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(54) HIGH STRENGTH HIGH DUCTILITY STEEL WITH SUPERIOR FORMABILITY

(57) This invention relates to relates to a high strength steel sheet as hot-rolled and cold-rolled products useful for frame components for vehicles and automobiles such as frames for trucks, or a component of a structure or engineering project.

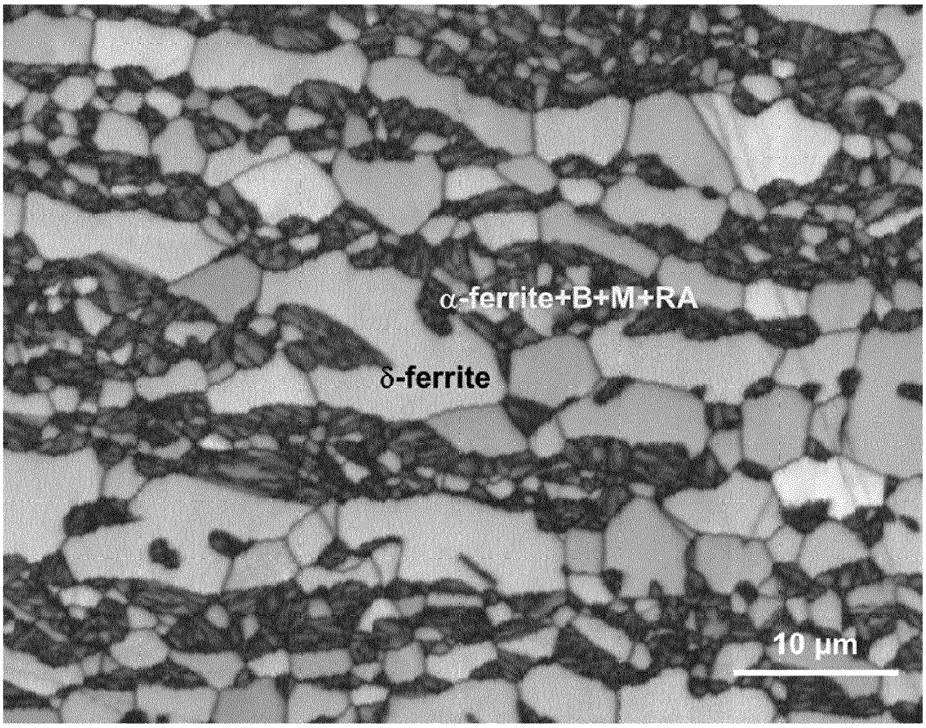

FIGURE 4

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Description

[0001] This invention relates to a high strength steel sheet as hot-rolled and cold-rolled products useful for frame components for vehicles and automobiles such as frames for trucks.

[0002] In recent years, (advanced) high strength steel sheets, AHSS, are increasingly used in car components to reduce weight and fuel consumption. A series of (advanced) high strength steels, such as HSLA, Dual phase (DP), Ferritic-bainitic (FB) including stretch-flangeable (SF), Complex phase (CP), Transformation-induced plasticity (TRIP), Hot-formed, Twinning-induced plasticity (TWIP) has been developed to meet the growing requirements.

[0003] However, AHSS sheet steels cannot be applied easily to a wide variety of car components because their formability is relatively poor. As steels became increasingly stronger, they simultaneously became increasingly difficult to form into automotive parts. Actually, the application of AHSS steels (DP, CP and TRIP) to car components is still limited by their formability. Therefore, improving formability and manufacturability is an important issue for AHSS applications.

[0004] To achieve a high yield strength/tensile strength ratio and an even higher tensile strength, i.e. above 800 MPa, steels having complex microstructures (ferrite, bainite martensite and/or retained austenite) have been developed.

[0005] Transformation-induced plasticity (TRIP) steel is one of these high-strength steels that utilize phase transformation to control the mechanical properties. Strain-induced martensitic transformation of metastable austenite plays a major role in improving the mechanical balance (tensile strength x elongation), allowing TRIP steel to be actively applied in the automotive industry. Currently, the tensile strength of commercially produced TRIP steel reaches approximately 1000 MPa. However, when the tensile strength exceeds 800 MPa, the elongation tends to decrease to less than 15 % and the mechanical balance is significantly deteriorated. A microstructural control ensuring higher stability as well as a sufficient fraction of retained austenite would be essential to obtain a higher tensile strength with desirable elongation.

[0006] Low-carbon, manganese TRIP steel (Mn TRIP steel) based on an alloy system of Fe-0.1C-5Mn was first introduced by Miller [R.L. Miller: Metall. Trans., 1972, vol. 3, pp. 905-12]. A retained austenite fraction of 20 ~ 40 % with optimized stability made it possible to exhibit an excellent mechanical balance after intercritical annealing. However, a prolonged heat treatment using a batch-type annealing process was required to obtain the desired properties.

[0007] Grain refinement of steels to submicron size and nano size has also been used to explore the improvement of the strength of metals. However, it has been reported that the ductility of ultra-fine grained (UFG) metals decreases as the grain size is reduced below 5 μm. The uniform elongation turns to almost zero when grain size becomes less than 2 μm. For the UFG materials, fracture occurs immediately after yielding during plastic deformation at room temperature. The low ductility in ultrafine-grained metals and alloys is attributed to their very poor work hardening capacity caused by their inability to accumulate dislocations because of their small grain size and saturation of dislocations, which seems to be a size effect intrinsic to small plastic domains. This indicates that it is difficult to manufacture products such as vehicle and aircraft components made of ultrafine-grained metals, particularly nano-crystalline metals, through secondary plastic deformation methods such as forging, pressing, and drawing.

[0008] It is an object of the present invention to provide a process for producing a steel grade which combines high yield and tensile strength with a good elongation.

[0009] It is also an object of the present invention to provide a steel grade which combines high yield and tensile strength with a good elongation.

[0010] According to a first aspect one or more of the objects of the invention may be reached with a process for producing a high strength cold-rolled and heat-treated steel strip, sheet, blank or hot formed product having a bimodal microstructure comprising the steps of:

- producing and casting a melt into a slab or cast strip having the following composition;

    0.05 - 0.50 wt.% C;
    0.50 - 8.0 wt.% Mn;
    0.05 - 6.0 wt.% Al_tot;
    0.0001 - 0.05 wt.% Sb;
    0.0005 - 0.005 wt.% of Σ (Ca + REM);
    5 - 100 ppm N;
    0 - 2.0 wt.% Si;
    0 - 0.01 wt.% S;
    0 - 0.1 wt. % P;
    0 - 1.0 wt.% Cr;
    0 - 2.0 wt.% Ni;
    0 - 2.0 wt.% Cu;
    0 - 0.5 wt.% Mo;

0 - 0.1 wt.% V;
0 - 50 ppm B;
0 - 0.10 wt.% Ti.

remainder iron and inevitable impurities,

- reheating the slab or cast strip to a reheating temperature of between 1100 and 1250 °C;
- hot-rolling the slab or cast strip to a hot-rolled strip wherein the finishing temperature is 800 to 950 °C;
- cooling and coiling the hot-rolled strip between 650 and 450 °C;
- pickling the hot-rolled strip;
- cold-rolling the pickled hot-rolled strip, preferably with a total cold rolling reduction of between 40 and 80 %;
- optionally producing sheet or blanks from the cold-rolled strip;
- heat treating the steel strip, sheet or blank by intercritically annealing, preferably at a temperature between 700 and 900 °C, for a duration of between 1 and 300 s.
- cooling the annealed steel strip, sheet or blank to an austempering temperature for an austempering treatment between 500 and 300 °C, preferably at most 480 and/or at least 350 °C, at a cooling rate which is higher than the critical rate for formation of pearlite, and maintained for a duration of 10 to 600s and subsequently cooled to ambient temperatures,

so as to achieve annealed steel strip, sheet or blank with bimodal grain microstructure consisting of a ferritic matrix phase having a grain size of between 5 and 20 μm and a second phase consisting of one or more of or bainite, martensite and retained austenite with a grain size of at most 5 μm, and wherein the final microstructure contains at least 20 vol.% of δ-ferrite.

