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- **FUJIMOTO, Hiroshi**, c/o Nisshin Steel Co., Ltd.
Shin-Nanyo-shi, Yamaguchi 746-8666 (JP)
- **MORIMOTO, Kenichi**, c/o Nisshin Steel Co., Ltd.
Shin-Nanyo-shi, Yamaguchi 746-8666 (JP)
- **HIRAMATSU, Naoto**, c/o Nisshin Steel Co., Ltd.
Shin-Nanyo-shi, Yamaguchi 746-8666 (JP)

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(71) Applicant: **NISSHIN STEEL CO., LTD.**

Chiyoda-ku Tokyo 100-8366 (JP)

(74) Representative: **Müller-Boré & Partner**

Patentanwälte

Grafinger Strasse 2

81671 München (DE)

(72) Inventors:

- **TOMIMURA, Kouki**, c/o Nisshin Steel Co., Ltd.
Shin-Nanyo-shi, Yamaguchi 746-8666 (JP)

(54) **DOUBLE PHASE STAINLESS STEEL STRIP FOR STEEL BELT**

(57) A high-strength dual-phase stainless steel strip has a chemical composition consisting of 0.04-0.15 mass % C, 10.0-20.0 mass % Cr, 0.5-4.0 mass % Ni and the balance being Fe except inevitable impurities, and a metallurgical structure composed of 20-85 vol. % martensite grains and the balance ferrite grains with prior austenite grains controlled to 10 µm or less in size. The stainless steel strip is conditioned to hardness of HV 300

or more. Transformation strains are uniformly distributed in a steel matrix during martensitic transformation, so that the steel strip is formed and straightened to a belt shape without Lüders band. Consequently, steel belts with fine external appearance are manufactured from the stainless steel strip.

EP 1 396 552 A1

Description

INDUSTRIAL FIELD OF THE INVENTION

[0001] The present invention relates to a dual-phase stainless steel strip useful as steel belts with fine external appearance free from Lüders band, which are likely to occur during straightening a steel sheet in a steel belt-manufacturing process.

BACKGROUND OF THE INVENTION

[0002] Stainless steel belts have been manufactured from work-hardening austenitic stainless steels such as SUS301 and SUS304, which are strengthened by cold-rolling, low-C martensitic stainless steels as disclosed in JP 51-31085B or precipitation-hardening martensitic stainless steels as disclosed in JP 59-49303B.

[0003] The work-hardening stainless steel has a semi-stable austenite phase, which is transformed to a martensite phase by application of strains during plastic forming. The strain-induced transformation causes Lüders band (as reported in Journal of the Japan Institute of Metals Vol. 55, No. 4, pp376-382 and Nisshin Steel Technical Report No. 69, pp.1-14), so that a steel sheet has a rugged surface unsuitable as a material for steel belts.

[0004] The martensitic or precipitation-hardening martensitic stainless steel is substantially transformed to a single martensite phase in a cooling step of annealing, but often deformed by volumetric expansion during transformation. A deformed profile is difficult to rectify, once a steel sheet is formed to a belt shape.

SUMMARY OF THE INVENTION

[0005] The present invention aims to provision of a stainless steel strip useful as steel belts with fine external appearance, without occurrence of Lüders band during straightening a steel sheet to a belt shape or transformation to a complete martensite phase difficult to rectify profiles of steel belts.

[0006] The present invention proposes a martensite/ferrite dual-phase stainless steel strip useful as steel belts. The stainless steel has a chemical composition consisting of 0.04-0.15 mass % C, 10.0-20.0 mass % Cr, 0.5-4.0 mass % Ni and the balance being essentially Fe. Its metallurgical structure is composed of 20-85 vol. % martensite grains and the balance being ferrite grains. The steel strip is conditioned to hardness of HV 300 or more.

[0007] Grain size of prior austenite grains is preferably controlled to 10 μm or less, so as to suppress volumetric expansion not more than 9% in average during martensitic transformation in a cooling step of annealing.

