



US 20140034196A1

(19) **United States**

(12) **Patent Application Publication**
Wedemeier et al.

(10) **Pub. No.: US 2014/0034196 A1**

(43) **Pub. Date: Feb. 6, 2014**

(54) **HOHERFESTER MEHRPHASENSTAHL MIT
AUSGEZEICHNETEN
UMFORMEIGENSCHAFTEN HIGH
STRENGTH MULTI-PHASE STEEL HAVING
EXCELLENT FORMING PROPERTIES**

C22C 38/00 (2006.01)
C22C 38/22 (2006.01)
C22C 38/06 (2006.01)
C22C 38/04 (2006.01)
C22C 38/02 (2006.01)
C22C 38/38 (2006.01)
C22C 38/26 (2006.01)

(76) Inventors: **Andreas Wedemeier**, Braunschweig (DE); **Thomas Schulz**, Salzgitter (DE); **Michael Pohl**, Braunschweig (DE); **Phillip Wüllner**, Braunschweig (DE); **Jörg Heinecke**, Salzgitter (DE); **Christian Schlegel**, Salzgitter (DE)

(52) **U.S. Cl.**
CPC *C21D 8/0247* (2013.01); *C22C 38/38* (2013.01); *C22C 38/32* (2013.01); *C22C 38/28* (2013.01); *C22C 38/26* (2013.01); *C22C 38/22* (2013.01); *C22C 38/06* (2013.01); *C22C 38/04* (2013.01); *C22C 38/02* (2013.01); *C22C 38/001* (2013.01)
USPC **148/661**; 148/537; 148/330

(21) Appl. No.: **13/981,870**

(22) PCT Filed: **Nov. 30, 2011**

(86) PCT No.: **PCT/DE2011/002094**

§ 371 (c)(1),
(2), (4) Date: **Oct. 3, 2013**

(57) **ABSTRACT**

(30) **Foreign Application Priority Data**

Jan. 26, 2011 (DE) 10 2011 010 256.6
Oct. 25, 2011 (DE) 10 2011 117 572.9

Publication Classification

(51) **Int. Cl.**
C21D 8/02 (2006.01)
C22C 38/32 (2006.01)
C22C 38/28 (2006.01)

The invention relates to a high strength multi-phase steel for a cold- or hot-rolled steel strip having excellent forming properties, in particular for light vehicle construction, comprising the elements (contents in mass %): C 0.060 to=0.115; Al 0.020 to=0.060; Si 0.100 to=0.500; Mn 1.300 to=2.500; P=0.025; S=0.0100; Cr 0.280 to=0.480; Mo<0.150; Ti=0.005 to=0.050; Nb=0.005 to=0.050; B=0.0005 to=0.0060; N=0.0100; the remainder being iron including the usual elements present in steel and which are not mentioned above.