[0011] Preferred embodiments are provided in the dependent claims 2 to 11.

[0012] The bimodal grain size distribution is essential in these steels. With the bimodal size distribution of grains in the microstructure, the restricted ductility of UFG steels due to the high strain-hardening capacity of the coarse grains and strengthening ability of the ultrafine grains can be overcome, and provides a good compromise between strength and elongation.

[0013] This invention is to provide steels with a high strength and a high deformability. The invented steel sheets are multi-phase steels including δ-ferrite, α-ferrite, martensite and/or bainite and retained austenite and having a bimodal microstructures, in which with δ-ferrite has a relative large grain size range from 5-20 μm, while the α-ferrite and other phases have a small grain size < 5 μm.

[0014] The matrix of the steel consists of δ and α ferrite, and for it to be a matrix phase, the minimum of $\sum(\delta+\alpha)$ is at least 50 vol.%. The sum of the bainite, martensite and retained austenite phases is between 5 and 50 vol.%. Consequently the maximum of $\sum(\delta+\alpha)$ is between 95 and 50%. A suitable maximum for δ-ferrite is 80 vol%, preferably 70 vol.%, more preferably 60 vol.%.

[0015] Figure 1 gives a schematic indication of the phases in pure iron during slow cooling from the liquid phase (L). As pure iron cools, it changes from one phase to another at constant temperatures. Pure iron solidifies from the liquid at 1538 °C (top of Fig. 1). A crystalline body-centered cubic lattice (bcc) structure, known as δ-ferrite, is formed (point a). As cooling proceeds further and point b (Fig. 1) is reached (1395 °C), the atoms rearrange into the face-centered cubic lattice (fcc), and this structure is called γ-iron or austenite. As cooling further proceeds to 910 °C (point c), the structure reverts to the bcc structure and this low temperature bcc-phase is called α-ferrite. The change at point d (770 °C) merely denotes a change from paramagnetic to ferromagnetic iron and does not represent a phase change (the magnetic transformation is usually considered to be a second order phase transformation, and the temperature at which this occurs is the Curie-temperature). The entire field below 910 °C is composed of α-ferrite, which continues down to room temperature and below. This principle applies also to iron-based alloys, although the transformation temperatures are strongly influenced by the alloying additions to the iron. These influences can be made visible with the so-called phase diagrams.

[0016] So the δ-ferrite is a ferritic phase originating from the solidified steel and the likelihood of it forming is increased as a result of the selected composition. Also, whether or not it remains stable at ambient temperatures upon cooling from the δ-ferrite field depends on the composition as well. The required amount of the δ-ferrite in the final microstructure of the steels according to the invention is at least 20 % in volume.

[0017] C is a necessary element for strength and hardenability.

[0018] The austenite phase is enriched with C on annealing in the α-γ intercritical region as well as during austempering of a bainitic structure. The higher carbon content in the austenite contributes to lowering the M_s transformation temperature of austenite into martensite. The C dissolved in the austenite stabilises the austenite to form residual austenite at ambient temperatures if the Ms is below ambient temperatures. Upon deforming some amount of the residual austenite or all of it transforms to martensite and thus contributes to the strength after deformation, whilst being relatively ductile before deformation. However, it is required that the C content is controlled at an appropriate level so as to control the desired microstructure and maintain the delicate balance of microstructure and properties. For the steels according to the invention the carbon content is from 0.05 to 0.5 wt.% (all compositional percentages are in weight percent (wt.%) unless otherwise indicated). A suitable minimum amount is 0.08 %, preferably at least 0.10 %. A suitable maximum amount is 0.46 %, more preferably at most 0.40 %.

[0019] Silicon and aluminium are ferrite forming elements which are added to promote the formation of the δ-ferrite in the microstructure. These elements also increase the concentration of C in austenite and suppress the formation of carbides and thus have the function to promote the formation of residual austenite. The sum total of Si and Al is from 0.1 to 6.5 %. Silicon is preferably between 0.05 % and 2.0 %, the upper boundary being dictated by surface quality. Aluminium is preferably between 0.05 and 6 %. A high content of Al results in a steel sheet exhibiting a high value in a total elongation while maintaining a high strength. However, if Al is excessively added, κ-carbide may be formed during intercritical annealing and a disorder (bcc_A2) to order (bcc_B2) transition will occur in the ferrite at a lower temperature. The formation of the ordered structure reduces the ductility of steel, so that the upper limit of aluminium is restricted to 6 %. A suitable minimum amount of aluminium is 0.75 %. In a preferable embodiment the minimum amount of aluminium is 1.5 %, or even 2.5 %.

[0020] The amount of Si and Al needs to be adjusted according to the total amount of (Mn+Cu+Ni) to guarantee the presence of the δ-ferrite and complete recrystallization in the δ-ferrite during annealing at the intercritical ($\gamma + \delta$) temperatures. To ensure the formation of δ-ferrite, the following equation has to be satisfied (in wt.%):

$$Al + (Si/3) \geq 4 \cdot C + 0.24 \cdot (Mn+Cu+Ni) + 0.9$$

[0021] The functions of the manganese are to stabilize the austenite and to harden the steel. Below 0.5 % these effects are not sufficiently marked. If the content of Mn increases, the phase transformation points A_3 and A_1, the martensite and the bainite transformation temperatures are lowered. The recrystallization temperature of the ferrite phase is increased and recrystallization kinetics of ferrite is decreased. Higher amounts of ferritic stabilizers, such as Al and Si are needed to increase A_1 and A_3 and to guarantee the formation of a ferritic matrix. Thus, the level of Mn is limited to at most 8 %, and preferably to at most 7 %, and even more preferably at most 6 %.

[0022] Cu and Ni can optionally be used at amounts of up to 2 % Cu and 2 % Ni to partly replace Mn, but the total amount of Cu, Mn and Ni ($\sum$(Mn+Cu+Ni)) must be in the range of 0.5 to 8 %. The added copper may provide precipitation hardening. Moreover, because the copper is insoluble in the cementite, it has a beneficial effect on the residual austenite, similar to silicon and aluminium.

[0023] Sb is an important element for steels containing high amounts of alloying elements such as Al, Mn and Si. Sb itself does not form an oxide thin film at high temperature, but is enriched into the surface and the grain boundaries. As a result, Sb inhibits Al, Mn and Si from diffusing to the surface, which results in inhibiting the oxidation of these elements. Thus, the addition of minute amounts of Sb has an unexpected and remarkable effect on the occurrence of MnO, SiO_2, Al_2O_3, etc. during annealing a cold-rolled steel sheet. In order to produce these effects only small amounts of Sb are required, and 0.0005 % (5 ppm) Sb already has an effect. So a preferable minimum amount is 0.0005 % Sb, more preferably at least 0.001 % (10 ppm). If Sb is added beyond a specified limit, it brings grain boundary embrittlement. Thus, the content of Sb is limited to the upper limit 0.05 %, preferably to the upper limit of 0.015 %, even more preferably 0.01 % (100 ppm).

