(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 356 127 B9

(12) CORRECTED EUROPEAN PATENT SPECIFICATION

Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see page(s) 3

(48) Corrigendum issued on:
11.01.2006 Bulletin 2006/02

(45) Date of publication and mention of the grant of the patent:
04.05.2005 Bulletin 2005/18

(21) Application number: **01991857.2**

(22) Date of filing: **17.12.2001**

(51) Int Cl.:
C21D 8/12 (1980.01) *C22C 38/02* (2000.01)

(86) International application number:
PCT/EP2001/014879

(87) International publication number:
WO 2002/050314 (27.06.2002 Gazette 2002/26)

(54) PROCESS FOR THE PRODUCTION OF GRAIN ORIENTED ELECTRICAL STEEL STRIPS

VERFAHREN ZUR HERSTELLUNG VON KORNORIENTIERTEN ELEKTROSTAHLBÄNDERN

PROCEDE DE PRODUCTION DE BANDES D'ACIER MAGNETIQUES A GRAINS ORIENTES

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

(30) Priority: **18.12.2000 IT RM20000672**

(43) Date of publication of application:
29.10.2003 Bulletin 2003/44

(73) Proprietor: **ThyssenKrupp Acciai Speciali Terni S.p.A.**
05100 Terni (IT)

(72) Inventors:
- **FORTUNATI, Stefano,**
  Centro Sviluppo Materiali
  I-00129 Rome (IT)
- **CICALE', Stefano,**
  Centro Sviluppo Materiali S.p.A.
  I-00129 Rome (IT)
- **ROCCHI, Claudia,**
  Centro Sviluppo Materiali S.p.A.
  I-00129 Rome (IT)
- **ABBRUZZESE, Giuseppe,**
  Centro Sviluppo Materiali
  I-00129 Rome (IT)

(74) Representative: **Gervasi, Gemma**
Studio Brevetti e Marchi
NOTARBARTOLO & GERVASI S.r.l.,
Corso di Porta Vittoria, 9
20122 Milano (IT)

(56) References cited:
EP-A1- 0 390 160
EP-A2- 0 326 912
EP-A2- 0 947 597
WO-A1-98/41659
WO-A1-98/41660

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the invention

[0001] The present invention refers to a process for the production of grain oriented electrical steel strips and, more precisely, refers to a process in which a strip directly obtained from continuous casting of liquid steel is cold rolled, and in which strip precipitation of a controlled precipitation of second phases particles has been induced, said second phases being intended to control the grain growth after the primary recrystallization (primary inhibitors). In a further step, during the continuous annealing of the cold rolled strip, a further precipitation of second phases particles is induced throughout the whole thickness of the strip, having the function, along with the primary inhibitors, to control the oriented secondary recrystallization, through which a texture is obtained favourable to the magnetic flux along the rolling direction.

State of the art

[0002] Grain oriented electrical steel strips (Fe-Si) are typically industrially produced as strips having a thickness comprised between 0,18 and 0,50 mm and are characterised by magnetic properties variable according to the specific product class. Said classification substantially refers to the specific power losses of the strip subjected to given electromagnetic work conditions (e.g. P^{50Hz} at 1,7 Tesla, in W/kg), evaluated along a specific reference direction (rolling direction). The main utilisation of said strips is the production of transformer cores. Good magnetic properties (strongly anisotropic) are obtained controlling the final crystalline structure of the strips to obtain all, or almost all, the grains oriented to have their easiest magnetisation direction (the <001> axis) aligned in the most perfect way with the rolling direction. In practice, final products are obtained having the grains mean diameter generally comprised between 1 and 20 mm having an orientation centred around the Goss orientation ({110} <001>). The minor the angular dispersion around the Goss one, the better the product magnetic permeability and hence the lesser the magnetic losses. The final products having low magnetic losses (core losses) and high permeability have interesting advantages in terms of design, dimensions and yield of the transformers.

[0003] The first industrial production of the above materials was described by the U.S. Firm ARMCO at the beginning of the thirties (USP 1.956.559). As well known to the experts, many important improvements have been since introduced in the production technology of grain oriented electrical strips, in terms both of magnetic and physical quality of products and of transformation costs and cydes rationalisation. All existing technologies exploit the same metallurgical strategy to obtain a very strong Goss structure in the final products, i.e. the process of oriented secondary recrystallisation guided by uniformly distributed second phases and/or segregating elements. The, non metallic, second phases and the segregating elements play a fundamental role in controlling (slowing down) the movement of grain boundaries during the final annealing which actuates the selective secondary recrystallisation process.

[0004] In the original ARMCO technology, utilising MnS as inhibitor of the grain boundaries movement, and in the subsequent technology developed by NSC, in which the inhibitors are mainly aluminium nitrides (AIN + MnS) (EP 8.385, EP 17.830, EP 202.339), a very important binding step common to both production processes is the heating of the continuously cast slabs (ingots, in old times), immediately before the hot rolling, at very high temperatures (around 1400 °C) for a time sufficient to guarantee a complete dissolution of sulphides and/or nitrides coarsely precipitated during the slab cooling after casting, to re-precipitate them in a very fine and uniformly distributed form throughout the metallic matrix of the hot rolled strips. According to said known technique, such a fine re-precipitation can be started and completed, as well as the precipitates dimensions adjusted, during the process, in any case, however, before the cold rolling. The slab heating to said temperatures requires using special furnaces (pushing furnaces, liquid-slag walking-beam furnaces, induction furnaces) due to the ductility at high temperatures of the Fe-3%Si alloys and to formation of liquid slags.

