 0.004wt.% or less O, 0.003wt.% or less N, 0.05wt.% or less Sb, and the balance being Fe and inevitable impurities;

said alloy sheet before annealing before press-forming having an average austenite grain size (D_{av}) of 10.5 to 15.0 μ m, a ratio of a maximum size to a minimum size of austenite grains (D_{max}/D_{min}) of 1 to 15, and a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of

$10 \times D_{av} + 80 > Hv > 10 \times D_{av} + 50$; and

said alloy sheet having gathering degrees of crystal planes on said alloy sheet surface of
 14% or less for {111} plane,
 5 to 75% for {100} plane,
 5 to 40% for {110} plane,
 20% or less for {311} plane,
 20% or less for {331} plane,
 20% or less for {210} plane, and
 20% or less for {211} plane.

28. The alloy sheet of Claim 27, wherein said Ni content is 35.5 to 37wt.%.

29. The alloy sheet of Claim 28, wherein said Ni content is 35.5 to 36.5wt.%.

30. The alloy sheet of Claim 27, wherein said O content is 0.0001 to 0.004wt.%.

31. The alloy sheet of Claim 27, wherein said B content is 0.001wt.% or less.

32. The alloy sheet of Claim 27, wherein said Si content is 0.001 to 0.2wt.%.

33. The alloy sheet of Claim 27, wherein said N content is 0.0001 to 0.003wt.%.

34. The alloy sheet of Claim 27, wherein said ratio of the maximum size to the minimum size of austenite grains, D_{max}/D_{min} , is 1 to 10.

35. The alloy sheet of Claim 27, wherein said degree of {100} plane is 8 to 46.

36. An alloy sheet consisting essentially of 34 to 38wt.% Ni, 0.01 to 3wt.% Cr, 1wt.% or less Co, 0.2wt.% or less Si, 0.005wt.% or less B, 0.004wt.% or less O, 0.003wt.% or less N, 0.05wt.% or less Sb, and the balance being Fe and inevitable impurities;

said alloy sheet before annealing before press-forming having an average austenite grain size (D_{av}) of 10.5 to 15.0 μ m, a ratio of a maximum size to a minimum size of austenite grains (D_{max}/D_{min}) of 1

to 15, and a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of

$$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50; \text{ and}$$

- 5 said alloy sheet having gathering degrees of crystal planes on said alloy sheet surface of
 14% or less for {111} plane,
 5 to 75% for {100} plane,
 5 to 40% for {110} plane,
 20% or less for {311} plane,
 10 20% or less for {331} plane,
 20% or less for {210} plane, and
 20% or less for {211} plane.
37. The alloy sheet of Claim 36, wherein said Ni content is 35.5 to 37wt.%.
- 15 38. The alloy sheet of Claim 37, wherein said Ni content is 35.5 to 36.5wt.%.
39. The alloy sheet of Claim 36, wherein said O content is 0.0001 to 0.004wt.%.
- 20 40. The alloy sheet of Claim 36, wherein said B content is 0.001wt.% or less.
41. The alloy sheet of Claim 36, wherein said Si content is 0.001 to 0.2wt.%.
42. The alloy sheet of Claim 36, wherein said N content is 0.0001 to 0.003wt.%.
- 25 43. The alloy sheet of Claim 36, wherein said ratio of the maximum size to the minimum size of austenite
 grains (D_{max}/D_{min}) is 1 to 10.
44. The alloy sheet of Claim 36, wherein said gathering degree of {100} plane is 8 to 46.
- 30 45. A alloy sheet consisting essentially of 28 to 38wt.% Ni, 0.01 to 3wt.% Cr, over 1wt.% to 7wt.% Co,
 0.2wt.% or less Si, 0.005wt.% or less B, 0.004wt.% or less O, 0.003wt.% or less N, 0.05wt.% or less
 Sb, and the balance being Fe and inevitable impurities;
 said alloy sheet before annealing before press-forming having an average austenite grain size (D_{av})
 35 of 10.5 to 15.0 μ m, a ratio of a maximum size to a minimum size of austenite grains (D_{max}/D_{min}) of 1
 to 15, and a Vickers hardness (Hv) of 165 to 220 and satisfying a relation of
- $$10 \times D_{av} + 80 \geq H_v \geq 10 \times D_{av} + 50; \text{ and}$$
- 40 said alloy sheet having gathering degrees of crystal planes on said alloy sheet surface of
 14% or less for {111} plane,
 5 to 75% for {100} plane,
 5 to 40% for {110} plane,
 20% or less for {311} plane,
 45 20% or less for {331} plane,
 20% or less for {210} plane, and
 20% or less for {211} plane.
46. The alloy sheet of Claim 45, wherein said Ni content is 30 to 33wt.% and said Co content is 3 to
 50 6wt.%.
47. The alloy sheet of Claim 45, wherein said O content is 0.0001 to 0.004wt.%.
48. The alloy sheet of Claim 45, wherein said B content is 0.001wt.% or less.
- 55 49. The alloy sheet of Claim 45, wherein said Si content is 0.001 to 0.2wt.%.
50. The alloy sheet of Claim 45, wherein said N content is 0.0001 to 0.003wt.%.