[0024] P is an element useful for maintaining desired retained austenite, and its effect is exerted by an amount of P of 0.001 % or larger, more preferably 0.003 % or larger, but when an amount of P is excessive, secondary processability is deteriorated. Therefore, an amount of P should be suppressed to 0.02 % or smaller, preferably 0.015 % or smaller.

[0025] S is a harmful element which forms sulphide based inclusions such as MnS, which may serve as a crack initiator, thereby deteriorating processability. Therefore, it is desirable to reduce the amount of S as much as possible. Accordingly, S is 0.02 % or smaller. Preferably S is 0.01 % or even 0.008 % or smaller.

[0026] Nitrogen (N) is inevitably present in the BOF steel making process and allowable in the steels according to the invention in amounts between 5 to 100 ppm. The N content is preferably 60 ppm or less. Desirably, the N content is decreased as much as possible. A suitable and practical minimum N content is 10 ppm.

[0027] Boron (B) is a potent hardenability enhancer in low C, low alloy steels. B is a very effective alloying element in increasing the yield strength. The B content should preferably be at most 25 ppm so as not to impair low temperature toughness. For the boron to be able to perform this role, it is essential that no free nitrogen is present so that the formation of BN is avoided. This is where the nitrogen scavenging effect of certain elements such as titanium or aluminium comes in. A suitable minimum amount of Boron is 5 ppm.

[0028] At least one element selected from Ca: 0.005 % or smaller and REM: 0.005 % or smaller is used. These Ca and REM (rare earth element) are elements effective for controlling a form of sulphide in the steel, and improving processability. Examples of the rare earth element include Scandium, Yttrium, and lanthanide. It is recommended that for these elements to be useful they have to be present in amounts of 0.0005 % or higher. However, when added excessively, the effect is saturated and the economic efficiency is reduced. Therefore, it is better to suppress an amount thereof to 0.005 % or smaller, preferably to 0.003 % or smaller.

[0029] Ti can also be added in a total amount not exceeding 0.3 %. Ti forms carbides, nitrides or carbonitrides which block grain growth at high temperature and increase strength by precipitation. Preferably Ti does not exceed 0.1 %.

[0030] It is desirable to avoid the addition of elements which slow down the bainitic transformation. This applies for instance to Cr, Mo and V. In any event, the contents of each of these elements individually must preferably not exceed 1 %. Preferably, their total concentration ($\sum$(Cr+Mo+V)) must not exceed 0.3 %.

[0031] The other elements present in the steel are those usually found as manufacturing impurities, in proportions which have no significant effect on the required properties of steel.

[0032] Figure 2 shows the phase diagram of Fe-5.8Mn-3.2Al-0.25Si-xC steels as an example according to the current invention.

[0033] In the process according to the invention a steel melt is conventionally cast in the form of a thick slab, a thin slab or a strip. After casting it is brought to hot-rolling temperatures by (re-)heating and/or homogenising and hot-rolled, depending on whether the cast was made as a thick slab, a thin slab or a strip. The slab reheating temperature (SRT) or homogenisation temperature has to be sufficiently high to dissolve coarse Ti and V carbides which may have precipitated in the slab during casting or to keep them in solution in case of a thin slab casting and direct-rolling process. The inventors found that a SRT of at between 1100 and 1300 °C is preferable. A suitable maximum SRT is 1250 °C. The reheating of the slab or cast strip to the reheating temperature is a known process per se and the time needed to reheat the slab or strip to the reheating temperature depends inter alia on the type of furnace, the thermal capacity of the furnace, the thickness of the slab or strip. Typical residence times in a reheating furnace of a conventional hot strip mill are between 2 and 5 hours when starting from cold slabs. In a thin slab casting and direct rolling mill the slabs are not cooled but homogenised at the reheating temperature. Typical residence times in a reheating furnace of such a mill is typically between 5 and 120 minutes.

[0034] The hot-rolling pass is performed on the steels within the two-phase (γ + δ) field. So the microstructure during hot-rolling consists of γ-grains and δ-ferrite grains. During hot-rolling, recovery and/or recrystallization occur in the two phases. However, due to the difference in the recrystallization behaviour, the grains in the γ phase are refined through recrystallization, while the grains in the δ phase are coarser and present as elongated shape as the recrystallization is incomplete. On the other hand, partitioning of elements, C, Mn and Al occurs between the δ- and γ-phases and some amount of the α-ferrite forms within the γ phase as the hot rolling temperature gradually decreases. The δ-ferrite does not transform to austenite upon cooling because it is stabilised by the alloying elements in the steel. The microstructure at hot rolling finish temperatures after hot-rolling consists of partially recrystallized bands of coarse grained δ-ferrite, bands of γ-austenite with smaller grains and small amount of α-ferrite within the γ bands. The hot-rolling finishing temperature is preferably between 800 °C to 950 °C. This temperature range is applied to produce fine grains in the austenite (γ) and elongated laminate grains in the δ-ferrite.

[0035] The thickness of the hot-rolled strip according to the invention is between 1.5 and 10 mm. Preferably the thickness is at least 2 and/or at most 8 mm, more preferably at least 3 and/or at most 6 mm.

[0036] After finish rolling the steel is cooled on the run-out table of the hot strip mill, preferably at an average cooling rate of between 5 and 200 °C/s, more preferably of at least 10 and/or at most 150 °C/s, or even more preferably of at most 100 °C, to a coiling temperature of between 650 and 450 °C followed by cooling of the coil by natural cooling down to ambient temperature. During cooling and coiling, the γ phase decomposes into α-ferrite and κ-carbide or other carbides. If the cooling rate is too low or the coiling temperature is too high, carbides may form in a larger size along grain boundaries, which is detrimental to cold rolling. So the formation of coarse carbides must be avoided. The preferred average cooling rate ensures that the formation of coarse carbides is avoided.

[0037] The hot-rolled steel sheet is coiled at a temperature between 450 °C to 650 °C. In this temperature range, elements such as Si, Mn and Al in steel react with an oxide scale (FeO) after coiling, thereby forming alloyed oxides at a scale/metal interface. This formation of the Si, Mn and Al oxides has a strong influence on concentrations of these elements in the outermost surface layer of the strip. The addition of Sb has a suppressing effect on the formation of these alloyed oxides at very low additions.

[0038] If the coiling temperature is lower than 450 °C, undesirable amounts of low temperature transformation structures, such as bainite and martensite may be formed, which adversely affect the cold-rollability. When the coiling temperature exceeds 650 °C, then internal oxidation of Si, Mn and Al become problematic, and the inhibiting effect of Sb is no longer able to prevent this if the coiling temperature exceeds 650 °C. This has an adverse influence on surface roughness and pickleability. Preferably the coiling temperature is at least 475 °C, preferably at least 500 °C, more preferably at least 525 °C. Preferably the coiling temperature is at most 625 °C, more preferably at most 600 °C. By decreasing the allowable range of coiling temperatures the homogeneity of the microstructure improves.

[0039] The hot-rolled material is subsequently pickled and cold-rolled, preferably with a reduction of at least 40 % and/or at most 80 %. The cold-rolled material is then annealed in a continuous annealing furnace. This is essential, because the batch annealed process does not result in the desired properties of the annealed strip, it is economically very unattractive, and as the heating and cooling during annealing determines the final microstructure and properties it results in an inhomogeneous product as a result of the very slow heating and cooling process which is different for each location in the coil. The time-temperature profile of the heat treatments following the cold rolling are schematically demonstrated in Figure 3. The thickness of the cold rolled-strip depends on the degree of cold rolling reduction and the hot-rolled strip serving as input. The thickness of the cold-rolled strip according to the invention is between 0.3 and 6 mm. Preferably the thickness is at least 0.4 and/or at most 6 mm, more preferably at least 0.6 and/or at most 3.6 mm.