[0005] Recently, new casting technologies were developed for the liquid steel, to simplify the production processes to make them more compact and flexible and to reduce costs. An innovative technology advantageously utilised in the production of electrical steels strips for transformers is the "thin slab" casting , consisting in the continuous casting of slabs having the typical thickness of conventional already roughened slabs, apt to a direct hot rolling, through a sequence of slabs continuous casting, treating in continuous tunnel-furnaces to rise/maintain the temperature of slabs, and finishing-rolling down to coiled strip. The problems connected to the utilisation of said technique for grain oriented products mainly consist in the difficulty to maintain and control the high temperatures necessary to keep in solution the elements forming the second phases, which have to be finely precipitated at the beginning of the finishing hot-rolling step, if desired best micro-structural and magnetic characteristics are to be obtained in the end-products.

[0006] The casting technique potentially offering the highest rationalisation level of the processes and the higher production flexibility is the one consisting in the direct production of strips from the liquid steel (Strip Casting), totally eliminating the hot rolling step. Strip Casting is well known and is utilised in the production of electrical strips, in general, and more precisely of grain oriented electrical strips.

[0007] The inventors believe that, for an industrial product, it is not convenient to adopt the strategy of directly producing the grain growth inhibitors necessary to the control of the oriented secondary recrystallisation by means of precipitation induced by rapid cooling of the cast strip, as proposed in the current scientific literature and patents. This opinion derives by the fact, well known to the experts, the level of necessary inhibition (drag force to the grain boundaries movement) is high and must remain comprised within a restricted field (1800 - 2500 cm^{-1}; in other words, with an inhibition level too low or too high the quality of the end products is impaired. Moreover, the inhibition have to be very evenly distributed through the metallic matrix, in that the local lack of necessary levels of inhibition produces texture defects which critically impair the quality of the end products.

[0008] This is particularly true if very high quality products (e.g. having B800>1900mT) have to be produced.

Summary of the invention

[0009] Present invention solves the above problems through an industrial process for the production of grain oriented electrical steel strips as defined in claim 1. Preferred embodiments of the invention are defined in claims 2-6. ***[deletion(s)]***

Brief description of the drawings

[0010] The final quality of the products obtained according to Example 1 are shown in the enclosed drawing table, in which:

- fig. 1 shows the results of permeability measurements obtained with reference with 29 different strips, as a function of the measured Primary Inhibition;
- fig. 2 shows the dispersion of said permeability measures, for each of said strips.

Detailed description of the invention

[0011] According to the invention, it is convenient to control the inhibitors content (distribution of second phases), present in the strip prior to the cold rolling, at intensity values lower than those necessary to the control of the secondary recrystallisation in order to maintain at an uniform level the recrystallisation structure after rolling of the strip, to guarantee a constant behaviour of the microstructure to the thermal treatment in all the points of the strip itself.

[0012] Hence, it is important to induce a homogeneous distribution of inhibitors between the casting step and the cold rolling one. This allows a greater freedom in choosing the industrial treatment conditions for the continuous annealing of the cold rolled strip in terms both of control of the process parameters and of temperatures to be utilised.

[0013] In fact, if there is absence or low quantity of grain growth inhibitors in the metal matrix, or a non- homogeneous distribution thereof, any even small fluctuation of annealing parametres (such as strip speed, strip thickness, local temperature) induces a high frequency of quality defects due to the microstructural irregularity, very sensible to the thermal treatment conditions. On the contrary, a controlled amount of inhibitors uniformly distributed in the matrix, greatly reduces the sensibility of the microstructure to the process parametres (slowing-down of grain boundaries), thus permitting an industrially stable process.

[0014] There is not a metallurgical limit to the inhibition maximum level in the strip prior to the rolling. From the practical point of view, however, the inventors studying various test conditions such as the alloy composition modification, the cooling conditions and so on, did recognise that it is not convenient, for an industrial process, to have inhibition levels higher than 1500 cm^{-1}, for the same reasons for which it is not convenient to have, at this stage, the whole inhibition amount necessary for the secondary recrystallisation control (higher than 1500 cm^{-1}). Going above said inhibition levels it is necessary to greatly reduce the dimensions of the precipitates, and from the process control point of view, the produced inhibition level is very sensible to even small fluctuations of the casting and treatment conditions, In fact, the nature of the inhibitors effect with reference to the grain boundaries movement is proportional to the surface of the second phases present in the matrix. This surface is directly proportional to the volume fraction of said second phases and inversely proportional to their dimensions. It can be demonstrated that the volume fraction of the precipitates, with the same alloy composition, depends from the temperature with reference to their solubility in the metal matrix, in that the higher the treatment temperature, the minor is the volume fraction of second phases present in the matrix. In a similar way, the particle dimensions are directly related to the treatment temperature. In fact, in a particle distribution as the temperature rises the smaller particles tend to dissolve into the matrix to be reprecipitated on the bigger ones, increasing their dimensions, diminishing their total surface (a process kmown as dissolution and growth). Said two phenomena, well known to the experts, control the level of the drag force of a second phases distribution within a thermal treatment. As the temperature rises, also rises the speed at which the inhibition reduces its strength, depending on the exponential relationship between the temperature and the phenomena of dissolution and diffusion.