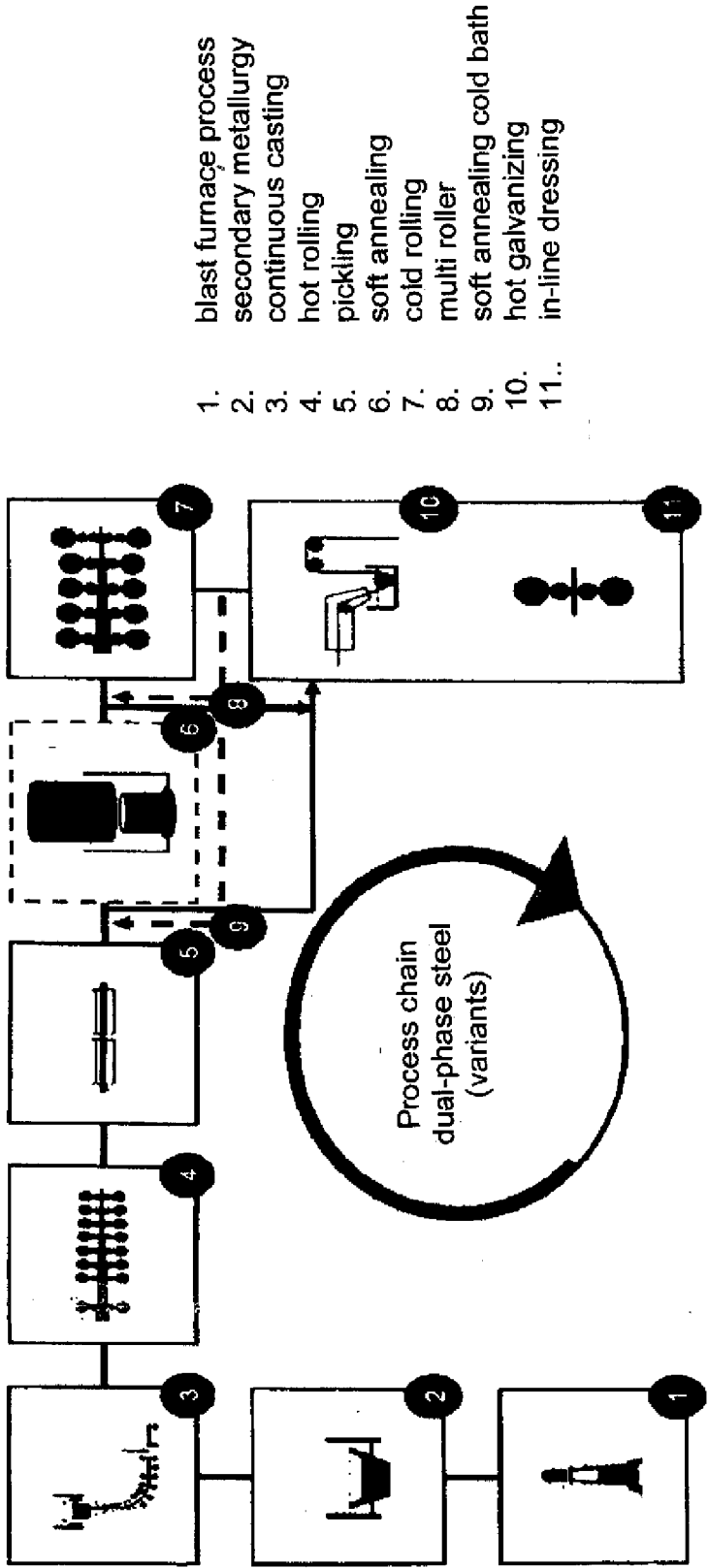


Figure 1

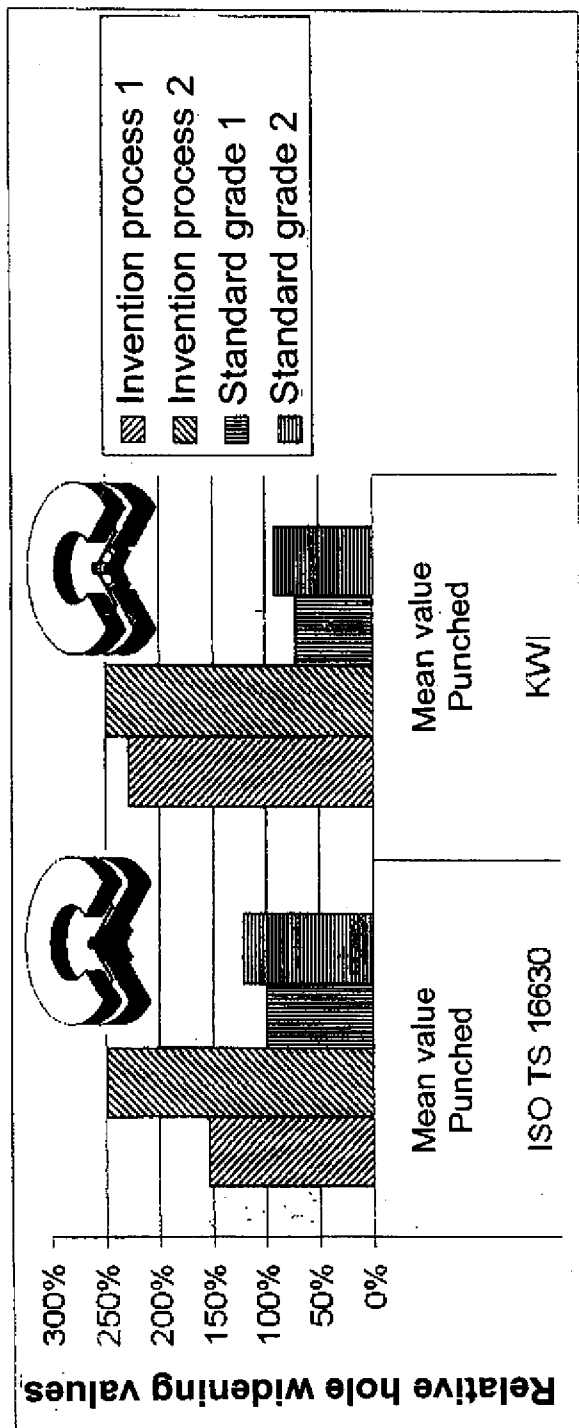


Figure 2

| | C [weight - %] | Ti [weight - %] | Nb [weight - %] | B [weight - %] |
|------------------|-------------------|--------------------|--------------------|-------------------|
| Standard grade 1 | 0.150 | 0.003 | 0.013 | 0.0000 |
| Standard grade 2 | 0.154 | 0.008 | 0.002 | 0.0001 |
| Invention | 0.099 | 0.03 | 0.027 | 0.0018 |

Figure 3

| | R _{p0.2} [Mpa] | R _m [Mpa] | A ₈₀ [%] |
|---------------------|----------------------------|-------------------------|------------------------|
| | transverse | transverse | transverse |
| Standard grade 1 | 519 | 851 | 15 |
| Standard grade 2 | 539 | 804 | 17 |
| Invention process 1 | 503 | 813 | 18 |
| Invention process 2 | 453 | 782 | 18 |