[0040] Subsequently, the cold-rolled sheet is annealed at an ($\delta + \gamma$) intercritical temperature. Because of the difference in recrystallization behaviour between the δ- and the γ-phases and the partially reverse transformation of γ to α during intercritical annealing, a microstructure with a bimodal grain size distribution can be obtained during annealing. The recrystallized δ-ferrite has a larger grain size, while the austenite and the α-ferrite have a smaller grain size. The annealing can be performed in a continuous annealing line in a temperature range of 700-900 °C for a duration of between 1 and 300s.

[0041] During an optional initial slow cooling section (see the dashed part (a) in Figure 3), some α-ferrite may form in the austenitic region. This slow cooling causes carbon to be further enriched into the austenite. The stability of the austenite increases as the C content is increased.

[0042] The cold-rolling reduction, the annealing time-temperature profile and the subsequent slow cooling process after the annealing are very important for obtaining the final microstructure and the properties of the cold-rolled and annealed strip. The volume fraction and the grain size of various phases as well as the stability of the retained austenite can be adjusted by changing the cold-rolling reduction, the annealing and the subsequent cooling process.

[0043] After intercritical annealing and the optional slow cooling, the steel sheet is quenched. Two possible cooling routes are available at this point:

i. direct quenching to ambient temperature
ii. quenching to an austempering temperature, austempering for a certain duration followed by cooling to ambient temperature

[0044] The first route involves direct quenching at a cooling rate sufficiently high to ambient room temperature. A cooling rate of higher than 10 °C/s is usually sufficient to prevent the decomposition of the austenite for the compositions of the steel according to the invention. A suitable maximum cooling rate is 100 °C/s, preferably at most 75 °C/s, more preferably 50 °C/s. At ambient temperature the final microstructure will consist of δ-ferrite, α-ferrite, martensite and retained austenite.

[0045] The second route involves quenching at a cooling rate sufficiently high to an temperature between 300 and 500 °C and austempering for a suitable period of 10 to 600s. The austempering temperature must be above the martensite start forming temperature (Ms) and below a bainite start forming temperature (Bs) of the austenitic phase, the exact temperatures of which depend on the steel composition and intercritical annealing temperatures and can be determined e.g. by means of dilatometric experiments. Preferably the austempering annealing takes between 30 and 300 seconds. After the austempering treatment, the steel is cooled to ambient temperatures. The cooling rate is preferably higher than 5 °C/s, and preferably at least 10 °C/s. A suitable maximum cooling rate is 100 °C/s, preferably at most 75 °C/s, more preferably 50 °C/s. In the austempering process, the austenite formed during intercritical annealing is decomposed into bainite and retained austenite. Due to the suppression of carbide formation by the high amounts of Al and/or Si during bainitic transformation, the concentration of carbon in the austenite is further increased, so that the stabilization of the retained austenite is further increased. In this case, in addition to the contribution for the ferritic matrix, this retained austenite may be transformed into martensite at room temperature by deformation, so that the ductility is further increased by the TRIP effect.

[0046] The average grain size of the δ-ferrite phase is between 5 to 20 μm, preferably at least 7 μm. The average size of the α-ferrite, bainite ferrite, martensite phases and retained austenite is less than 5 μm, preferably less than 3 μm.

[0047] The cold-rolled steel may be provided in a known way with a known metallic coating by means of electroplating or hot-dipping, e.g. by hot dip galvanising, preferably wherein the metallic coating is an aluminium based alloy or a zinc based alloy. Preferably, the galvanizing is carried out in a hot dip galvanizing bath between 400 °C to 500 °C, and then the alloying treatment is carried out at a temperature of 500 °C to 580 °C.

[0048] According to a second aspect the invention is also embodied in a steel according to claim 12 and a preferred embodiment is provided in claim 13.

[0049] The principles for the alloy design are:

- The steels have complex phase microstructures, including δ-ferrite, α-ferrite, bainitic ferrite and retained austenite, which have a bimodal grain size distribution.
- The steels contains a quantity of δ-ferrite at all temperatures and at least 20 % in the final microstructure.
- The δ-ferrite has a larger grain size of 5-20 μm. The α-ferrite and remaining phases have a smaller grain size < 5 μm.
- The TRIP effect from the retained austenite transformation contributes to the enhanced formability.
- The δ-ferrite can be retained permanently in the microstructure so that fully martensitic regions are not produced in

the heat-affected zone of the spot weld, so the steels may have good weldability.

[0050] This microstructure is obtained through composition design and by means of a two-step heat treatment that includes intercritical annealing and quenching (austempering and quenching) for specified compositions. The composition design ensures the presence of the δ-ferrite under equilibrium condition. Al and Si are added to shrink the γ phase field and to obtain the required amount of the δ-ferrite. In the as-cast state, δ-ferrite is generated as dendrites, while pearlitic microstructure is present among the dendritic aims. During reheating and hot-rolling some amount of the δ-ferrite still persists as the reheating and hot-rolling are conducted in the $(\delta + \gamma)$ two phase field. The microstructure after hot-rolling shows a banded structure: layers of the δ-ferrite and austenite, which are elongated along the rolling direction. Depending on the compositions and cooling conditions, the austenite layers may decompose into pearlite, martensite, carbide and retained austenite in the following cooling, as a multi-phase region. During cold-rolling, the δ-phase layers and multiphase layers are further elongated along the rolling direction.

[0051] During the intercritical annealing, recrystallization in the δ-phase of the cold-rolled microstructure and reverse transformation in the multiphase regions to austenite occur. Some amount of α-ferrite forms in the original austenite layer during intercritical annealing and during slow cooling in the two phase area. Bainite ferrite and martensite form during rapid cooling and austempering and following quenching. Depending on the composition, some residual austenite might be stabilized to room temperature during the final cooling.

[0052] In the final microstructure, δ-ferrite presents as layers and has a coarser grain size range from 5 to 20 μm, while the α-ferrite and other microstructure in the multiphase regions are much smaller in size, making it a ferrite-(original) austenite duplex steel having a bimodal grain structure, as shown in Figure 4.

[0053] According to a third aspect the invention is also embodied in a car, truck or structural or engineering component, such as an automotive chassis component, a component of the body in white, a component of the frame or the subframe, or a component of a structure or engineering project, said component having been produced from the steel sheet according to the invention.

[0054] The invention will now be described with reference to the following non-limiting examples.

[0055] Steels having compositions shown in Table 1 were cast into ingots of 200 mm x 110 mm x 110 mm in dimensions. The ingots were reheated to 1250 °C and soaked for 1 hour and then rough hot-rolled to 35 mm thickness. The shrinkage and segregation zone from both ends were cut off. The cut blocks were reheated at 1200 °C for 30 min and then hot-rolled to 3 mm thickness in 5 passes. The finish rolling temperature was about 900 °C. It was then cooled in a furnace from 650 °C, after holding at this temperature for 1 h to simulate a coiling procedure. The cooled hot-rolled steel strips were subjected to removal of high-temperature iron oxides from the surface using 10 % HCl solution.