[0008] The wording "steel strips" in this specification involves steel sheets.

PREFERRED EMBODIMENTS OF THE INVENTION

[0009] The inventors have researched effects of various factors such as chemical compositions, metallurgical structures and materialistic properties on occurrence of Lüders band, and discovered that Lüders band is significantly influenced by distribution of strains and volumetric expansion during martensitic transformation. From experimental results, the inventors have reached the conclusion that Lüders band is effectively suppressed by reduction of residual austenite and uniform distribution of expansion strains to a whole of a steel strip during martensitic transformation in a cooling step of annealing.

[0010] The dual-phase stainless steel strip proposed by the invention contains various alloying elements at specified ratios, as follows:

0.04-0.15 mass % of C

[0011] C is an austenite former, which hardens a martensite phase. A ratio of martensite grains, which are formed after heating the steel strip at a temperature higher than A_{c1} , is controlled by C content. An effect of C on hardening is noted at 0.04 mass % or more. However, excess C above 0.15 mass % causes precipitation of chromium carbide at grain boundaries during cooling in a dual-phase annealing step, resulting in degradation of intergranular corrosion-resistance and fatigue strength.

10.0-20.0 mass % of Cr

[0012] Cr is an essential alloying element for imparting corrosion-resistance to a stainless steel. An effect of Cr on corrosion-resistance is noted at 10.0 mass % or more. However, excess Cr above 20.0 mass % degrades toughness and workability of the stainless steel strip. Moreover, excess Cr necessitates increase of austenite formers such as C, N, Ni, Mn and Cu. Increase of austenite formers raises a steel cost but also stabilizes an austenite phase at a room temperature, resulting in poor strength. In this sense, an upper limit of Cr is determined at 20.0 mass %.

0.5-4.0 mass % of Ni

[0013] Ni is an austenite former for formation of a ferrite/austenite structure in a high-temperature zone (which is

transformed to a ferrite/martensite structure at a room temperature). As increase of Ni, a ratio of martensite grains becomes larger, and a steel sheet is more hardened. The element Ni promotes nucleation for austenite grains during austenite/ferrite dual-phase annealing, so as to form a fine austenite/ferrite microduplex structure. The effect of increased Ni content on formation of the fine microduplex structure probably explained, as follows: As increase of Ni, growth of nuclei for austenitizing is retarded beyond critical nuclei determined by classic nucleation theory, and nuclear sites for austenite grains increase in number due to dynamic motion for formation of an austenite phase until an equilibrium state. The effect of Ni on refinement of the microduplex structure is noted at 0.5 mass % or more. However, Ni is an expensive element, and excess Ni leads to existence of residual austenite harmful on strength of a stainless steel due to incomplete transformation of high-temperature austenite to a martensite phase in a cooling step to a room temperature. In this sense, an upper limit of Ni content is determined at 4.0 mass %.

[0014] The dual-phase stainless steel may further contain one or more austenite formers, e.g. Mn, Cu and N, and/or one or more ferrite formers, e.g. Si, Ti, Nb and Al, other than C, Cr and Ni, so as to produce a ferrite/martensite dual-phase structure at a room temperature. Other elements, e.g. Mo for corrosion-resistance, Y, Ca and REM (rare earth metals) for hot-workability, B and V, may be added to the stainless steel. Ratios of these optional elements are determined, as follows:

Si up to 2.0 mass %

[0015] Si is an element, which is added as a deoxidizing agent in a steelmaking process. Due to a solution-hardening power of Si, excess Si above 2.0 mass % solution-hardens a stainless steel too much and degrades its ductility. Mn up to 2.0 mass %

[0016] Mn is an austenite former for promotion of austenitizing while suppressing formation of δ -ferrite in a high-temperature zone. However, excess Mn above 2.0 mass % allows existence of residual austenite in an annealed state. The residual austenite causes unfavorable strain-induced martensitic transformation during plastically forming a stainless steel sheet to a product shape, resulting in occurrence of strains.