Figure 4

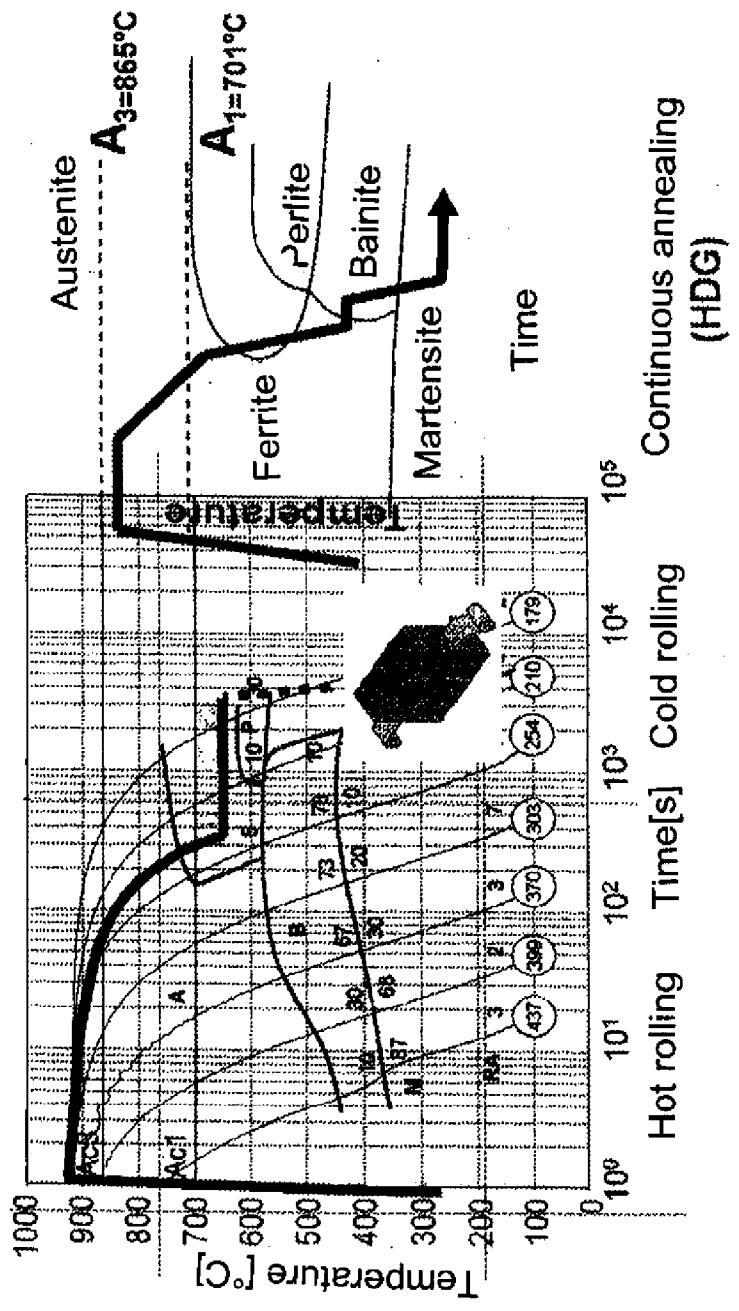


Figure 5

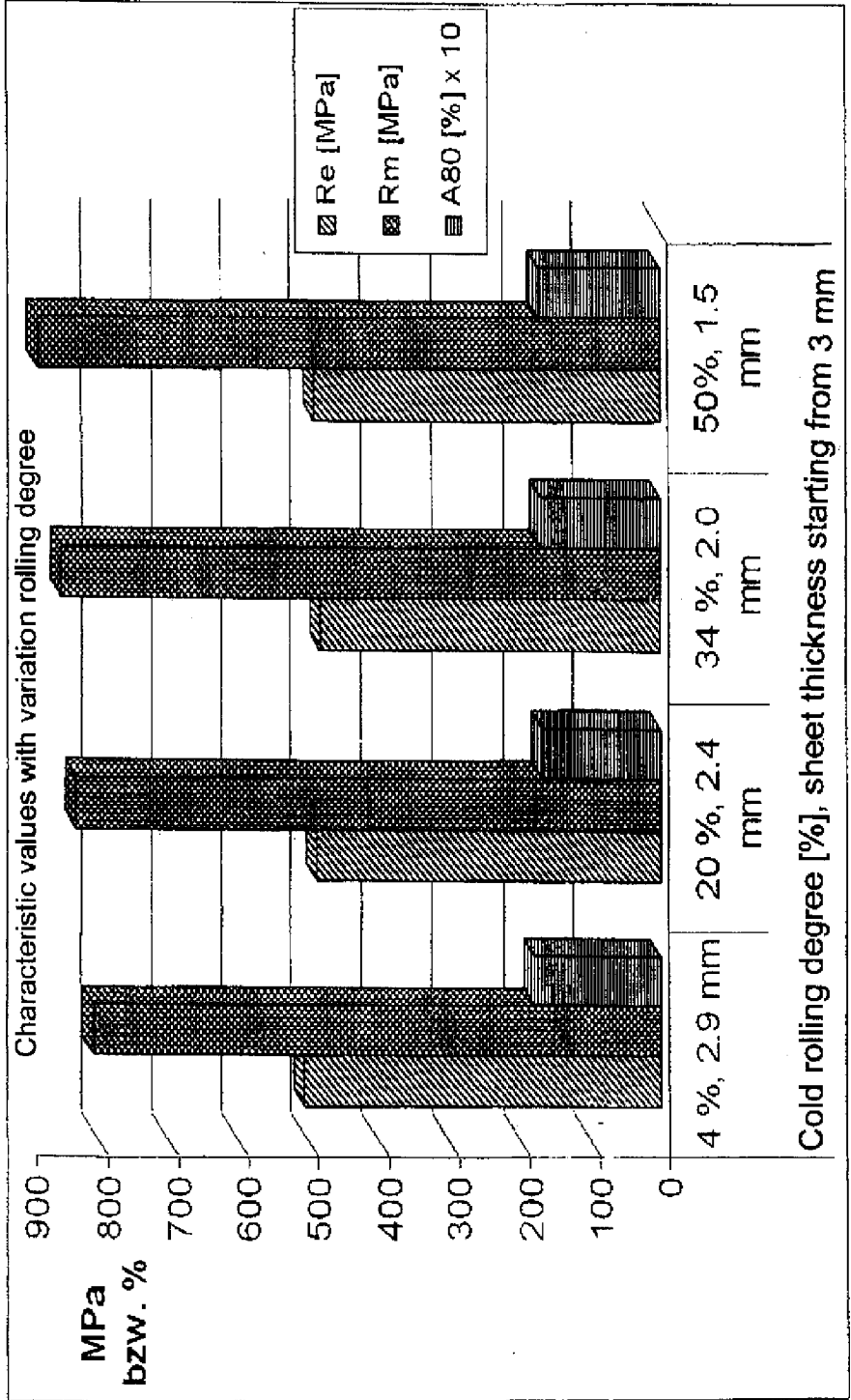


Figure 7

| Carrier material | Re/MPa | Rm/MPa | A80 | Ferri te% | Martensi te% | Bainite % |
|---|--------|--------|-------|-----------|--------------|-----------|
| 1. Pickled hot strip (HDT580X) | 360 | 719 | 20.35 | 70 | 30 | 0 |
| 2. Pickled hot strip (HDT750XD*) | 435 | 819 | 16.90 | 70 | 30 | 0 |
| 3. Pickled hot strip (HDT750C) | 524 | 842 | 13.75 | 45 | 40 | 15 |
| 4. Cold re-rolled hot strip (dressed) (HCT780XD) | 463 | 843 | 14.85 | 65 | 15 | 10 |
| 5. Cold strip with minimized rolling degrees (HCT780XD) | 463 | 843 | 14.85 | 65 | 15 | 10 |
| 6. Cold strip with high rolling degrees (HCT780X) | 473 | 883 | 14.40 | 5 | 40 | 55 |
| 7. Cold strip with high rolling degrees (HCT780C) | 507 | 916 | 12.40 | 5 | 45 | 50 |
| | 709 | 887 | 7.25 | 10 | 0 | 90 |
| 8. Cold strip with high rolling degrees (HCT980) | 928 | 998 | 5.30 | 5 | 0 | 95 |

* not standardized

Figure 8

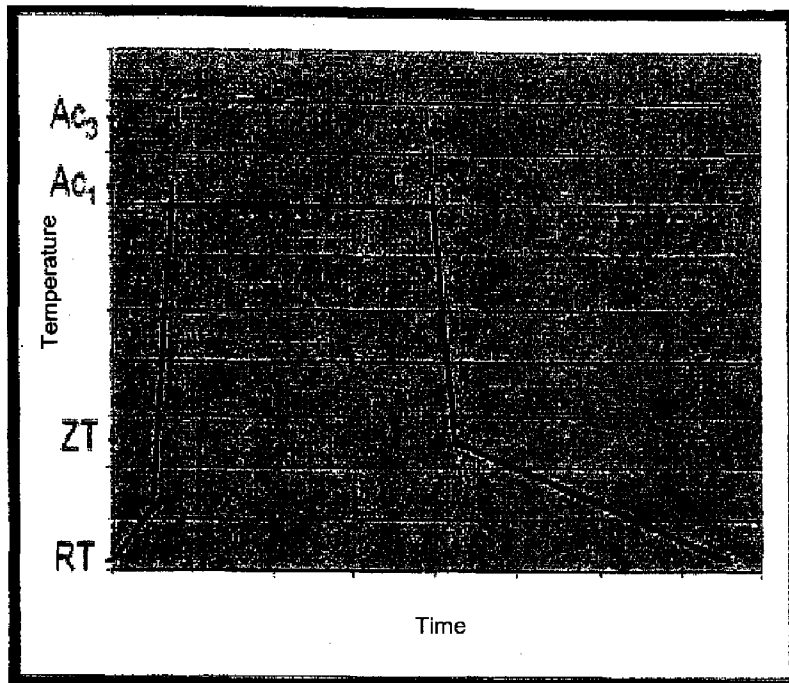


Figure 9a (Legend ZT= intermediate temperature, RT = room temperature)

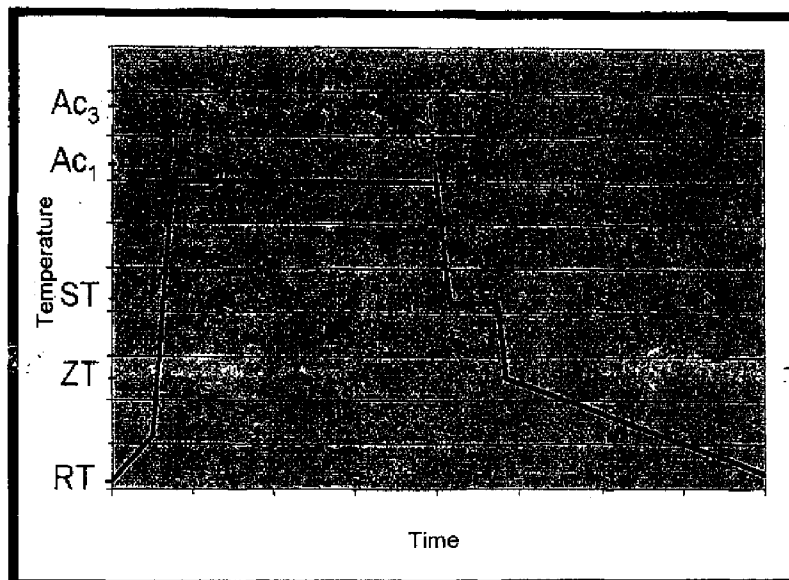


Figure 9b (Legend ST= melt bath temperature, ZT = intermediate temperature, RT =-room temperature)

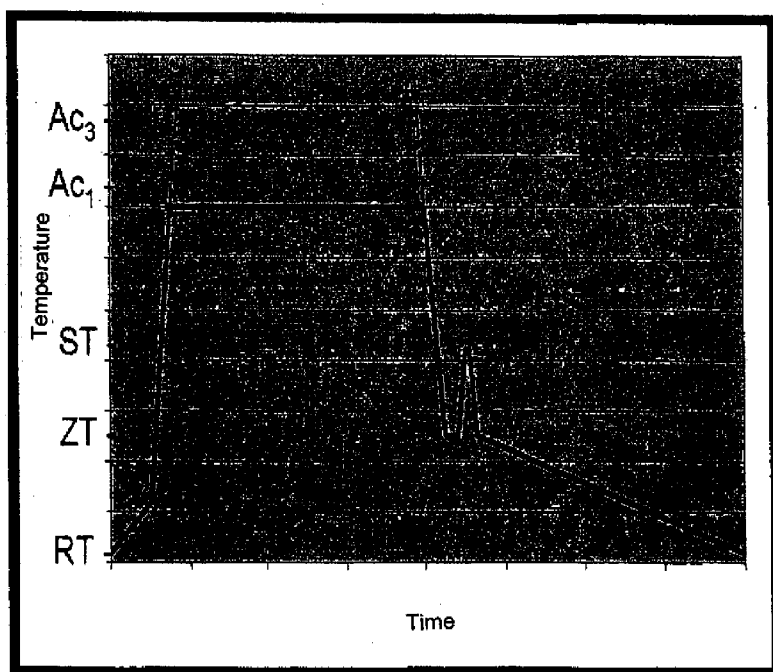


Figure 9c (Legend ST = melt bath temperature, ZT = intermediate temperature, RT = room temperature)

**HOHERFESTER MEHRPHASENSTAHL MIT
AUSGEZEICHNETEN
UMFORMEIGENSCHAFTEN HIGH
STRENGTH MULTI-PHASE STEEL HAVING
EXCELLENT FORMING PROPERTIES**

DESCRIPTION

[0001] The invention relates to a high-strength multiphase steel with dual bainite or complex phase microstructure and excellent forming characteristics in particular for the light-weight vehicle construction and a method for producing a steel flat product according to the preamble of patent claim 1. The invention further relates to a method for producing such a steel according to claim 14.