[0056] The strip was cold-rolled to produce a 1.2 mm thick steel sheet (60 % reduction). The cold-rolled steel sheet was annealed in a N_2-10 % H_2 atmosphere at a temperature of between 700 and 900 °C for 60 to 180 s, slowly cooled with a cooling rate 2 °C/s to a temperature between 800 and 650 °C, cooled at a rate of 15 to 30 °C/s to a temperature between 480 and 350 °C, maintained at a temperature for a time between 30 and 100 s, and finally cooled to ambient temperature at a rate of 15 to 30 °C/s.

[0057] JIS No. 5 tensile test piece (gauge length = 50 mm) were machined from each annealed sample so that the load axis was parallel to the rolling direction. Room temperature tensile tests were performed in a Schenk TREBEL testing machine following NEN-EN10002-1:2001 standard to determine tensile properties (yield strength YS (MPa), ultimate tensile strength UTS (MPa), total elongation TE (%)). For each condition, three tensile tests were performed and the average values of mechanical properties are reported.

Table 1. The compositions of the cast steels*

Steel	C	Mn	Si	Al	Cu	Cr	Ti	N	B	P	S	Sb	Al+Si/3	Σ**
A	0.18	3.5	0.06	4.7	0.05	0.12	0.010	0.005	-	0.004	0.003	0.001	4.72	2.46
C	0.13	5.8	0.25	3.2	0.01	0.02	0.020	0.003	-	0.005	0.002	0.002	3.28	2.81
D	0.13	5.8	1.46	2.8	0.01	0.01	0.010	0.003	-	0.005	0.005	0.002	3.29	2.81
E	0.32	5.9	0.45	4.3	0.01	0.01	0.020	0.002	-	0.005	0.005	0.002	4.45	3.60
F	0.35	3.5	0.06	4.4	0.01	0.01	0.040	0.002	-	0.005	0.004	0.001	4.42	3.14
G	0.39	3.5	0.15	5.9	0.05	0.05	0.005	0.003	-	0.008	0.005	0.002	5.95	3.30
H	0.38	1.2	0.22	3.0	0.01	0.02	0.005	0.003	-	0.005	0.005	0.002	3.07	2.71
I	0.38	0.6	0.21	4.1	0.02	0.02	0.005	0.003	-	0.006	0.004	0.003	4.17	2.56

(continued)

Steel	C	Mn	Si	Al	Cu	Cr	Ti	N	B	P	S	Sb	Al+Si/3	∑**
J	0.38	1.3	0.29	4.1	0.10	0.22	0.02	0.001	0.001	0.01	0.001	0.005	4.20	2.73
* The Ca content in these steels ranges from 0.001 to 0.002. ** ∑=4C+0.24Mn+0.9														

Table 2. Intercritical annealing, austempering process, tensile properties and volume fraction of the ferritic phase

Steel	Annealing		CR	Austempering		CR °C/s	YS MPa	UTS MPa	TE %	δ Vol. %	δ+α Vol. %
	T (°C)	Time (s)	°C/s	T (°C)	Time (s)						
A	800	120	20°	400	120	15	489	652	28.5	73	79
C1	720	120	20	RT*			814	854	21.7	30	68
C2	780	120	20	RT			714	994	27.5	30	60
C3	840	120	20	RT			444	1161	12.4	30	52
D	800	180	20	450	120	15	790	1038	22.8	25	60
E	800	180	20	450	120	15	810	1245	15.6	28	50
F	830	60	10	450	180	15	620	810	28.8	46	60
G	830	60	10	400	180	10	677	906	22	35	70
H	850	180	30	450	120	15	545	750	25.6	22	50
I	850	180	30	450	120	15	505	661	26.4	53	64
J1	850	180	30	RT			590	895	22.7	50	62
J2	850	180	30	450	60	15	510	800	30.2	50	62
*RT, room temperature											

Figure 1 - This figure shows the various phases occurring in pure iron when slowly cooled from the liquid phase to ambient temperatures.
Figure 2 - This shows the phase diagram of steel C, with the (γ + δ) intercritical annealing temperature of 700 to 900 marked by the dashed lines.
Figure 3 - This diagram shows the formation of various microstructures during and after the annealing process. RA' denotes a C-enriched RA.
Figure 4 - The SEM micrograph shows a typical example of the bimodal microstructure in the invented steel C after annealing at 780 °C for 120s. The δ-ferrite is revealed as the banded structure with large grain size of average 8 μm, whereas α-ferrite, together with martensite and retained austenite are shown as blocky islands having a finer grain size less than 2 μm.

Claims

1. Process for producing a high strength cold-rolled and heat-treated steel strip, sheet, blank or hot formed product having a bimodal microstructure comprising the steps of:

   - producing and casting a melt into a slab or cast strip having the following composition;

     0.05 - 0.50 wt.% C;
     0.50 - 8.0 wt.% Mn;
     0.05 - 6.0 wt.% Al_tot;
     0.0001 - 0.05 wt.% Sb;
     0.0005 - 0.005 wt.% of ∑ (Ca + REM);
     5 - 100 ppm N;

0 - 2.0 wt.% Si;
0 - 0.01 wt.% S;
0 - 0.1 wt. % P;
0 - 1.0 wt.% Cr;
0 - 2.0 wt.% Ni;
0 - 2.0 wt.% Cu;
0 - 0.5 wt.% Mo;
0 - 0.1 wt.% V;
0 - 50 ppm B;
0 - 0.10 wt.% Ti.

remainder iron and inevitable impurities,
- reheating the slab or cast strip to a reheating temperature of between 1100 and 1250 °C;
- hot-rolling the slab or cast strip to a hot-rolled strip wherein the finishing temperature is 800 to 950 °C;
- cooling and coiling the hot-rolled strip between 650 and 450 °C;
- pickling the hot-rolled strip;
- cold-rolling the pickled hot-rolled strip, preferably with a total cold rolling reduction of between 40 and 80 %;
- optionally producing sheet or blanks from the cold-rolled strip;
- heat treating the steel strip, sheet or blank by intercritically annealing, preferably at a temperature between 700 and 900 °C, for a duration of between 1 and 300 s.
- cooling the annealed steel strip, sheet or blank to an austempering temperature for an austempering treatment between 500 and 300 °C, preferably at most 480 and/or at least 350 °C, at a cooling rate which is higher than the critical rate for formation of pearlite, and maintained for a duration of 10 to 600s and subsequently cooled to ambient temperatures,

so as to achieve annealed steel strip, sheet or blank with bimodal grain microstructure consisting of a ferritic matrix phase having a grain size of between 5 and 20 μm and a second phase consisting of one or more of or bainite, martensite and retained austenite with a grain size of at most 5 μm, and wherein the final microstructure contains at least 20 vol.% of δ-ferrite.

2. Process according to claim 1 wherein the blank undergoes the heat treating in a reheating furnace for a hot forming press, and wherein the intercritical annealing of the blank takes place before hot deformation in the hot forming press, and wherein the intercritically annealed blank is hot-pressed and cooled to the austempering temperature of between 500 and 300 °C, preferably at most 480 and/or at least 350 °C, in the hot press and i). held in the hot-press for the duration of the austempering treatment or ii). taken from the hot-press and entered into an austempering furnace, followed by cooling to ambient temperatures, preferably at a cooling rate of at least 5 °C/s, more preferably of at least 10 °C/s.