P not more than 0.050 mass %

[0017] P is an impurity disadvantageous for hot-workability of a stainless steel strip. The effect of P on hot-workability is typically noted at 0.050 mass % or more.

S not more than 0.020 mass %

[0018] S is also an impurity, which is likely to segregate at grain boundaries. Segregation of S makes the grain boundaries brittle and degrades hot-workability of a stainless steel strip. These defects are suppressed by controlling S content to 0.020 mass % or less.

0-0.10 mass % of Al

[0019] Al is an element, which is added as a deoxidizing agent in a steelmaking process. However, excess Al above 0.10 mass % increases non-metallic inclusions, which cause degradation of toughness and occurrence of surface defects.

0-0.10 mass % of N

[0020] N is an austenite former for promoting formation of an austenite phase while suppressing formation of δ -ferrite in a high-temperature zone. But, excess N above 0.10 mass % allows existence of residual austenite in an annealed state. The residual austenite causes unfavorable strain-induced martensitic transformation during plastically forming a stainless steel sheet to a product shape, resulting in occurrence of strains. Furthermore, ductility of a cold-rolled stainless steel sheet is degraded in an annealed state as increase of N.

0-1.0 mass % of Mo

[0021] Mo is an alloying element effective for corrosion-resistance, but excess Mo above 1.0 mass % degrades hot-workability of a stainless steel strip due to its effect on solution-hardening and retarding dynamic recrystallization.

Cu not more than 2.0 mass %

[0022] Cu is an impurity included in a stainless steel from raw materials such as scraps. Since excess Cu degrades hot-workability and corrosion-resistance of the stainless steel, Cu content is determined at 2.0 mass % or less.

0.01-0.50 mass % of Ti, 0.01-0.50 mass % of Nb,

0.01-0.30 mass % of V and 0.01-0.30 mass % of Zr

[0023] Ti, Nb, V and Zr are elements effective for workability and toughness. Ti, Nb and V stabilize dissolved C as carbides, while Zr captures O as an oxide in a steel matrix. Ratios of these elements are preferably determined to 0.01-0.50 mass % of Ti, 0.01-0.50 mass % of Nb, 0.01-0.30 mass % of V and 0.01-0.30 mass % of Zr, since excess addition of these elements degrades productivity of a stainless steel strip.

0.0010-0.0100 mass % of B

[0024] B is an element, which disperses transformed grains uniformly in a hot-rolled steel sheet and minimizes the transformed grains during dual phase-annealing. The effect of B is typically noted at 0.0010 mass % or more, but excess B above 0.0100 mass % degrades hot-workability and weldability of the stainless steel strip.

0-0.02 mass % of Y, 0-0.05 mass % of Ca and 0-0.1 mass % of REM

[0025] Y, Ca and REM are alloying elements effective for hot-workability, but excess addition of these elements

causes surface defects. In this sense, upper limits of Y, Ca and REM are preferably determined at 0.02, 0.05 and 0.1 mass %, respectively.

[0026] Metallurgical structure, prior austenite grains and an expansion ratio during martensitic transformation are controlled in addition to the specified alloying design, in order to suppress effects of strains and volumetric expansion, which are originated in the martensitic transformation, on occurrence of Lüders band.

Metallurgical structure: 20-85 vol. % martensite grains and the balance being ferrite grains.

[0027] A ratio 20-85 vol. % of martensite grains at a room temperature corresponds to the same ratio % of austenite grains in a high-temperature zone. A high-temperature austenite phase is transformed to a martensite phase in a cooling step to a room temperature, but transformation strains, which derived from dislocations in the martensite phase and volumetric expansion during the transformation, are introduced into a cooled stainless steel strip.