[0002] The hotly contested automobile market forces manufacturers to constantly seek solutions for lowering the fleet consumption while at the same time maintaining a greatest possible comfort and occupant protection. For this, on one hand weight reduction of all vehicle components plays an important role, but on the other hand also an optimal behavior of the individual components in case of high static and dynamic stress during operation and also in the case of a crash. To meet these requirements, the distributors of raw material provide high strength and ultra-high-strength steels to thereby allow reducing the sheet thickness of the vehicles at improved forming and component behavior during manufacture and operation. These steels therefore have to meet relatively high standards regarding their strengths and ductility, energy absorption and during their processing such as for example during coching, hot and cold forming, welding and/or surface finishing (for example metallic finishing, organically coating).

[0003] Newly developed steels thus besides satisfying the required weight reduction have to satisfy the high material demands regarding stretch limit, tensile strength, and elongation at break at good formability as well as the components requirements for high tenacity edge break resistance, energy absorption and strength via the Work-Hardening-Effect and the Bake-Hardening-Effect.

[0004] Therefore, dual-phase steels are increasingly used in vehicle construction, which consist of a ferritic base structure in which a martensitic second phase and possibly a further phase with bainite and residual austenite is incorporated.

[0005] The processing properties of the dual phase steels which determine the steel types, such as a very low stretch limit ratio at very high tensile strength, a strong strain hardening and a good cold formability are sufficiently known.

[0006] Increasingly, multiphase steels are also used, such as complex phase steels, ferritic-bainitic steels, bainitic steels and martensitic steels which are characterized by different microstructure compositions.

[0007] Complex phase steels of the hot or cold rolled type are steels which contain small proportions of martensite, residual austenite and/or perlite in a ferritic/bainitic base structure, wherein an extreme grain refinement as a result a delayed recrystallization or of precipitation of micro alloying elements.

[0008] Ferritic-bainitic steels in hot-rolled configuration are steels, which contain bainite or hardened bainite in a matrix of ferrite and/or hardened ferrite.

[0009] The hardening of the matrix is caused by a high dislocation density, by grain refinement and by the precipitation of micro-alloying elements.

[0010] Bainitic steels in hot-rolled or cold-rolled configuration are steels, which are characterized by a very high stretch limit and tensile strength at sufficiently high stretching for cold forming processes. The chemical composition results in a good weldability. The microstructure typically consists of bainite. In some cases, smaller proportions of other phases such as martensite and ferrite can be contained.

[0011] Martensitic steels in hot-rolled configuration are steels, which as a result of thermo-mechanical rolling contain small proportions of ferrite and/or bainite in a basic structure of martensite. These steel types are characterized by a very high stretch limit and tensile strength at sufficiently high stretching for cold forming processes. Within the group of multiphase steels, the martensitic steels have the highest tensile strengths.

[0012] These steels are used inter alia in structure-relevant, chassis-relevant and crash-relevant components as well as flexibly cold-rolled sheets. These Tailor Rolled Blank light-weight construction technology (TRB®) enables a significant weight reduction by choosing a sheet thickness over the component length that is adjusted to the stress.

[0013] With the currently known alloys and available continuous annealing systems, the production of TRB®'s is not possible without limitations for strongly varying sheet thicknesses with multiphase microstructure, such as heat treatment before cold-rolling. Due to the temperature gradient occurring in the conventional process windows in regions of different sheet thickness, no uniform multiphase microstructure can be established in cold-rolled and hot rolled steel strips.

[0014] For economic reasons, cold-rolled steel strips are usually re-crystallizingly annealed in the continuous annealing method to well formable fine steel sheet. Depending on the alloy composition and the strip cross-section, the process parameters such as throughput speed, annealing temperatures and cooling speed are adjusted according to the required mechanical—technological properties with the microstructure required therefore.

[0015] For adjusting the dual-phase microstructure, the hot or cold strip is heated in the continuous annealing furnace to such a temperature, that the required microstructure is formed during the cooling. The same is true for adjusting a steel with complex-phase microstructure, martensitic, ferritic-bainitic and purely bainitic microstructure.

[0016] When for reason of high corrosion protection requirements the surface of the hot or cold strip is to be hot-dip coated, the annealing usually occurs in a continuous annealing furnace located upstream of the galvanizing bath.

[0017] Also in the hot strip, the required microstructure is only adjusted in the annealing in the continuous furnace depending on the alloying concept in order to realize the required mechanical properties.

[0018] In the continuous annealing of hot or cold-rolled steel strips with alloying concepts that are for example known from the printed publications EP 0152665B1, EP 0691415B1, and EP 0510718 B1, the problem is that only a narrow process window is available for the annealing parameters in order to ensure uniform mechanical properties over the strip length without adjusting the process parameters in the case of jumps in cross-section.

[0019] A narrow process window means here that depending on the cross-section of the strip to be annealed, the process parameters have to be adjusted in order to achieve the required microstructure and the mechanical—technological properties through homogenous temperature distribution in

the strip and during cooling. Increased process windows also enable the required strip properties at different cross-sections of the strips to be annealed while using same process parameters.

[0020] Besides flexibly rolled strips with different sheet thicknesses over the strip length, oftentimes strips with different thicknesses for example with 1.5 and 2.0 mm and/or different width for example 900 and 1400 mm have to be annealed successively.

[0021] A homogenous temperature distribution is difficult to achieve especially in the case of different thicknesses in the transitional region from one band to another. In the case of alloy compositions with a too small process window this can lead to the thinner band being moved through the furnace too slowly during continuous annealing, resulting in lowering of the productivity, or lead to the thicker strip being moved through the furnace too quickly and the required annealing temperature and with this the required microstructure is not achieved. This results in increased scrap and even reclamation by the client.

[0022] The deciding process parameter is thus the adjustment of the speed during continuous annealing because the phase transition occurs in dependence on temperature and time. The more tolerant the steel is with regard to the uniformity of the mechanical properties when changing the temperature and time course during the continuous annealing, the greater is the process window.

[0023] The problem of a too narrow process window during the annealing is particularly pronounced, when stress-optimized components are to be produced from hot or cold strip which have varying sheet thicknesses over the strip length and strip width, and are for example rolled flexibly.

[0024] A method for producing a steel strip with different thickness over the strip length is described for example in DE 100-378-67A1.

[0025] When using the known alloy concepts for the group of the multiphase steels, the narrow process windows already make it very difficult in the continuous annealing of strips with different thicknesses to adjust homogenous mechanical properties over the entire length of the strip. Complex-phase steels in addition have an even narrower process window than dual-phase steels.

[0026] In the case of flexibly rolled cold strips from steels of known composition, the regions with small sheet thickness have either excessive strengths due to great martensite proportions as a result of the transformation processes during cooling, or the regions with greater sheet thickness attain too low strengths as a result of insufficient martensite proportions. Homogenous mechanical—technological properties over the strip length or strip width cannot practically be achieved with the known alloy concepts in the continuous annealing.