51. The alloy sheet of Claim 45, wherein said ratio of the maximum size to the minimum size of austenite grains (D_{\max}/D_{\min}) is 1 to 10.

52. The alloy sheet of Claim 45, wherein said gathering degree of $\{100\}$ plane is 8 to 46.

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53. The use of an alloy sheet according to any of the preceding claims for the making of a shadow mask.

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FIG.1

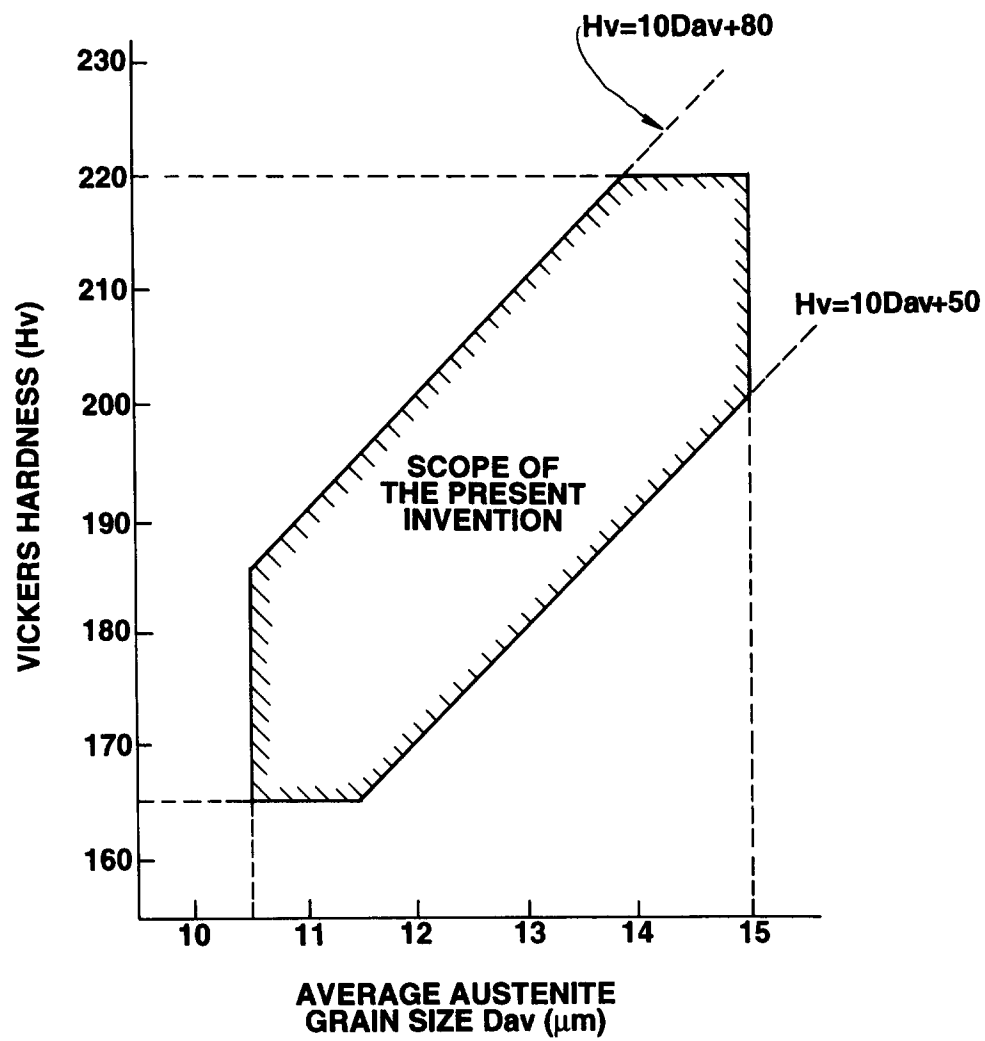


FIG.2

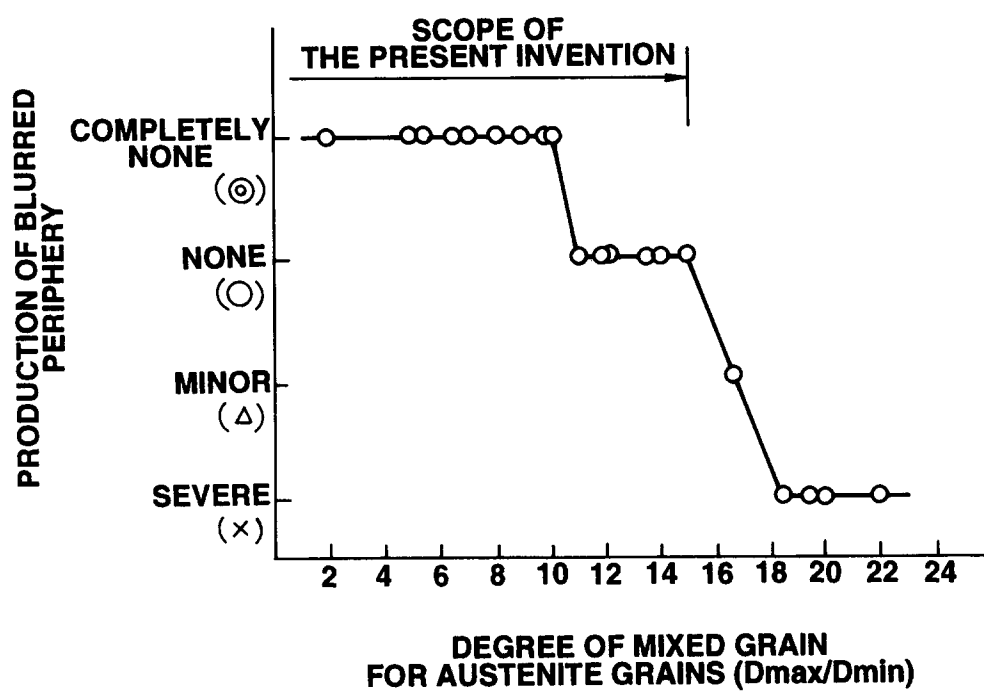