[0028] Transformation strains are uniformly dispersed and absorbed in soft ferrite grains in the vicinity of martensite grains by minimization of prior austenite grains so as to enlarge intergranular areas between the prior austenite and ferrite grains in a high-temperature zone. As a result, an external surface of a steel strip is prevented from deformation originated in the transformation. When the stainless steel strip formed to a belt shape is straightened by application of 1-2% tensile strain after uniform dispersion and absorption of the transformation strains, the transformation strains are absorbed in strains caused by straightening. Consequently, the steel strip is plastically formed to the objective belt shape without occurrence of Lüders band.

[0029] Efficient absorption of the uniformly dispersed transformation strains in work strains without occurrence of Lüders band is realized by controlling a ratio of martensite grains, which accumulates the transformation strains, to 20 vol. % or more. If a ratio of martensite grains is less than 20 vol. %, tensile strains of 1-2%, which are applied to a stainless steel strip during straightening, exceeds a capacity for accumulation of transformation strains and causes appearance of Lüders band on a surface of the stainless steel strip. A small ratio of martensite grains also means presence of excess soft ferrite grains, resulting in poor strength of the steel strip. But, a ratio of martensite grains above 85 vol. % is substantially equal to complete martensitic transformation, which produces large strains, degrades a profile and transubstantiates the steel strip to a difficult-straightening state.

Prior austenite grains of 10 μm or less in average size

[0030] Ferrite grains and martensite grains, which are formed in a cooling step of annealing, become smaller in size as minimization of prior austenite grains, so that domains for martensitic transformation are advantageously distributed to a state suitable for uniform dispersion of strains originated in the martensitic transformation. Consequently, a steel strip is straightened to a belt shape without inhomogeneous deformation or Lüders band. The effect of prior austenite grains on uniform dispersion of transformation strains, in other words suppression of Lüders band, is noted at grain size of 10 μm or less.

Martensitic transformation with an average expansion ratio of 9% or less

[0031] According to martensitic transformation, a stainless steel strip changes its crystalline structure from f.c.c. to b.c.c. or b.c.t. and number of atoms packed in one crystalline structure, resulting in volumetric expansion. An expansion ratio caused by the martensitic transformation is not simply proportional to a ratio of martensite grains formed by transformation, but depends on distribution of martensite and ferrite grains. As the formed martensite grains are distributed in finer size, transformation strains are efficiently absorbed and accumulated in soft ferrite grains in the vicinity of the martensite grains. Such distribution of fine martensite grains is attained by minimizing prior austenite grains so as to enlarge intergranular areas between ferrite grains and martensite grains formed by the transformation.

[0032] A total expansion rate of a stainless steel strip is reduced by absorption and accumulation of transformation strains. Due to the effect of fine martensite grains on suppression of transformation strains, the stainless steel strip is formed to a belt shape without inhomogeneous deformation or Lüders band during straightening. In this meaning, prior austenite grains are minimized to 10 μm or less in size, a martensite/ferrite dual-phase structure is refined in grain size so as to enlarge intergranular areas between martensite and ferrite grains, and an expansion rate of martensitic transformation is controlled not more than 9% in average.

Hardness of HV 300 or more

[0033] A dual-phase stainless steel strip is conditioned to proper hardness by controlling C and Ni contents as well as a ratio of martensite grains. In the case where the steel strip is used as a material for a steel belt, which is driven at a high speed with rapid response under the condition that a demand for fatigue strength is intensified in response to miniaturization of pulleys, it is hardened to HV 300 or more.

[0034] The other features of the present invention will be clearly understood from the following examples.

EP 1 396 552 A1

[0035] Several stainless steels with chemical compositions shown in Table 1 were vacuum-melted, cast, forged and hot-rolled to thickness of 3.0 mm. Steel Nos. 1-5 in Table 1 had compositions defined by the present invention, while Steel Nos. 6-8 were out of the scope of the present invention.