[0015] On the basis of many experiments starting from the direct continuous casting of silicon steel strips, in which were measured through electron microscopy the inhibition levels, expressed as:

$$Iz = 1{,}9\ Fv/r \quad (cm^{-1})$$

[0016] In which Fv is the volume fraction of non metallic second phases stable at temperatures lesser than 800 °C, and r is the mean radius of the same precipitates, expressed in cm, present inventors did found that the better results are obtained in the interval:

$$600\ cm^{-1} < Iz < 1500\ cm^{-1}$$

[0017] It was demonstrated that below 600 cm^{-1} the primary recrystallisation structure is exceedingly sensible to the process fluctuations, with particular reference to temperature and strip thickness, while for values above 1500 cm^{-1} it is very difficult to ensure a constant behaviour throughout the strip profile.
[0018] Said inhibition interval (for primary inhibition) is necessary for the precipitation of second phases required for the control of the oriented secondary recrystallisation (secondary inhibition) according to present invention.
[0019] Present inventors did found that, to obtain a fine and homogeneously distributed precipitation of second phases particles apt to control, along with the inhibitors already present in the matrix, the selective secondary recrystallisation process, it is convenient to let an element, apt to react with micro-alloying elements thus precipitating second phases, to permeate by means of solid phase diffusion the strip having the desired final thickness. Nitrogen was found to be the most convenient element, in that it forms sufficiently stable nitrides and carbonitrides, it is an interstitial element thus being very mobile within the metallic matrix, and particularly much more mobile than the elements to which it react to form nitrides.
[0020] The above characteristic allows, adopting the opportune treatment conditions, to homogeneously precipitate the required nitrides throughout the strip thickness.
[0021] The technique utilised to generate a nitriding atmosphere during the strip annealing is not important. However, to guarantee that the nitrogen diffusion front forms the desired inhibition for the control of the oriented secondary recrystallisation, it is necessary the presence in the metal matrix of evenly distributed micro-alloying elements forming nitrides stable at high temperature. Very convenient from the industrial point of view is the utilisation of $NH_3 + H_2 + H_2O$ mixtures permitting to easily modulate the amount of nitrogen diffused into the steel strip by contemporary controlling the nitriding power, proportional to the pNH_3/pH_2 ratio, as well as the oxidising potential, proportional to the pH_2O/pH_2ratio.
[0022] The nitriding temperature according to present invention cannot be below 800 °C.
[0023] In fact, at lower nitriding temperatures the nitrogen reaction with silicon (typically present in amounts between 3 and 4 wt%) prevails forming silicon nitrides and blocking nitrogen at the strip surface, preventing its penetration towards the strip core and hence the formation of a homogeneous distribution of inhibitors throughout the strip thickness. The higher the silicon content in the matrix, the higher will have to be the nitriding temperature.
[0024] There is no upper limit to the nitriding temperature, the choice of the best temperature being determined by the balance between the desired nitride distribution and the process exigencies.
[0025] In the absence, in the metal matrix, of a given minimal and controlled distribution of second phase particles (as primary inhibition) according to present invention, the capability to nitride at high temperature is limited in view of the risk to generate temperature-activated local and undesired evolutions of the micro-structure, with consequent development of eterogeneities and defects of final quality. On the contrary, the presence within the above mentioned interval of a given level of primary inhibition before the nitriding treatment ensures the micro-structural stability even at high process temperatures.
[0026] To obtain such a precipitation of second phases in the strip, in addition to the presence in the liquid steel of sulphur and/or nitrogen in limited quantities, however higher than 30 ppm, present inventors identified in the group consisting of Al, V, B, Nb, Ti, Mn, Mo, Cr, Ni, Co, Cu, Zr, Ta, W, the elements and mixtures thereof which, when present in the chemical composition of the steel, usefully partecipate to formation of the inhibition. Analogously, the presence of at least one of the elements Sn, Sb, P, Se, Bi, as micro-alloying additions, tend to improve the homogeneity level of the microstructure.
[0027] The control of the primary inhibitors distribution and the level of the deriving drag force are obtained, according to present invention, balancing the control elements of the following process steps, (i) the concentration of the micro-alloying elements and (ii) a controlled in-line deformation of the cast strip before its coiling within an interval of defined thickness reduction conditions.
[0028] More particularly, present inventors found, on the basis of many laboratory and industrial tests with strip-casting plants, that below a reduction ratio of 15%, unwanted conditions of non-homogeneous precipitation can occur in the rolled strip matrix, perhaps because of not controlled thermal gradients as well as of irregular deformation patterns,

tending to localise in certain zones of the strip the conditions for the preferential nucleation of the second phases particles. It was also defined an upper deformation limit of 60%, in that above this limit no differences in the distribution of precipitates are found, with the addition of technological troubles, due to difficulties in controlling of the sequence casting-rolling-coiling of the strip.