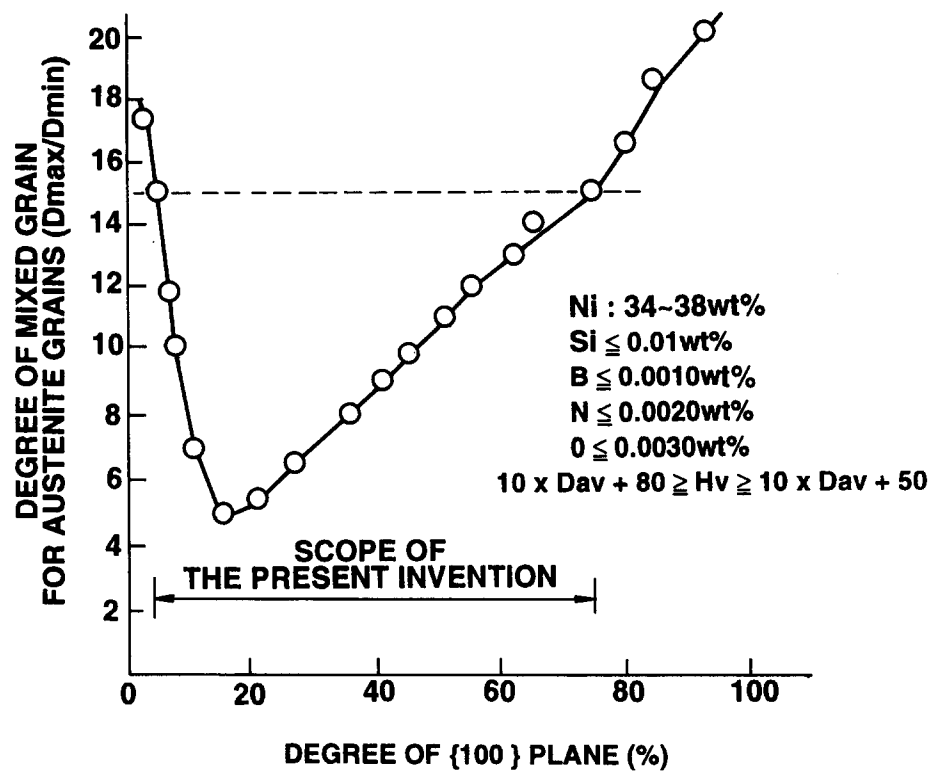
FIG.3

FIG.4

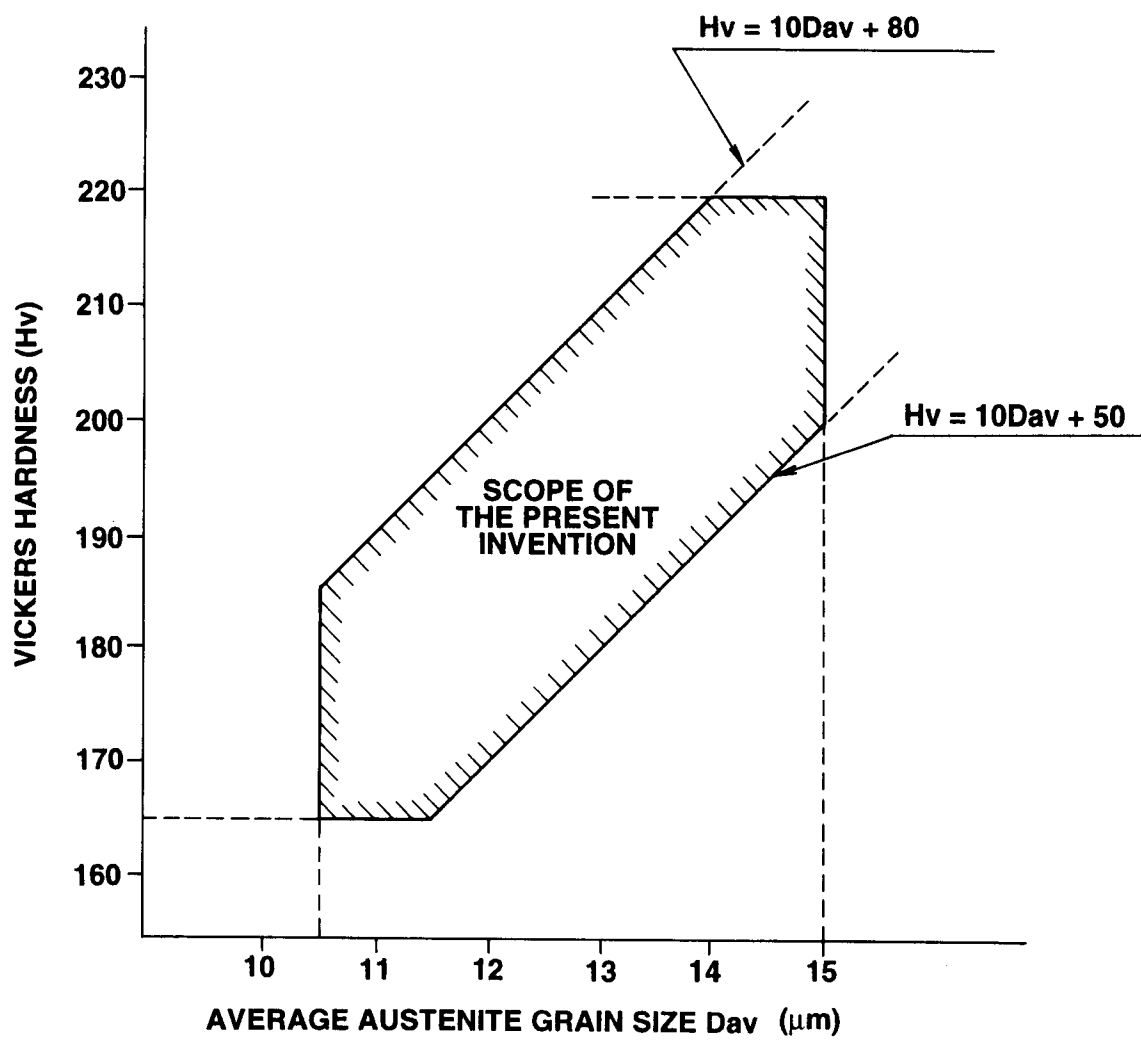


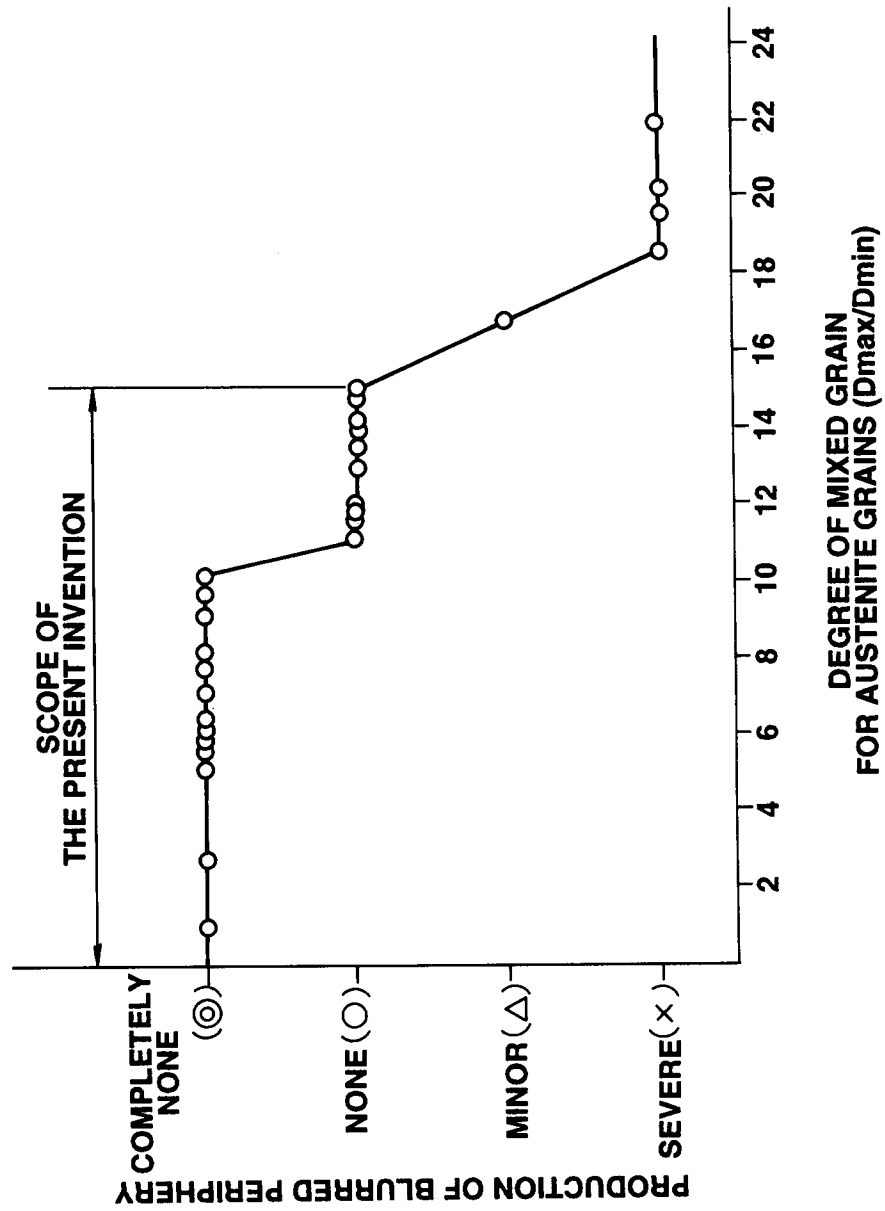
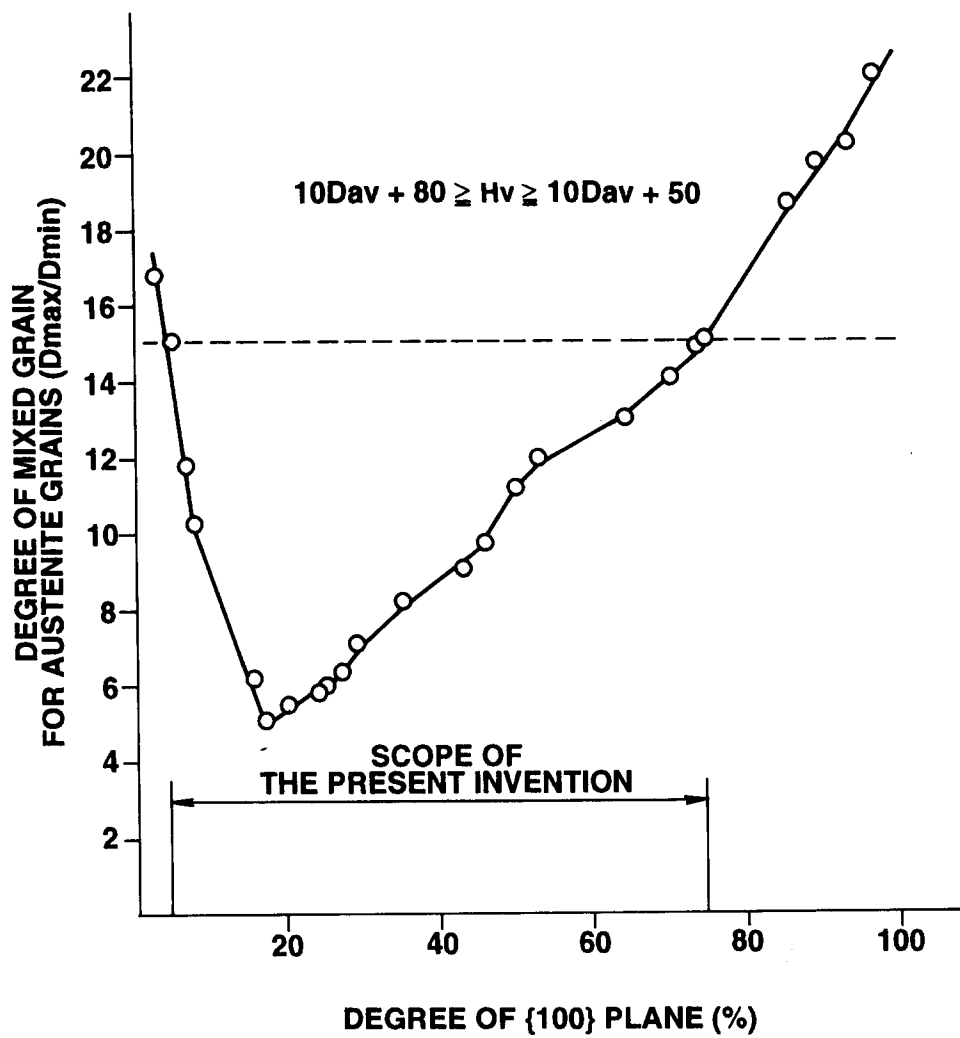
FIG.5

FIG.6



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 0509

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
P,Y	EP-A-0 552 800 (NKK CORPORATION) *Claims 1-14; p.7, Table 1* ---	1-7,53	C22C38/08 H01J29/07
P,Y	EP-A-0 561 120 (NKK CORPORATION) *Claims 1-22* ---	1-7,53	
Y	FR-A-2 668 498 (NKK CORPORATION) *Claims 1-6* ---	1-4,6,7, 53	
Y	FR-A-2 664 908 (NKK CORPORATION) *Claims 1-4* -----	1-3,6,53	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C22C H01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 August 1994	Examiner Lippens, M
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