[0027] The goal to achieve the final mechanical—technological properties in a narrow region over strip width and strip length through the controlled adjustment of the volume proportions of the microstructure phases has the highest priority and is therefore only possible through an increased process window. The known alloy concepts for multiphase steels are characterized by a too narrow process window and are therefore not suited for solving the present problem in particular in the case of flexibly rolled strips. With the known alloy concepts only steels of one strength class with defined cross-

sectional regions can be produced so that for different strength classes and or cross-sectional regions different alloy concepts are required.

[0028] The invention is therefore based on the object, to propose a different alloy concept for a high-strength multiphase steel with a broad spectrum of different microstructure compositions with which the process window for the continuous annealing of hot or cold strips can be increased so that besides strips with different cross-sections also steel strips having varying thickness over strip length and strip width can be produced with mechanical—technological properties that are as homogenous as possible. Further, an alloy concept is proposed with which also allows meeting the demand for different strength classes. In addition, a method for producing a strip that is produced from this steel is proposed.

[0029] According to the teaching of the invention, this object is solved by a steel with the following contents in weight %:

| | |
|----|----------------------|
| C | 0.060 to = 0.115 |
| Al | 0.020 to = 0.060 |
| Si | 0.100 to = 0.500 |
| Mn | 1.300 to = 2.500 |
| P | = 0.025 |
| S | = 0.0100 |
| Cr | 0.280 to = 0.480 |
| Mo | = 0.150 |
| Ti | = 0.005 to = 0.050 |
| Nb | = 0.005 to = 0.050 |
| B | = 0.0005 to = 0.0060 |
| N | = 0.0100 |

[0030] Remainder iron, including common steel tramp elements not mentioned above.

[0031] The steel according to the invention has the advantage of a significantly increased process window compared to the known steels. This results in an increased process reliability in the continuous annealing of cold and hot strip with multiphase microstructure. Thus, more homogenous mechanical—technological properties can be ensured in the strip for continuously annealed hot or cold strips even in the case of different cross-sections and otherwise same process parameters.

[0032] This applies for the continuous annealing of successive strips with different strip cross-sections as well as for strips with varying sheet thickness over the strip length or strip width. This for example allows processing in selected thickness regions of smaller than 1 mm strip thickness, 1 to 2 mm strip thickness and greater than 2 mm strip thickness.

[0033] When high strength hot or cold strips are produced from multiphase steel with varying sheet thickness in the continuous annealing method, stress-optimized components can be advantageously produced from these materials by forming.

[0034] The produced material can be produced as cold strip as well as hot strip via a galvanizing line or a pure continuous annealing system in the dressed and undressed state (intermediate annealing).

[0035] At the same time, it is possible by varying the process parameters in a targeted manner to adjust the microstructure proportions so that steels can be produced in different strength classes.

[0036] The steel strips produced with the alloy composition according to the invention are characterized by a significantly broader process window with regard to temperature and throughput speed when manufacturing a multiphase or bainitic steel in the inter-critical annealing between A_{C1} and A_{C3} or in an austenizing annealing over A_{C3} with final controlled cooling compared to the known alloy concepts.

[0037] Annealing temperatures of 700 to 950° C. and cooling speeds of 15 to 100° C./s to a temperature of 420 to 470° C. with holding at an intermediate temperature of 200 to 250° C. and also with prior optional reheating have proven advantageous, with which the required multiphase microstructures can be evenly adjusted over the strip length. This is particularly advantageous when annealing flexibly rolled strips or in subsequent annealing of strips with different cross sections, which thus allows achieving very uniform material properties.

[0038] The prerequisite for achieving a broad process window is the combination according to the invention of the micro-alloy elements titanium, niobium and boron with optional addition of molybdenum.

[0039] Fine titanium precipitations act in the same way as niobium-carbides and together enhance this effect. Titanium binds nitrogen, which therefore is no longer available for the formation of boron-nitride, through which the boron alloy can act. In this case, the addition of boron, which is present as free boron, causes an increase of the hardenability.

[0040] Boron is one of the elements that besides a high hardening is also characterized by a high hardness penetration. The microstructure becomes more isotropic because differences in the cooling rates, which are caused by the process conduction or the geometry of the strip, have a smaller influence, which also leads to a greater process window.

[0041] Free boron is able to produce a relatively homogeneous microstructure (same microstructure proportions) viewed over the sheet thickness. The same is true for the less pronounced influence of temperature gradients, which occur over the length of the strip or with regard to its width.

[0042] In classic two-phase steels, beside manganese, chromium and silicon, carbon is also responsible for the transformation of austenite into martensite. Due to the Boron, a portion of the carbon can therefore be substituted. This also has a positive influence on the microstructure because carbon is one of the most strongly segregating elements in the steel. Thereby, segregations, which leads to locally different thermodynamic driving forces, are less pronounced which in turn results in a higher robustness against process and geometry related temperature fluctuations.

[0043] It is characteristic for the material that the additional addition of titanium and boron besides niobium significantly shifts the ferrite region to later points in time after the cooling. This enables the potential for complex-phase steels and bainitic steels.

[0044] The proportions of ferrite are more or less reduced by increased proportions of bainite depending on the process parameters. The combination of the three micro-alloy elements, enables the previously described material diversity.

[0045] Tests have shown that the micro-element combination of niobium and boron alone is not sufficient to achieve a broad process window and the tensile strength range typically required therefore of at least 750 MPa for hot strip and at least 780 MPa for cold-rolled hot strip and cold strip. This only became possible through the addition of titanium.

[0046] The adjustment of a low carbon content of $\approx 0.115\%$ allows reducing the carbon equivalent, which improves the weldability and avoids excessive hardening during welding. In resistance spot welding, the service life of the electrodes can be significantly increased.

[0047] Carbide and nitride formation only starts above temperatures of about 1000 C or after the α/β transformation, i.e., significantly later than in the case of titanium and niobium. Thus, vanadium has hardly a grain refining effect due to the low number of precipitations in the austenite. Also growth of austenite grains is not inhibited by the late precipitation of the vanadium carbides. Thus the strength increasing effect is almost solely based on the precipitation hardening.

[0048] An advantage of vanadium is the high solubility in the austenite and the large volume proportion of fine precipitations caused by the low precipitation temperature.

[0049] In the following, the effect of the elements in the alloy according to the invention is described in more detail. The chemical composition of multiphase steels is typically such that like elements are combined with and without micro-alloy elements. Tramp elements round off the analysis concept.

[0050] Tramp elements are elements, which are already present in the iron ore or are introduced into the steel due to manufacture. Due to their predominantly negative effect however they are usually not desired. It is sought to remove them to a tolerable content or to convert them into less deleterious forms.

[0051] Hydrogen(H) is the only element that can diffuse through the iron lattice without causing lattice stresses. As a result, hydrogen is relatively mobile in the iron lattice and can be absorbed relatively easily during manufacture. Hydrogen can only be taken up in the iron lattice in atomic (ionic) form.

[0052] Hydrogen has a strong embrittling effect and preferably diffuses to energetically favorable sites (gaps, grain boundaries etc). Gaps act as hydrogen traps and can significantly increase the retention time of the hydrogen in the material.

[0053] Recombination to molecular hydrogen, can lead to cold cracks. This behavior occurs in the hydrogen embrittlement or hydrogen-induced tension crack corrosion. Hydrogen is also often identified as the cause in the so-called delayed fracture, which occurs without outer tensions.

[0054] Therefore, hydrogen should be kept as low as possible in the steel.

[0055] Oxygen(O): in the molten state, the steel has a relatively high absorption capacity for gases, at room temperature however, oxygen can only diffuse into the material in atomic form. Due to the strong embrittling effect and the negative effect on ageing resistance, oxygen is sought to be reduced as much as possible during manufacture.