3. Process according to claim 1 wherein the blank is deformed in a press to form a product and wherein the product subsequently undergoes the heat treating in an annealing furnace wherein the intercritical annealing of the product takes place and wherein

i) the intercritically annealed product is cooled to the austempering temperature of between 500 and 300 °C, preferably at most 480 and/or at least 350 °C, in the annealing furnace and held for the duration of the austempering treatment, followed by cooling to ambient temperatures, preferably at a cooling rate of at least 5 °C/s, more preferably of at least 10 °C/s, or
ii) wherein the intercritically annealed product is taken from the annealing furnace and entered into an austempering furnace at the austempering temperature of between 500 and 300 ° C, preferably at most 480 and/or at least 350 °C, followed by cooling to ambient temperatures, preferably at a cooling rate of at least 5 °C/s, more preferably of at least 10 °C/s.

4. Process according to claim 1 or 2 wherein the coiling temperature is at least 475 °C, preferably at least 500 °C, more preferably at least 525 °C and/or at most 625 °C, preferably at most 600 °C.

5. Process according to any one the preceding claims wherein the duration of the intercritical annealing is at least 30s and/or at most 240 s.

6. Process according to any one the preceding claims wherein the duration of the austempering annealing is at least

30 s and/or at most 300 s.

7. Process according to any one of the preceding claims wherein the austempering temperature is at least 350 °C and preferably at least 375 °C and/or at most 475 °C, and preferably at most 450 °C.

8. Process according to any one of the preceding claims wherein the Sb content is at least 0.0005 wt.%.

9. Process according to any one of the preceding claims wherein the second phase consisting of one or more of or bainite, martensite and retained austenite has a grain size of at most 3 μm

10. Process according to any one of the preceding claims wherein:

- $\sum$(Mn+Cu+Ni) is between 0.5 and 8.0 wt.%, and/or
- $\sum$(Al+Si) is between 0.1 and 6.0 wt.%, and/or
- $Al+Si/3 \geq 4C+0.24Mn+0.9$.

11. Process according to any one of the preceding claims wherein the total cold-rolling reduction is between 40 and 80 %, and/or wherein the strip, sheet or blank is provided with a metallic coating by means of plating or hot-dipping, preferably wherein the metallic coating is an aluminium based alloy or a zinc based alloy.

12. High strength cold-rolled and heat-treated steel strip, sheet, blank or hot formed product having a bimodal microstructure having the following composition;

0.05 - 0.50 wt.% C;
0.50 - 8.0 wt.% Mn;
0.05 - 6.0 wt.% Al_tot;
0.0001 - 0.05 wt.% Sb;
0.0005 - 0.005 wt.% of $\sum$ (Ca + REM);
5 - 100 ppm N;
0 - 2.0 wt.% Si;
0 - 0.01 wt.% S;
0 - 0.1 wt. % P;
0 - 1.0 wt.% Cr;
0 - 2.0 wt.% Ni;
0 - 2.0 wt.% Cu;
0 - 0.5 wt.% Mo;
0 - 0.1 wt.% V;
0 - 50 ppm B;
0 - 0.10 wt.% Ti.

remainder iron and inevitable impurities, remainder iron and inevitable impurities,

- wherein the heat treated steel strip, sheet or blank has a bimodal grain microstructure consisting of a ferritic matrix phase consisting of δ-ferrite and α-ferrite, wherein the δ-ferrite has a grain size of between 5 and 20 μm, wherein the α-ferrite has a grain size of at most 5 μm and a second phase consisting of one or more of or bainite, martensite and retained austenite with a grainsize of at most 5 μm, and wherein the final microstructure contains at least 20 % of δ-ferrite, said high strength cold-rolled and heat-treated steel strip, sheet, blank or hot formed product being obtainable by the process according to any one of claims 1 to 11.

13. Steel according to claim 12 wherein the steel is coated with a metallic coating by means of plating or hot-dipping, preferably wherein the metallic coating is an aluminium based alloy or a zinc based alloy.

14. Component, e.g. a car or truck component, such as an automotive chassis component, a component of the body in white, a component of the frame or the subframe, or a component of a structure or engineering project, said component having been produced from the steel sheet according to any one of claim 1 to 11, wherein the component has a bimodal grain microstructure consisting of a ferritic matrix phase consisting of δ-ferrite and α-ferrite, wherein the δ-ferrite has a grain size of between 5 and 20 μm, wherein the α-ferrite has a grain size at most 3 μm and a second phase consisting of one or more of or bainite, martensite and retained austenite with a grain size of at most

3 μm.

15. Component, e.g. a car or truck component, such as an automotive chassis component, a component of the body in white, a component of the frame or the subframe, or a component of a structure or engineering project, said component having been produced from the steel sheet according to any one of claims 1 to 11 by means of the process according to claim 12 or 13 wherein the component has a bimodal grain microstructure consisting of a ferritic matrix phase consisting of δ-ferrite and α-ferrite, wherein the δ-ferrite has a grain size of between 5 and 20 μm, wherein the α-ferrite has a grainsize at most 3 μm and a second phase consisting of one or more of or bainite, martensite and retained austenite with a grain size of at most 3 μm.