[0036] Hot-rolled steel strips Nos. 1-7 were diffusion-annealed 8 hours at 780°C, pickled, cold-rolled to thickness of 1.0 mm, dual-phase annealed 1 minute at 1050°C and then pickled again. A hot-rolled steel strip No. 8 (corresponding to SUS 301) of 2.0 mm in thickness was annealed 6 hours at 1050°C and cold-rolled to thickness of 1.0 mm.

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TABLE 1: Chemical Compositions of Stainless Steels

Steel No.	Alloying Elements (mass %)									Note	Inventive Examples	Comparative Examples
	C	Si	Mn	Ni	Cr	Cu	N	Mo	Al	Others		
1	0.058	0.48	0.18	1.87	16.74	0.18	0.008	0.24	0.012			
2	0.039	0.77	0.25	0.67	16.18	0.14	0.029	0.18	0.009	Nb 0.05 V 0.09		
3	0.087	0.58	0.88	0.89	17.98	0.67	0.027	0.33	0.007	Ti 0.15 B 0.008		
4	0.125	0.28	0.49	1.28	17.29	0.44	0.018	0.29	0.004	Y 0.007 REM 0.007		
5	0.042	0.29	0.47	3.98	13.25	0.49	0.026	0.36	0.003	Ca : 0.005		
6	0.087	0.22	0.87	<u>0.22</u>	16.58	0.12	0.039	0.02	0.065			
7	<u>0.027</u>	0.47	0.39	<u>0.26</u>	18.25	0.34	0.028	0.29	0.001			
8	0.107	0.67	1.08	<u>6.85</u>	16.88	0.25	0.046	0.15	0.012			

The underlined figures are out of the definitions of the present invention.

[0037] Test pieces sampled from each steel strip were subjected to tests for quantification of metallurgical structure, measurement of surface hardness with a load of 1 kg and measurement of size of prior austenite grains. Ratios of ferrite and martensite grains were measured by etching the test piece with an etchant of hydrofluoric acid 2 : nitric acid 1 : glycerine 1, and counting number of ferrite or martensite grains. A ratio of austenite grains was measured by a magnetic method. Grain size of a prior austenite phase was measured by intercept method on a field observed with a

microscope. An expansion rate originated in martensitic transformation was calculated as a volumetric expansion by measuring a rate of unidirectional expansion caused by transformation in a cooling step of dual-phase annealing and cubing the measurement values. Results are shown in Table 2.

[0038] A test piece of 50 mm in width and 200 mm in length was sampled from each stainless steel strip along its rolling direction, and subjected to a simulation test for straightening a steel sheet to a belt shape. In the simulation test, a tensile strain at 5% at most was applied to the test piece at a strain rate of 1 mm/minute by a tensile tester, and a surface of the stretched test piece was observed for detection of Lüders band. Prior to application of the tensile strain, the test piece was repeatedly bent 10 times by bending stress with a radius of 50 mm, so as to imitate driving situation of a steel belt which was affected by bending stress at pulleys. Results are shown in Table 2.

TABLE 2: Metallurgical Structures and Properties of Stainless Steel Strips

Steel No.	Phase (vol. %)			Grain size (μm) of prior austenite	Hardness HV	Average expansion rate (vol. %)	Occurrence of Lüders band	Note
	Martensite	Ferrite	Austenite					
1	63	37	0	6.5	375	6.3	no	Inventive Examples
2	38	62	0	4.2	302	3.2	no	
3	65	35	0	6.5	395	5.9	no	
4	78	22	0	5.9	432	7.0	no	
5	65	35	0	7.2	382	7.7	no	
6	75	25	0	<u>12</u>	316	<u>9.2</u>	yes * 1	Comparative Examples
7	<u>12</u>	<u>88</u>	0	<u>15</u>	<u>235</u>	1.3	yes	
8	65	<u>0</u>	<u>35</u>	<u>35</u>	456	0.0	yes	

The underlines figures are out of the definitions of the present invention.

* : cracked during bending

[0039] Results shown in Table 2 prove that any of the inventive stainless steel strips Nos. 1-5 was formed and straightened to a belt shape without Lüders band.