[0056] In order to reduce oxygen, on one hand process technical approaches such as the vacuum treatment and on the other hand analytical approaches are available. By adding certain alloy elements, oxygen can be converted into less dangerous states. Thus, binding of oxygen via manganese, silicon and/or aluminum is common. The oxides generated thereby however, can cause negative properties in the material in the form of gaps. In case of a fine precipitation especially of aluminum oxides however, a grain refinement can also occur.

[0057] For these reasons, the oxygen content in the steel should be as low as possible.

[0058] Nitrogen(N) is also a tramp element in steel production. Steels with free nitrogen are prone to a strong aging

effect. Nitrogen already diffuses at low temperature at dislocations and blocks the dislocations. With this, it causes a strength increase associated with a rapid loss of tenacity. Binding of nitrogen in form of nitrides is possible by adding aluminum or titanium to the alloy.

[0059] For these reasons, the nitrogen content is limited to=0.0100%, advantageously to=0.0090% or optimally to=0.0070% or to unavoidable tramp amounts.

[0060] Like phosphorus, sulfur(S) is bound in the iron ore as trace element. It is undesired in the steel (exception automate steels) because it has a strong tendency for segregation and acts strongly embrittling. It is therefore sought to achieve an amount of sulfur in the melt that is as small as possible (for example by ultra vacuum treatment). Further, the present sulfur is converted into the relatively harmless component manganese sulfide (MnS) by adding manganese.

[0061] The manganese sulfides are rolled out row-like during the rolling process and act as nuclei for the transformation. Especially in the case of diffusion-controlled transformation this leads to a microstructure that is configured band-like and can lead to poorer mechanical properties in the case of strongly pronounced microstructure banding (for example pronounced martensite bands instead of distributed martensite islands, no isotropic material properties, decreased elongation at break).

[0062] For these reasons, the sulfur content is limited to=0.0100% or to unavoidable tramp amounts.

[0063] Phosphorus (P) is a trace element from the iron ore and is dissolved in the iron lattice as substitution atom. Through solid solution hardening, phosphorus increases strength and improves hardenability.

[0064] However, it is usually sought to lower the phosphorus content as much as possible because due to its low diffusion speed it has a strong tendency for segregation and strongly decreases tenacity. Deposition of phosphorus at the grain boundaries normally leads to grain boundary fractures. In addition, phosphorus increases the transition temperature from tenacious to brittle behavior to 300° C. During hot-rolling, surface proximate phosphorus oxides can lead to fracture separation at the grain boundaries.

[0065] In some steels, however it is used in small amounts (<0.1%) as micro-alloy element due to the low costs and the high strength increase. Thus, phosphorus is sometimes also used in dual-phase steels as strength carrier.

[0066] For the aforementioned reasons, the phosphorus content is limited to=0.025% or to unavoidable tramp amounts.

[0067] Alloy elements are usually added to the steel in order to influence certain properties in a targeted manner. An alloy element can influence different properties in different steels. Generally, the effect strongly depends on the amount and the solution state of the material.

[0068] For example, in dissolved form, even small amounts of chromium can already significantly increase the hardenability of steels. In form of chromium carbides it can cause a direct increase of strength as a result of particle hardening. Through the increase of nuclei and by lowering the amount of dissolved carbon however, the hardenability is reduced.

[0069] The circumstances can thus be rather diverse and complex. In the following, the effect of the alloy elements is explained in more detail.

[0070] Carbon(C) is regarded as the most important alloy element in the steel. Its presence causes the iron to become steel in the first place. In spite of this fact, the carbon content

is drastically lowered during steel production. In dual-phase steels for a continuous hot-dip coating, its proportion according to DIN EN 10346 depending on grade is maximally 0.23%, a minimal value is not given.

[0071] Due to its small atom radius, carbon is interstitially dissolved in the iron lattice. The solubility in the α -iron is maximally 0.02% and in the β -iron maximally 2.06%. In solubilized form, carbon significantly increases the hardenability of steel.

[0072] Due to the caused lattice stresses in the dissolved state, diffusion processes are impeded and thus transformation processes delayed. In addition, carbon facilitates the formation of austenite i.e., it expands the austenite region to lower temperatures. With increasing force-dissolved carbon content, the lattice distortions increase and with this the strength values of the martensite.

[0073] Carbon is also required to form carbides. An example is cementite (Fe₃C), which is present in almost every steel. However, significantly harder special carbides can form together with other metals such as for example chromium, titanium, niobium, vanadium. Not only the type but also the distribution and size of the precipitations is of significant importance for the resulting strength increase. In order to on one hand ensure a sufficient strength and on the other hand a good weldability, the minimal C-content is 0.060% and the maximal C-content is 0.115%.

[0074] Silicon (Si) binds oxygen during casting and thus decreases segregations and contaminations in the steel. In addition, silicone increases the strength and the stretch limit ratio of the ferrite through hybrid Crystal hardening at only minimally decreasing elongation at break. They further important effect is that silicone shifts the formation of ferrite to shorter times and thus enables the formation of sufficient ferrite prior to the quenching. Through the ferrite formation the austenite is enriched with carbon and stabilized. In addition, silicon stabilizes the austenite in the lower temperature range particularly in the range of the bainite formation by preventing carbide formation (no depletion of carbon).

[0075] In the continuous galvanizing, silicon can diffuse to the surface during the annealing where it can lead to silicon oxides. During the dip phase in the zinc bath, silicone oxides can interfere with the formation of a closed adhesive layer between steel and zinc (inhibition layer). This results in a poor zinc adhesion and un-galvanized sites.

[0076] In addition, at high silicon contents a strongly adhering scale can form during hot-rolling, which can have a negative influence on further processing.

[0077] For the above stated reasons, the minimal Si content is 0.100% and the maximal Si-content is 0.500%.

[0078] Manganese(Mn) is added to almost all steels for de-sulfurization in order to convert the deleterious sulfur into manganese sulfide. In addition, manganese increases strength of the ferrite by solid solution strengthening and shifts the α - β transformation to low temperatures.

[0079] A main reason for adding manganese into the alloy in dual-phase steels is the significant improvement of the hardness penetration. Due to the impeding of diffusion, the perlite and bainite transformation is shifted to longer times and the martensite start temperature is lowered.

[0080] Analogous to silicon, manganese can lead to manganese oxides at the surface at high concentrations, which can negatively influence the adhesion properties of zinc and the surface aesthetics.

[0081] The manganese content is therefore set to 1.300 to 2.500%.

[0082] Chromium(Cr): the addition of Chromium in dual-phase steels mainly improves the hardness penetration. In the dissolved state, chromium shifts the perlite and bainite transformation to longer times and lowers at the same time the martensite start temperature.

[0083] A further important effect is that chromium significantly increases the tempering resistance so that almost no strength losses occur in the zinc bath.

[0084] In addition, chromium is a carbide former. When chromium is present, the austenization temperature has to be selected to be sufficiently high to dissolve the chromium carbides. Otherwise the increased number of nuclei can lead to a deterioration of the hardness penetration.

[0085] The Cr-content is therefore set to values of 0.280 to 0.480%.

[0086] Molybdenum (Mo): similar to Chromium, molybdenum is added to improve hardenability. The perlite and bainite transformation is shifted to longer times and the martensite start temperature is lowered.

[0087] Molybdenum also significantly increases the tempering resistance so that in the zinc bath no strength losses are to be expected and causes through solid solution strengthening a strength increase of the ferrite.

[0088] The Mo-content is optionally added to the alloy depending on the dimensions the system configuration and the microstructure adjustment, wherein then the minimal addition should be 0,050% to achieve an effect. For reasons of costs, the Mo content is set to maximally 0.150%.