[0029] The inhibitors control, moreover, cannot be obtained if the thickness reduction temperature is lesser than 750 °C, in that the spontaneous precipitation due to the cooling before rolling becomes predominant thus preventing the rolling conditions to significantly control the inhibition.

[0030] The present invention, however, does not utilise the measure of the inhibition content as a factor to directly control on-line the process.More particularly, the present invention claims a process for the production of grain oriented electrical steel strips in which a silicon steel, comprising at least 30 ppm of sulphur and/or nitrogen, and at least an element of the group consisting in Al, V, Nb, B, Ti, Mn, Mo, Cr, Ni, Co, Cu, Zr, Ta, W, at least an element of the group consisting in Sn, Sb, P, Se, Bi, ti continuously cast directly in the form of a strip with a thickness comprised between 1,5 and 4,5 mm, and cold rolled to a final thickness comprised between 1,00 and 0,15 mm, said cold rolled strip being then continuously annealed for primary recrystallisation, if necessary in an oxydising atmosphere to decarburise the strip and/or to carry out a controlled surface oxidisation thereof, followed by a secondary recrystallisation annealing at temperatures higher than those of the primary recrystallisation. The process is characterised in that along the production cycle the following group of steps is sequentially carried out:

- cooling cycle of the as solidified strip comprising a step of deformation at controlled temperature, so as to obtain in the metal matrix a homogeneous distribution of non-metallic second phases able to inhibit the grain boundaries movement with a drag force specifically comprised in the interval

$$800\ cm^{-1} < Iz < 1500\ cm^{-1}$$

  Iz being defined as Iz = 1,9 Fv/r (cm^{-1}), in which Fv is the volume fraction of non-metallic second phases stable at temperatures below 800 °C and r is the mean radius of said precipitates, in cm;
- in-line hot rolling of said strip between its solidification stage and its coiling, utllising a reduction ratio comprised between 15 and 60% at a temperature higher than 750 °C; optionally annealing the strip after colling;
- single-stage cold rolling, or multiple stage cold rolling with intermediate annealing, with a reduction ratio comprised between 60 and 92% in at least one of the rolling passages;
- primary recrystallisation continuous annealing of the cold rolled strip at a temperature comprised between 750 and 1100 °C, in which the nitrogen content in the metal matrix is rised; with respect to as cast value, by at least 30 ppm at the strip core, by means of a nitriding atmosphere;
- oriented secondary recrystallisation annealing at a temperature higher that the one of the primary recrystallization one.

[0031] The following Examples are intended solely for illustration purposes, not as a limitation of tha invention and relevant scope.

Example 1

[0032] A number of steel compositions were cast as strip by solidification between two counter-rotating cooled rolls, starting from alloys comprising from 2,8 to 3,5% SI, from 30 to 300 ppm S, from 30 and 100 ppm N, end different amounts of micro-alloying elements according to the following Table 1 (concentrations in ppm).

TABLE 1

	Al	Mn	Cu	Ti	Nb	V	W	Ta	B	Zr	Cr	Bi	Sn	Sb	P	Se	Mo	Ni	Co
1	300	1500	-	-	-	-	-	-	-	-	200	-	800	-	-	-	300	230	-
2	220	1300	2000	-	-	-	50	-	-	-	500	-	-	-	100	-	120	100	-
3	50	200	-	-	60	-	-	40	-	-	-		70	-	-	-	-	120	-
4	-	-	3000	20	-	-	-	-	15	30	400	30	-	-	-	80	220	-	
5	-	-	700	20	30	40	-	-	-		300	-	1000		-	60	200	100	
6	280	2000	1000	-	-	40	-	-	-	-	1000	-	-	-	100	-	180	800	60
7	130	500	-	30	-	-	-	-	-	-	-	-	400	400	40	40	-	-	-
8	350	1400	2500	40	-	-	-	-	-	-	600	-	700	-	50	-	-	600	80
9	200	700	1000	30	200	-	-	-	15	-	800	-	600	-	100	-	100	220	-

[0033] All the strips were continuously rolled before coiling according to a defined deformation program, so that any strip contained a sequence of lengths having a decreasing thickness as a function of an increasing reduction ratio comprised between 5 and 50%. All the strips were cast with a thickness comprised between 3 and 4,5 mm and with variable casting speed, with strip temperatures at the beginning of the rolling comprised between 790 and 1120 °C.

[0034] The lengths having different thickness of each strip were cut and separately coiled in small coils; each length was characterised in detail by means of electron microscopy to ascertain the second phases distribution obtained in each case, from which the mean value of the inhibtion intensity Iz was calculated, in cm^{-1}, according to the invention.

[0035] Figure 1 shows the characterisation results, organised according to increasing primary inhibition values measured.

[0036] The materials under test were then transformed, at laboratory scale, into finished strips 0,22 mm thick, according to the following cycle:

- cold rolling to 1,9 mm thickness;
- annealing at 850°C in dry nitrogen for 1 min.;
- cold rolling down to 0,22 mm;
- continuous annealing comprising the steps of recrystallisation and nitriding, in sequence, respectively in damp hydrogen + nitrogen atmosphere with a pH_2O/pH_2 ratio of 0,58 and temperatures of 830, 850 and 870 °C for 180 s for the primary recrystallisation, and in damp hydrogen + nitrogen atmosphere with the addition of ammonia, with a pH_2O/pH_2 ratio of 0,15 and a pNH_3/pH_2 ratio of 0,2 at 830 °C for 30 s;
- coating of the strips with an MgO-based annealing separator, and box-annealing in hydrogen + nitrogen, with a heating speed of 40 °C/h from 700 to 1200 °C, holding at 1200 °C for 20 h in hydrogen and subsequent cooling.