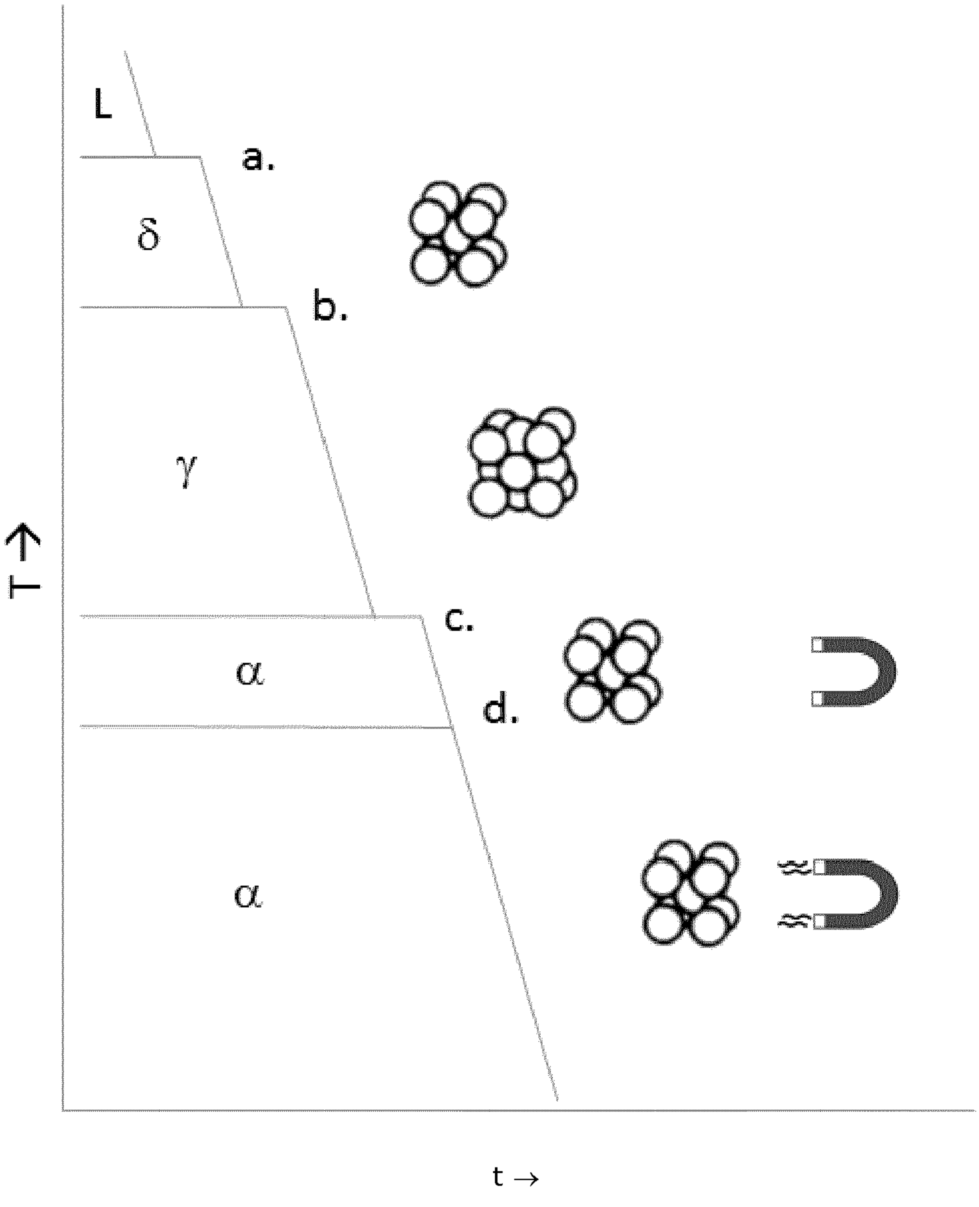

FIGURE 1

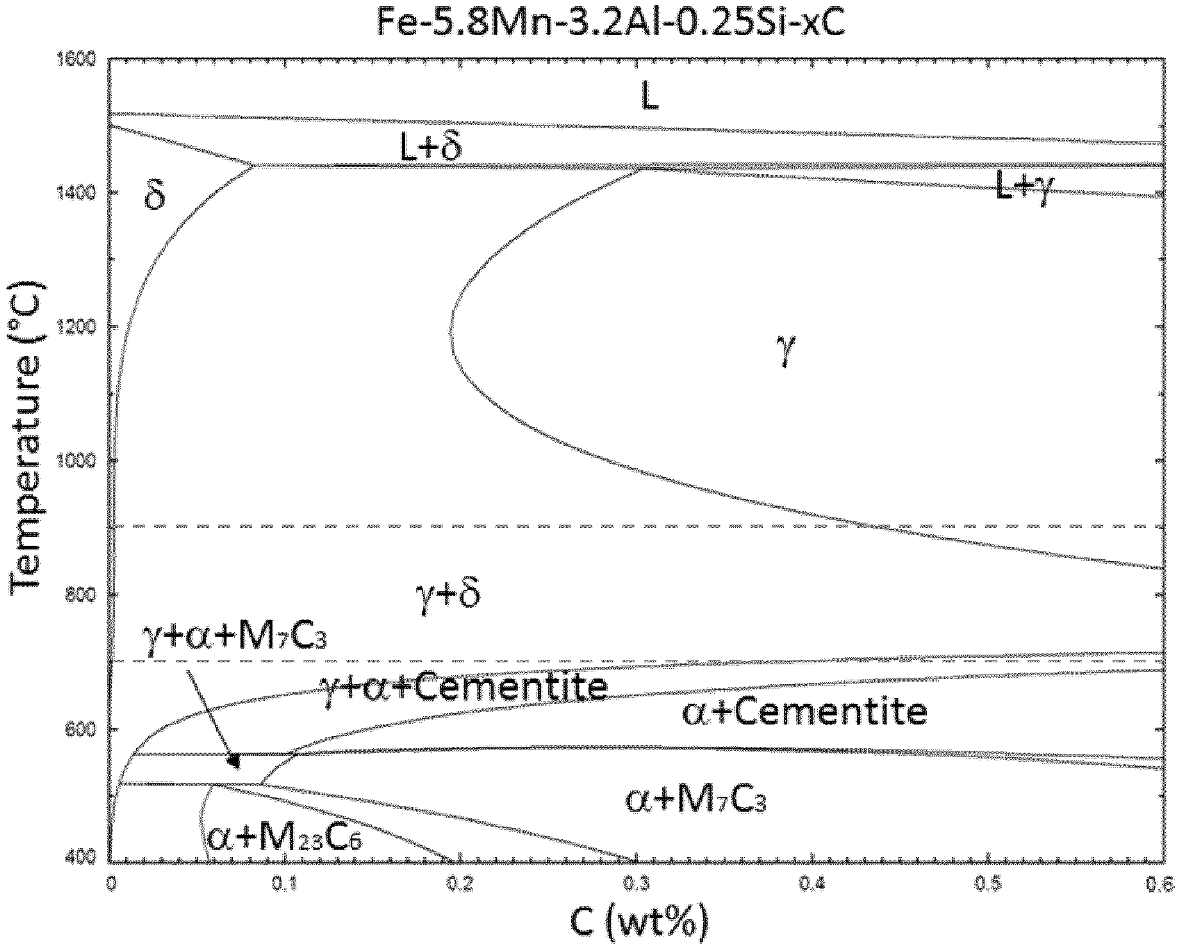
Fe-5.8Mn-3.2Al-0.25Si-xC
Temperature (°C)
1600
1400
1200
1000
800
600
400
C (wt%)
0
0.1
0.2
0.3
0.4
0.5
0.6
L
L+δ
L+γ
δ
γ
γ+δ
γ+α+M7C3
γ+α+Cementite
α+Cementite
α+M7C3
α+M23C6

FIGURE 2

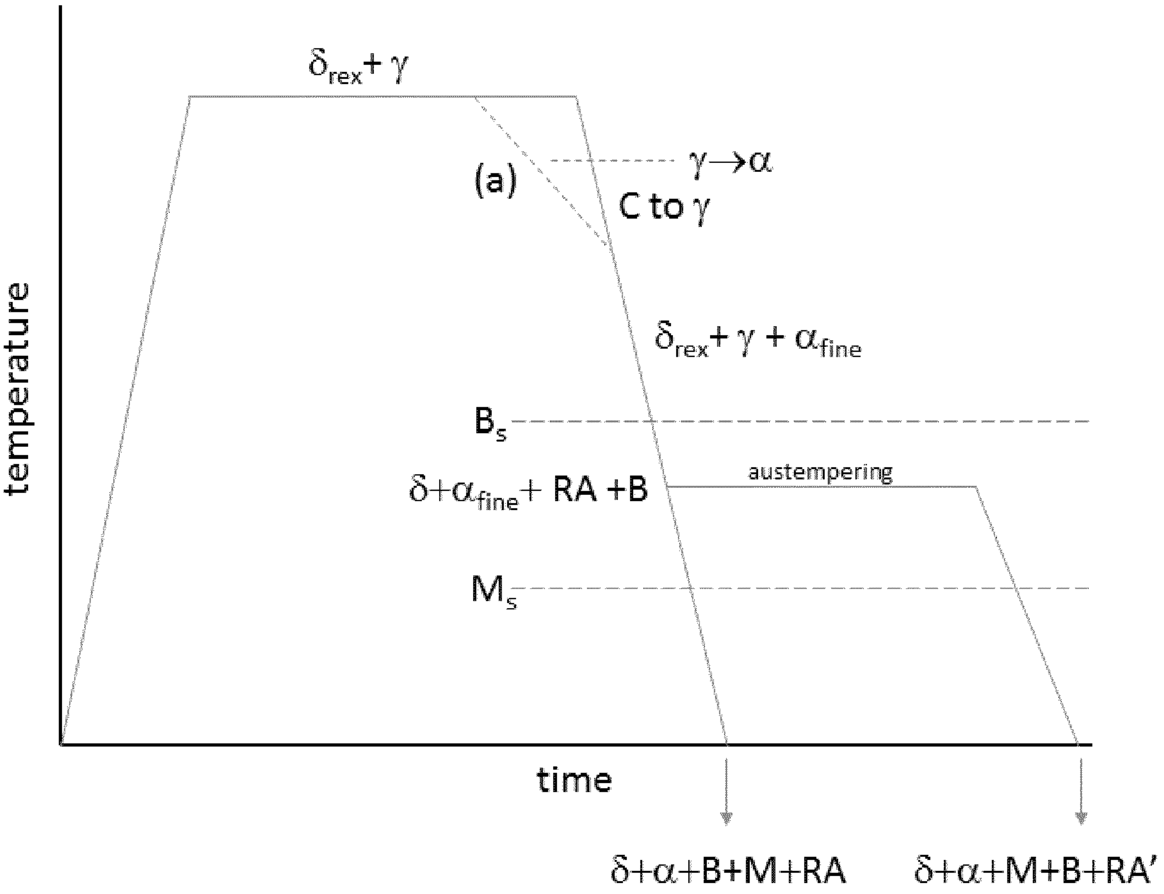
$\delta_{rex}+\gamma$
(a)
$\gamma\rightarrow\alpha$
C to γ
$\delta_{rex}+\gamma+\alpha_{fine}$
B_s
austempering
$\delta+\alpha_{fine}+RA+B$
M_s
temperature
time
$\delta+\alpha+B+M+RA$
$\delta+\alpha+M+B+RA'$