[0040] As for the comparative steel strip No. 6, formation of nuclei for prior austenite was insufficient due to shortage of Ni, and Lüders band was detected since prior austenite grains were bigger than 10 µm in size and an expansion rate was more than 9% in average. The insufficient Ni content also led to poor strength, so that the test piece was sometimes cracked during repetition of bending in prior to the tensile test.

[0041] A ratio of martensite grains in the comparative steel strip No. 7 was smaller due to shortage of C, and transformation strains were insufficient for homogeneous deformation during straightening the steel strip to a belt shape, resulting in inhomogeneous deformation, in other words Lüders band. Ni content of the comparative steel No. 7 was reduced to the same level as the steel No. 6, but C content was also reduced, so that the steel strip No. 7 was not cracked during repetition of bending.

[0042] The comparative steel No. 8 had a structure including a lot of residual austenite due to excess Ni. Since the residual austenite was transformed to a martensite phase during tensile deformation, Lüders band was detected on the stretched test piece.

INDUSTRIAL APPLICABILITY

[0043] According to the present invention as above-mentioned, transformation strains, which are generated during martensitic transformation in a cooling step of annealing, are uniformly dispersed in a steel matrix and accumulated in soft ferrite grains, by minimizing prior austenite grains so as to enlarge intergranular areas between ferrite and martensite grains. The transformation strains accumulated in the ferrite grains are absorbed in work strains, which are applied to a steel strip during straightening it to a belt shape, without occurrence of Lüders band. Consequently, the ferrite/martensite dual-phase stainless steel strip is useful as steel belts with good profile and fine external appearance free from Lüders band, in comparison with conventional work-hardening and precipitation-hardening stainless steel belts.

Claims

1. A dual-phase stainless steel strip for use as steel belts, which has:

a chemical composition consisting of 0.04-0.15 mass % C, 10.0-20.0 mass % Cr; 0.5-4.0 mass % Ni and the balance being Fe except inevitable impurities,
a transformed structure composed of 20-85 vol. % martensite grains and the balance being ferrite grains with prior austenite grains controlled to 10 µm or less in size, and hardness of HV 300 or more.

2. The dual-phase stainless steel strip defined by Claim 1, wherein the chemical composition further contains one or more of Si up to 2.0 mass %, Mn up to 2.0 mass %, not more than 0.050 mass % of P, not more than 0.020 mass % of S, 0-0.10 mass % of Al, 0-0.10 mass % of N, 0-1.0 mass % of Mo, 0-2.0 mass % of Cu, 0.01-0.50 mass % of Ti, 0.01-0.50 mass % of Nb, 0.01-0.30 mass % of V, 0.01-0.30 mass % of Zr, 0.0010-0.0100 mass % of B, 0-0.02 mass % of Y, 0-0.05 mass % of Ca and 0-0.1 mass % of REM (rare earth metals).

3. The dual-phase stainless steel strip defined by Claim 1 or 2, wherein an expansion rate during martensitic transformation of austenite is controlled to 9% or less in average.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/05572

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁷ C22C38/00, 38/40, 38/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁷ C22C38/00-38/60, C21D8/00-8/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95/13405 A1 (NISSHIN STEEL CO., LTD.), 18 May, 1995 (18.05.95), & EP 682122 A1 & US 5624504 A & JP 07-138704 A	1-3
Y	JP 9-263912 A (NISSHIN STEEL CO., LTD.), 07 October, 1997 (07.10.97), (Family: none)	1-3
Y	JP 10-265907 A (Nippon Kinzoku Co., Ltd.), 06 October, 1998 (06.10.98), (Family: none)	1-3
Y	JP 2000-129400 A (NISSHIN STEEL CO., LTD.), 09 May, 2000 (09.05.00), (Family: none)	1-3

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
01 August, 2002 (01.08.02)Date of mailing of the international search report
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Japanese Patent Office

Authorized officer

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Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/05572

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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