[0037] Specimens were obtained from each strip for a laboratory measurement of magnetic characteristics.

[0038] Outside the primary inhibition interval according to the invention, the orientation. level of the finished products (Fig. 2), measured as magnetic permeability, is either too low or too instable.

Example 2

[0039] A steel comprising: Si 3,1 wt%; C 300 ppm; Al_{sol} 240 ppm; N 90 ppm; Cu 1000ppm; B 40 ppm; P 60 ppm; Nb 60 ppm; Ti 20 ppm; Mn 700 ppm; S 220 ppm, was cast as strip, annealed at 1100 °c for 30 s, quenched in water and steam starting from 800 °C, pickled, sanded and then divided into five coils. Initially, the mean thickness of strip was 3,8 mm, reduced by rolling at 2,3 mm before coiling, with a temperature, at the beginning of rolling, of 1050-1080 °C maintained throughout the strip lenght.

[0040] Each of the five coils was then cold rolled at a final thickness of around 0,30 mm according to the following scheme:

a first coil (A) was directly rolled down to 0,28 mm;
the second coil (B) was directly rolled down to 0,29 mm, with a rolling temperature at the 3°, 4° and 5° passage of about 200 °C;
the third coil (C) was cold rolled down to 1,0 mm, annealed at 900 °C for 60 s and
then cold rolled down to 0,29 mm;
the fourth coil (D) was cold rolled down to 0,8 mm, annealed at 900 °C for 40 s and then cold rolled down to 0,30 mm;
the fifth coil (E) was cold rolled to 0,6 mm. Annealed at 900 °C for 30 s and then cold rolled down to 0,29 mm.

[0041] Each of the above cold rolled coils was divided into a number of shorter strips, to be treated in a continuous pilot line to simulate different primary recrystallisation annealing, nitriding and secondary recrystallisation annealing cycles. Each strip was subjected to the following scheme:

- the first teatment of primary recrystallisation annealing was carried out utilising three different temperatures, i.e. 840, 860 and 880 °C in a damp hydrogen + nitrogen atmosphere with a pH_2O/pH_2 ratio of 0,62 and for 180 s (of which 50 s for the heating-up stage);
- the second treatment of nitriding was carried out in a damp hydrogen + nitrogen atmosphere with a pH_2O/pH_2 ratio of 0,1, with an ammonia addition of 20%, for 50 s;
- the third treatment of secondary recrystallisation was carried out at 1100 °C in a damp hydrogen + nitrogen atmosphere with a pH_2O/pH_2 ratio of 0,01 and for 50s.

[0042] After coating the strips with an MgO based annealing separator, the same were box-annealed by heating-up with a gradient of about 100 °C/h up to 1200 °C in a 50% hydrogen + nitrogen atmosphere, holding this temperature for 3 h in pure hydrogen, followed by a first cooling down to 800 °C in hydrogen and then to room temperature in nitrogen.

[0043] The 8800 magnetic characteristics, in Tesla, measured on the strips treated as above described, are shown in Table 2.

TABLE 2

STRIP	840 °C	860 °C	880 °C
A	1,890	1,920	1,900
B	1,890	1,930	1,950
C	1,900	1,900	1,860
D	1,890	1,900	1,840
E	1,750	1,630	1,620

Example 3

[0044] The strip cold rolled according to the above defined cycle B, was treated according to a further set of treatment conditions, in which different temperatures for the precipitation of the secondary inhibition by nitriding were adopted. The strip first underwent a primary recrystallisation annealing at a temperature of 880 °C, utilising the same general conditions of Example 2; then, the nitriding annealing was carried out at the temperatures of 700, 800, 900, 1000, 1100 °C. Each strip was then transformed into finished product, sampled and measured, as in Example 2. The magnetic characteristics measured (B800, mT) are shown in Table 3, along with some chemical information.

TABLE 3

Nitriding Temp. (°C)	**Total Added Nitrogen** ppm*	**Nitrogen Added at core****	**B800 (mT) End Product**
700	70	0	**1540**
800	160	10	**1630**
900	270	70	**1940**
1000	230	100	**1950**
1100	200	95	**1950**

(*) The added nitrogen is evaluated by measuring the nitrogen in the matrix before and after the nitriding treatment.

(**) The measure of nitrogen diffused to the strip core is evaluated by measuring the nitrogen in the matrix after symmetrical erosion by 50% of the specimens, before and after nitriding.

Example 4

[0045] A silicon steel was produced comprising Si 3,0 wt%; C 200 ppm; Al_{sol} 265 ppm; N 40 ppm; Mn 750 ppm; Cu 2400 ppm; S 280 ppm; Nb 50 ppm; B 20 ppm; Ti 30 ppm.