[0089] Copper (Cu): the addition of copper can increase the tensile strength and the hardness penetration. Together with nickel, chromium and phosphorous copper can form a protective oxide layer at the surface, which significantly reduces the corrosion rate.

[0090] In connection with oxygen, copper can form deleterious oxides at the grain boundaries, which can have negative effects, especially for hot forming processes. The content of copper is therefore limited to unavoidable tramp elements.

[0091] Other alloy elements such as for example nickel (Ni) or tin (Sn) are limited in their contents to unavoidable steel tramp amounts.

[0092] Micro-alloy elements are normally only added in very low amounts (<0.1%). In contrast to the alloy elements, they act mainly through formation of precipitations but can also influence the properties in dissolved state. In spite of the small amounts added, the micro-alloy elements strongly influence the production conditions and the processing and end properties.

[0093] These properties can be used advantageously in that the generally deleterious elements sulfur and oxygen can be bound. However, the binding can also have negative effects when sufficient amounts of microelements are no longer available for the formation of carbides.

[0094] Typical micro-alloy elements are aluminum, vanadium, titanium, niobium and boron. These elements can be dissolved in the iron lattice and together with carbon and nitrogen form carbides or nitrides due to a reduction in the free enthalpy.

[0095] Aluminum (Al) is normally added to the steel to bind the oxygen that is dissolved in the iron. Oxygen and nitrogen are thus converted to aluminum oxides and aluminum nitrides. These precipitations can cause a grain refine-

ment via an increase of the nuclei and thus increase the tenacity properties and strength values.

[0096] Aluminum nitride does not precipitate when titanium is present in sufficient amounts. Titanium nitrides have a lower binding enthalpy and therefore form at higher temperatures.

[0097] In the dissolved state aluminum, like silicon, shifts the ferrite formation to shorter times and thus enables the formation of sufficient ferrite in the dual-phase steel. In addition, it suppresses the carbide formation and thus leads to a stabilization of the austenite.

[0098] The Al-content is therefore limited to 0.020 to maximally 0.060%.

[0099] Titanium (Ti) already forms very stable nitrides (TiN) and sulfides (TiS₂) at high temperatures. These dissolve in dependence on the nitrogen content partly only in the melt. When the thus generated precipitations are not removed with the slag, they form relatively large particles due to the high formation temperature and are normally not beneficial for the mechanical properties.

[0100] A positive effect on the tenacity is caused by the binding of free nitrogen and oxygen. In this way, titanium protects other micro-alloy elements such as niobium from being bound by oxygen. These can then optimally exert their effect. Nitrides, which due to the lowering of the oxygen and nitrogen content are generated only at lower temperatures, can cause an effective impediment of the austenite growth.

[0101] Not bound titanium forms titanium carbides at temperatures above 1150° C. and can thus cause a grain refinement (inhibition of the austenite growth, grain refinement through delayed recrystallization and/or increase of the number of nuclei at α/β transformation) and a precipitation hardening.

[0102] The Ti-content has therefore values of more than 0.005 and less than 0,050%. Advantageously, Ti is limited to contents of =0.045 or =0.040%.

[0103] Niobium (Nb) causes a strong grain refinement because it is most effective among all micro-alloy elements in delaying recrystallization and in addition inhibits the austenite growth.

[0104] The strength increasing effect is however higher than that of titanium due to the increased grain refining effect and the larger amount of strength increasing particles (bonding of the titanium to TiN at high temperatures).

[0105] Niobium carbides form above about 1200° C. In connection with titanium, which as mentioned binds nitrogen, niobium can increase its strength-increasing effect through carbide formation in the lower temperature range (smaller carbide sizes).

[0106] A further effect of niobium is the delay of the α/β -transformation and the lowering of the martensite start temperature in the dissolved state. On one hand, this occurs through the solute drag effect and on the other hand through the grain refinement. This causes a strength increase of the microstructure and thus also a higher resistance against the expansion in the martensite formation.

[0107] The use niobium is limited by the relatively low solubility limit. The latter limits the amount of precipitations however causes an early precipitation formation with relatively coarse particles.

[0108] The precipitation hardening can thus become effective mostly in steels with low C-content (greater over saturation possible) and in hot forming processes (deformation induced precipitation).

[0109] The Nb-content is therefore limited to values between 0.005 and 0.050%, wherein the max. contents are advantageously limited to ≈ 0.045 or $\approx 0.040\%$.

[0110] Vanadium(V): the carbide and nitride formation of vanadium only starts above temperatures of about 1000°C . or still after the α/β transformation, i.e., significantly later than in the case of titanium and niobium. Vanadium has thus hardly a grain refining effect due to the low number of precipitations that are present in the austenite. Also the austenite growth is not inhibited by the late precipitation of the vanadium carbides.

[0111] Thus, the strength increasing effect is almost exclusively based on the precipitation hardening. An advantage of vanadium is the high solubility in the austenite and the great volume proportion of fine precipitations caused by the low precipitation temperature.

[0112] Because addition of vanadium is not required in the present alloy concept, the content of vanadium is limited to unavoidable steel tramp amounts.

[0113] Boron (B) together with nitrogen and carbon, forms nitrides or carbides, which however is normally not desired. On one hand as a result of the poor solubility, only a small amount of precipitations forms and on the other hand these mostly precipitate at the grain boundaries. A strength increase at the surface is not achieved (exception boronation with formation of $\text{FeB}(2)$ at the surface).

[0114] In order to prevent nitride formation, it is normally sought to bind the nitrogen by more affine elements. In ascending order, nitrogen is more affine to beryllium, aluminum, cerium, titanium and zirconium. In particular titanium can ensure binding of the entire nitrogen. Aluminum is less capable for this.

[0115] In the dissolved state, very small amounts of boron lead to a significant improvement of the hardness penetration. The mode of action of boron can be described in that boron atoms preferably accumulate at the grain boundaries where they inhibit the diffusion and the grain boundary sliding by lowering the grain boundary energy. In addition, the reduction of the precipitation formation at the grain boundaries results in a decrease of the nuclei.

[0116] The effectiveness of boron is lowered with increasing grain size and increasing carbon content ($>0.8\%$). An amount of over 60 ppm causes a decreasing hardenability because boron carbides function as nuclei on the grain boundaries.

[0117] Boron has a very high affinity for oxygen, which can lead to a decrease of the boron content in regions close to the surface (up to 0.5 mm). In this context, it is advised against an annealing of over 1000°C . This is to be recommended because boron can lead to a strong coarse grain formation at annealing temperatures above 1000°C .

[0118] For the aforementioned reasons, the B-content is limited to values of 0.0005 to 0.0060%. Advantageously, the values are however below 0.0050 or 0.0040%.

[0119] In addition, it was found in the tests that a complex phase steel with a minimal tensile strength of 750 MPa can be achieved by an austenizing annealing over A_{C3} .

[0120] With an inter critical annealing between A_{C1} and A_{C3} or an austenizing annealing over A_{C3} with subsequent controlled cooling a multiphase steel strip with a thickness of 1 and 3 mm was produced which was characterized by a great tolerance towards process fluctuations and very homogenous properties at same process parameters.

[0121] With this, a significantly widened process window is established for the alloy composition according to the invention compared to the known alloy concepts.

[0122] The annealing temperatures for the steel according to the invention lie between 700 and 950°C ., with this a partial austenitic (two phase region) or a full austenitic structure (austenitic region) is achieved depending on the microstructure to be achieved (complex-phase microstructure).

[0123] The tests have shown that the adjusted structural proportions after the inter critical annealing between A_{C1} and A_{C3} or the austenizing annealing over A_{C3} with final controlled cooling are also retained after the process step hot-dip coating at temperatures between 420 to 470°C . for example in the case of Z (zinc) and ZM (zinc-magnesium).