FIGURE 3

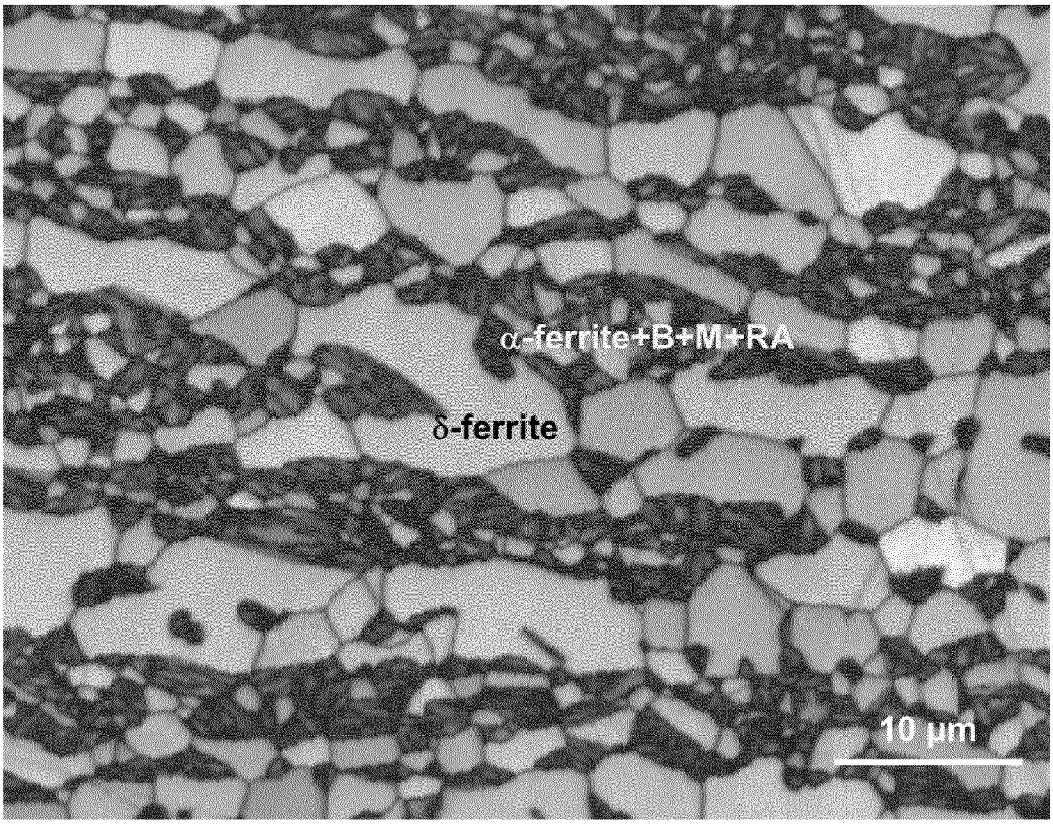

FIGURE 4

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EUROPEAN SEARCH REPORT

Application Number
EP 17 17 8502

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2016/067626 A1 (JFE STEEL CORP [JP]) 6 May 2016 (2016-05-06) * the whole document * -----	1-15	INV. C22C38/00
A	US 2014/261914 A1 (JAMWAL RANBIR SINGH [US] ET AL) 18 September 2014 (2014-09-18) * the whole document * -----	1-15	
A	WO 2016/067624 A1 (JFE STEEL CORP) 6 May 2016 (2016-05-06) * the whole document * -----	1-15	
A	US 2014/141279 A1 (JAMWAL RANBIR [US] ET AL) 22 May 2014 (2014-05-22) * the whole document * -----	1-15	
A	EP 3 034 646 A1 (JFE STEEL CORP [JP]) 22 June 2016 (2016-06-22) * the whole document * -----	1-15	
A	CN 1 531 604 A (NIPPON STEEL CORP [JP]) 22 September 2004 (2004-09-22) * the whole document * -----	1-15	TECHNICAL FIELDS SEARCHED (IPC) C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	6 December 2017	Radeck, Stephanie

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons
& : member of the same patent family, corresponding document

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 17 17 8502

06-12-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2016067626 A1	06-05-2016	CN 107075642 A	18-08-2017
		EP 3214196 A1	06-09-2017
		JP 6179677 B2	16-08-2017
		JP WO2016067626 A1	27-04-2017
		KR 20170072333 A	26-06-2017
		US 2017298482 A1	19-10-2017
		WO 2016067626 A1	06-05-2016
US 2014261914 A1	18-09-2014	US 2014261914 A1	18-09-2014
		WO 2014149505 A1	25-09-2014
WO 2016067624 A1	06-05-2016	CN 107075643 A	18-08-2017
		EP 3214193 A1	06-09-2017
		JP 6179675 B2	16-08-2017
		JP WO2016067624 A1	25-05-2017
		KR 20170074995 A	30-06-2017
		US 2017327919 A1	16-11-2017
		WO 2016067624 A1	06-05-2016
US 2014141279 A1	22-05-2014	US 2014141279 A1	22-05-2014
		WO 2014081774 A1	30-05-2014
EP 3034646 A1	22-06-2016	CN 105452517 A	30-03-2016
		EP 3034646 A1	22-06-2016
		JP 5862833 B2	16-02-2016
		JP 6094649 B2	15-03-2017
		JP 2016027208 A	18-02-2016
		JP WO2015022778 A1	02-03-2017
		KR 20160043012 A	20-04-2016
		US 2016194744 A1	07-07-2016
		WO 2015022778 A1	19-02-2015
CN 1531604 A	22-09-2004	AU 2002309283 B2	14-04-2005
		CN 1531604 A	22-09-2004
		KR 20040007718 A	24-01-2004
		KR 20070087240 A	27-08-2007
		KR 20070119096 A	18-12-2007
		KR 20080108163 A	11-12-2008
		TW I317383 B	21-11-2009
		WO 02103073 A2	27-12-2002

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- **R.L. MILLER.** *Metall. Trans.,* 1972, vol. 3, 905-12 **[0006]**