[0046] A 4,6 mm thick cast strip was obtained, in-line hot rolled down to 3,4 mm, coiled at a mean temperature of about 820 °C, and divided into four shorter strips. Two of said strips were double-stage cold rolled down to 0,60 mm, with an intermediate annealing on the 1 mm thick strip at 900 °C for about 120 s. The other two strips were single-stage cold rolled to the same thickness, starting from 3,0 mm. All the strips were then annealed for primary recrystallisation at 880 °C in hydrogen + nitrogen atmosphere having a dew point of 67,5 °C. Then said strips were nitrided in hydrogen + nitrogen atmosphere, with the addition of 10% ammonia, having a dew point of 15 °C. The strips were then coated with an MgO-based annealing separator and box-annealed with a temperature increase between 750 and 1200 °C in 35 hours in hydrogen + nitrogen atmosphere, stop at this temperature for 15 hours and cooling. The magnetic characteristics of the obtained end products are shown in Table 4.

TABLE 4

Cold Rolling	% Last Reduction	B800 (mT)
Single stage 1	82 %	1920
Single stage 2	82 %	1930
Double stage 1	40 %	1560
Double stage 2	40%	1530

Claims

1. A process for the production of grain oriented electrical steel strips in which a silicon steel is continuously cast in the form of a strip 1.5 to 4.5 mm thick, hot rolled, coiled and then cold rolled to a strip 0.15 to 1 mm thick, subjected to a primary recrystallisation and decarburisation annealing and to a further annealing for secondary recrystallisation at a temperature higher than the one of said primary recrystallisation annealing, and in which a first precipitation of non-metallic second phases is promoted able to inhibit grain boundaries movement with a drag force specifically comprised in the interval

$$600\ cm^{-1} < Iz < 1500\ cm^{-1}$$

Iz being defined as Iz = 1.9 Fv/r (cm^{-1}), in which Fv is the volume fraction of said non-metallic second phases stable at a temperature below 800 °C and r is the mean radius of said second phases, a second precipitation of non-metallic second phases being promoted after cold rolling, **characterised in that**

- said first precipitation of non-metallic second phases is obtained though a controlled in-line deformation of the as cast strip before its coiling, utilising a reduction ratio of between 15% and 60% at a temperature higher than 750 °C,
- said hot rolled strip is cold rolled in at least one stage, with intermediate annealing, with a reduction ratio of between 60 and 92% in at least one of the rolling passages,
- said second precipitation of non-metallic second phases is obtained during said decarburisation annealing by rising the nitrogen content in the steel strip, by means of a nitriding atmosphere.

2. The process of claim 1 in which the primary recystallisation continuous annealing is carried out in an oxidising atmosphere, to decarburise the strip and/or to carry out a controlled surface oxidation thereof.

3. The process of claim 1 in which the strip is annealed between the steps of coiling and of cold rolling.

4. The process of claim 1 in which the finishing cold rolling temperature is higher than 180 °C in at least two contiguous passes.

5. The process of claim 1 in which during the continuous annealing of the cold rolled strip a nitriding treatment of the strip is carried out in a controlled atmosphere, in which a mixture comprising at least $NH_3 + H_2 + H_2O$ is present, and at a temperature higher than 800 °C, so that nitrogen penetration and nitrides precipitation down to the strip core is obtained, directly during the continuous annealing.

6. The process of claim 1 **characterised in that** it comprises at least 30 ppm of S and/or N, at least an element chosen from the group consisiting in Al, V, Nb, B, Ti, Mn, Mo, Cr, Ni, Co, Cu, Zr, Ta, W and at least an element chosen from the group consisting in Sn, Sb, P, Se, Bi.

Patentansprüche

1. Verfahren zur Herstellung von komorientierten Elektrobändern, bei dem Siliziumstahl in der Form eines 1,5 bis 4,5 mm dicken Bands stranggegossen wird, heiß gewalzt wird. gewickelt wird und dann kalt zu einem 0,15 bis 1 mm dicken Band gewalzt wird, einer primären Rekristallisation und Entkohlung durch Glühen sowie bei einer Temperatur, die höher ist als diejenige, bei der das genannte primäre Rekristallisationsglühen erfolgt, einem zweiten Glühen zur sekundären Rekristallisation unterzogen wird und bei dem eine erste Kondensation nicht-metallischer zweiter Phasen veranlasst wird, die in der Lage sind die Bewegung der Komgrenzen mit einer Widerstandskraft zu hemmen und deren Größe insbesondere in dem Intervall

$$600\ cm^{-1} < Iz < 1500\ cm^{-1}$$

liegt, wobei Iz durch Iz = 1,9 Fv/r (cm^{-1}) definiert ist, wobei Fv der Volumenteil der genannten nicht-metallischen

Phasen ist, der bei Temperaturen unter 800 °C stabil ist, und r der mittlere Radius der genannten zweiten Phasen ist, und wobei eine zweite Kondensation nicht-metallischer Phasen nach dem Kaltwalzen veranlasst wird, **dadurch gekennzeichnet, dass**

- die genannte erste Kondensation nicht-metallischer zweiter Phasen durch eine kontrollierte In-line-Verformung des gegossenen Bands erfolgt, bevor es gewickelt wird, wobei die Dicke bei einer Temperatur über 750 °C um 15 % bis 60 % reduziert wird,
- das genannte heiß gewalzte Band in wenigstens einer Stufe kalt gewalzt wird' mit dazwischen eingelegtem Glühen, wobei die Dicke in wenigstens einem der Walzdurchgänge um 60 bis 92 % reduziert wird,
- die genannte zweite Kondensation nicht-metallischer zweiter Phasen während des genannten Eritkohlens durch Glühen erfolgt, indem der Stickstoffgehalt in dem Stahlband mittels einer nitrierenden Atmosphäre erhöht wird.

2. Verfahren gemäß Anspruch 1, wobei die primäre Rekristallisation durch kontinuierliches Glühen in einer oxidierenden Atmosphäre erfolgt, um das Band zu Entkohlen und/oder um die kontrollierte Oxidation seiner Oberfläche zu bewirken.

3. Verfahren gemäß Anspruch 1, wobei das Band zwischen den Schritten des Wickelns und des Kaltwalzens geglüht wird.

4. Verfahren gemäß Anspruch 1, wobei die Temperatur beim abschließenden Kaltwalzen in wenigstens zwei aufeinander erfolgenden Durchgängen über 180 °C liegt.

5. Verfahren gemäß Anspruch 1, wobei während des kontinuierlichen Glühens des kalt gewalzten Bands in einer kontrollierten Atmosphäre eine Nitirierbehandlung des Bands erfolgt, in Gegenwart einer Mischung, die wenigstens $NH_3 + H_2 + H_2O$ enthält, und bei einer Temperatur über 800 °C, so dass die Durchdringung mit Stickstoff und die Kondensation von Nitriden bis zum Kern des Bands direkt während des kontinuierlichen Glühens stattfindet.

6. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** wenigstens 30 ppm S und/oder N, wenigstens ein Element aus der Gruppe Al, V, Nb, B, Ti, Mn, Mo, Cr, Ni, Co, Cu, Zr, Ta, W und wenigstens ein Element aus der Gruppe Sn, Sb, P, Se, Bi enthalten sind.

Revendications

1. Un procédé de production de bandes d'acier magnétique à grains orientés dans lequel un acier au silicium est coulé en continu sous la forme d'une bande de 1,5 à 4,5 mm d'épaisseur, laminé à chaud, bobiné et ensuite laminé à froid pour donner une bande de 0,15 à 1 mm d'épaisseur, soumis à une recristallisation primaire et à un recuit de décarburisation et à un recuit supplémentaire pour recristallisation secondaire à une température plus élevée que celle dudit recuit de recristallisation primaire, et dans lequel est activée une première précipitation de secondes phases non métalliques susceptible d'empêcher un mouvement des limites des grains avec une force de traînage comprise spécifiquement dans l'intervalle

$$600\ cm^{-1} < Iz < 1500\ cm^{-1}$$

|z étant défini comme étant |z = 1,9 Fv/r (cm^{-1}), où Fv est la fraction volumique desdites secondes phases non métalliques stables à une température en dessous de 800°C et r est le rayon moyen desdites secondes phases, une seconde précipitation de secondes phases non métalliques étant activée après laminage à froid, **caractérisé en ce que**

- ladite première précipitation de secondes phases non métalliques est obtenue par l'intermédiaire d'une déformation en ligne régulée de la bande telle que coulée avant son bobinage, en utilisant un rapport de réduction d'entre 15% et 60% à une température supérieure à 750°C,
- ladite bande laminée à chaud est laminée à froid en au moins un stade, avec recuit intermédiaire, en présentant un rapport de réduction d'entre 60 et 92% dans au moins un des passages de laminage,
- ladite seconde précipitation de secondes phases non métalliques est obtenue pendant ledit recuit de décar-

burisation en élevant la teneur d'azote dans la bande d'acier au moyen d'une atmosphère de nitruration.

2. Le procédé de la revendication 1 dans lequel le recuit continu de recristallisation est mis en oeuvre dans une atmosphère oxydante, afin de décarburer la bande et/ou de mettre en oeuvre une oxydation de surface régulée de celle-ci.

3. Le procédé de la revendication 1 dans lequel la bande est recuite entre les étapes de bobinage et de laminage à froid.

4. Le procédé de la revendication 1 dans lequel la température finale de laminage à froid est supérieure à 180°C dans au moins deux passes contiguës.

5. Le procédé de la revendication 1 dans lequel, pendant le recuit continu de la bande laminée à froid, un traitement de nitruration de la bande est mis en oeuvre dans une atmosphère régulée, dans laquelle est présent un mélange comprenant au moins $NH_3 + H_2 + H_2O$, et à une température supérieure à 800°C, de sorte que l'on obtient une pénétration de l'azote et une précipitation des nitrures jusqu'à la partie centrale de la bande, directement pendant le recuit continu.

6. Le procédé de la revendication 1 **caractérisé en ce qu'**il comprend au moins 30 ppm de S et/ou de N, au moins un élément choisi dans le groupe se composant de Al, V, Nb, B, Ti, Mn, Mo, Cr, Ni, Co, Cu, Zr, Ta, W et au moins un élément choisi dans le groupe se composant de Sn, Sb, P, Se, Bi.

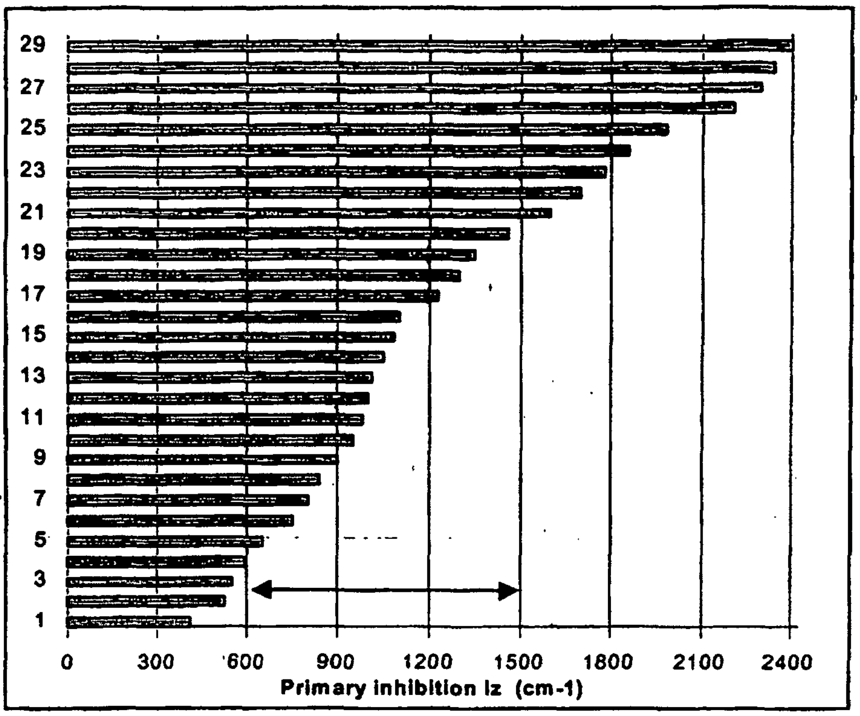
29
27
25
23
21
19
17
15
13
11
9
7
5
3
1
0
300
600
900
1200
1500
1800
2100
2400
Primary inhibition Iz (cm-1)

Fig. 1

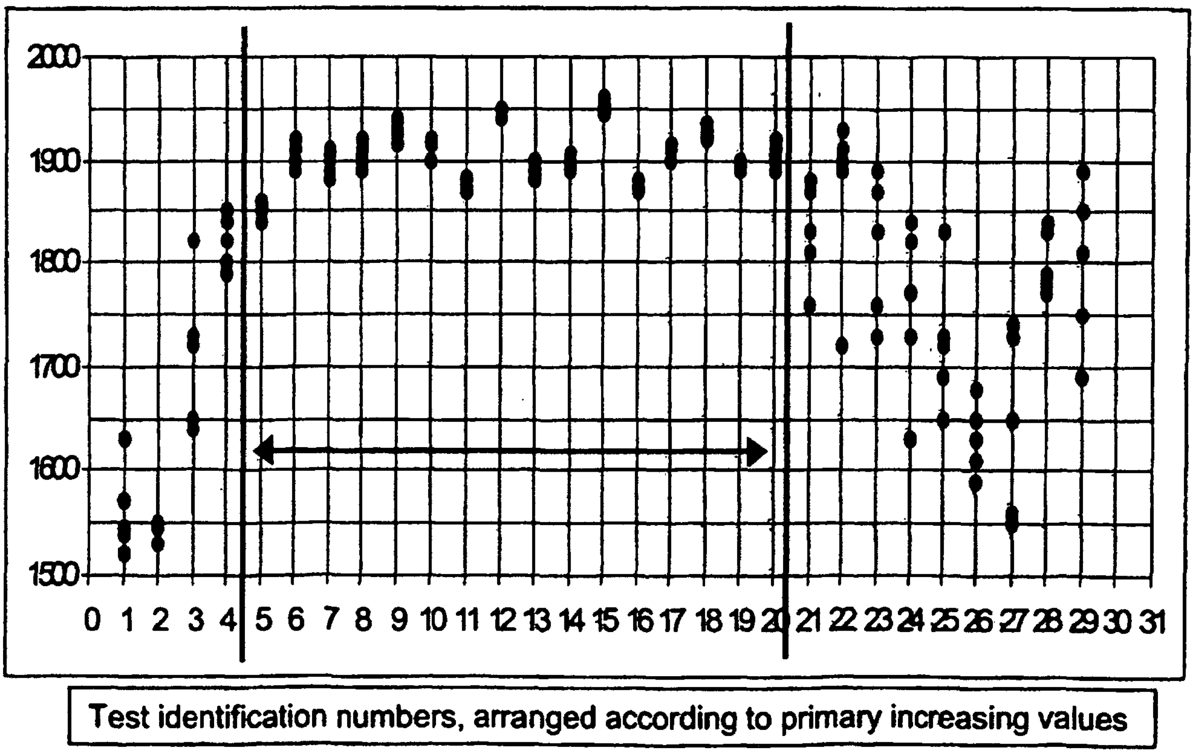
2000
1900
1800
1700
1600
1500
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Test identification numbers, arranged according to primary increasing values

Fig. 2