[0124] The hot-dip coated material can be manufactured as hot strip, as cold temper rolled hot strip or cold strip in the dressed (cold after rolled) or stretch bent straightened state (undressed).

[0125] Steel strips, in the present case as hot strip, cold temper rolled hot strip or cold strip made of the alloy composition according to the invention are further characterized by a high resistance against edge proximate fracture formation during further processing.

[0126] As a result of a quasi isotropy of the steel strip, the material can also be used transverse, longitudinal and diagonally to the rolling direction.

[0127] In order to ensure the rollability of a hot strip that was produced from the steel according to the invention, the hot strip is according to the invention produced with finishing rolling temperatures in the austenitic range above A_{C3} and coiling temperature above the recrystallization temperature.

[0128] Further features, advantages and details of the invention become apparent from the following description of exemplary embodiments shown in the drawing. It is shown in: [0129] FIG. 1 schematically the process chain for the production of the steels according to the invention,

[0130] FIG. 2 results of the hole-widening test,

[0131] FIG. 3 examples for analytical differences of the steel according to the invention relative to the state of the art, [0132] FIG. 4 examples for mechanical characteristics for the steel according to the invention compared to the state of the art (sheet thickness $t=2.0$ mm),

[0133] FIG. 5 schematically the time temperature course of the process steps hot rolling and continuous annealing,

[0134] FIG. 6 ZTU-diagram for a steel according to the invention,

[0135] FIG. 7 mechanical characteristics in case of variation of the rolling degrees,

[0136] FIG. 8 overview over the strength classes that can be adjusted with the alloy concept according to the invention,

[0137] FIG. 9: temperature time curve (schematic).

[0138] FIG. 1 shows schematically the process chain for the production of the steels according to the invention. Shown are the different process routes that relate to the invention. Up to position 5 (pickling) the process route is the same for all steels, after that the corresponding processing occurs according to the desired results. For example, the pickled hot strip can be galvanized or cold-rolled and galvanized. Or it can be soft annealed, cold-rolled and galvanized.

[0139] FIG. 2 shows results of the hole-widening test (relative values in comparison). Shown are the results of the hole widening tests for the steel according to the invention compared to the standard grades. All materials have a sheet thickness of 2.00 mm. On the left hand partial picture, the results

for the test ISO TS 16630 are shown, on the right hand side the results for the KWI-test (Kaiser Wilhelm Institute). It can be seen that the steels according to the invention achieve the best widening values in punched holes independent of the type of processing. Process 1 corresponds here to an annealing for example on a fire galvanization with combined directly fired furnace and radiation tube furnace. Process 2 corresponds for example to a process control in a continuous annealing system. In addition, a reheating of the steel by means of induction furnace can be optionally achieved prior to the galvanization bath. As a result of the different temperature courses according to the invention inside the mentioned range, characteristics result that are different from each other or also different hole widening tests, which are significantly improved for both processes compared to the standard grades. The principle difference is thus the temperature time parameter during the heat treatment and the subsequent cooling.

[0140] FIG. 3 shows the relevant alloy elements of the steel according to the invention compared to steels of the same grade, which correspond to the state of the art. In the steels, which correspond to the state of the art, the main difference is the carbon content, which lies in the ultra peritectic range. Some steels are micro-alloyed with Nb, Ti, and B but not in this combination.

[0141] FIG. 4 shows the mechanical characteristics of the steel according to the invention compared to those of the state of the art. All characteristics correspond to the normative standard.

[0142] FIG. 5 shows schematically the time temperature course of the process steps hot rolling and continuous annealing of strips having the alloy composition according to the invention. Shown is the time and temperature dependent transformation for the hot rolling process and also for a heat treatment after the cold rolling. Of particular interest is the shift of the ferrite phase to later times. This enables the potential for complex phase steels and bainitic steels.

[0143] FIG. 6 shows a ZTU-Diagram for a steel according to the invention. In this, the determined ZTU diagram with corresponding chemical composition and the A_{C1} and A_{C3} temperature is shown. By setting corresponding temperature time courses during the cooling, a broad spectrum of microstructure compositions can advantageously be established in the steel material.

[0144] FIG. 7 shows the mechanical characteristics with same parameters of continuously annealed strips at variation of the rolling degrees of different material thickness. Shown are the characteristics tensile strength, stretch limit and elongation at break in dependence on selected rolling degrees. Only the tensile strength slightly increases. All values lie within the standard for an HCT780XD and show that also in the case of different sheet thicknesses practically same mechanical properties are present after the continuous annealing.

[0145] FIG. 8 shows schematically the temperature time courses during the annealing treatment and cooling with 3 different variants.

[0146] Variant 1 (FIG. 9a) shows the annealing and cooling of produced cold or hot rolled steel strip in a continuous annealing system. First, the strip is heated to a temperature of 700 to 950° C. The annealed steel strip is subsequently cooled from the annealing temperature with a cooling speed between 15 and 100° C./s to an intermediate temperature of 200 to 250° C. subsequently, the steel strip is cooled on air with a cooling speed of 2 and 30° C. until reaching room tempera-

ture or the cooling speed between 15 and 100° C./s is maintained until reaching room temperature, i.e., the intermediate temperature corresponds to the room temperature.

[0147] Variant 2 (FIG. 9b) shows the process according to variant 1, however, the cooling of the steel strip is shortly interrupted during passage through the hot dip container for the purpose of a hot-dip coating, in order to subsequently continue the cooling with a cooling speed between 15 and 100° C./s until reaching an intermediate temperature of 200 to 250° C. Subsequently, the steel strip is cooled on air with a cooling speed of 2 and 30° C./s until reaching room temperature.

[0148] Variant 3 (FIG. 9c) also shows the process according variant 1 in a hot-dip coating, however, the cooling of the steel strip is interrupted by a short break (1 to 20 s) at an intermediate temperature of 200 to 250° C. and reheated to the temperature that is required for the hot-dip coating. Subsequently, the steel strip is cooled to an intermediate temperature of 200 to 250° C. With a cooling speed of 2 and 30° C./s the final cooling of the steel strip is carried out on air until reaching room temperature.

What is claimed is:

1.-18. (canceled)

19. A high strength multiphase steel for a cold or hot-rolled steel strip with excellent forming properties, in particular for lightweight vehicle construction comprising in weight %:

| | |
|----|--------------------------------|
| C | 0.060 to \leq 0.115 |
| Al | 0.020 to \leq 0.060 |
| Si | 0.100 to \leq 0.500 |
| Mn | 1.300 to \leq 2.500 |
| P | \leq 0.025 |
| S | \leq 0.0100 |
| Cr | 0.280 to \leq 0.480 |
| Mo | \leq 0.150 |
| Ti | \geq 0.005 to \leq 0.050 |
| Nb | \geq 0.005 to \leq 0.050 |
| B | \geq 0.0005 to \leq 0.0060 |
| N | \leq 0.0100 |

Remainder iron including common steel tramp elements not mentioned above.

20. The steel of claim 19, wherein the Mo content is \leq 0.100%.

21. The steel of claim 19, wherein the Mo content is \leq 0.050%.

22. The steel of claim 19, wherein the Nb content is \leq 0.045%.

23. The steel of claim 19, wherein the Nb content is \leq 0.040%.

24. The steel of claim 19, wherein the Ti content is \leq 0.045%.

25. The steel of claim 19, wherein the Ti content is \leq 0.040%.

26. The steel of claim 19, wherein the B content is \leq 0.005%.

27. The steel of claim 19, wherein the B content is \leq 0.0040%.

28. The steel of claim 19, wherein the N content is \leq 0.0090%.

29. The steel of claim 19, wherein the N content is \leq 0.0070%.

30. The steel of claim 19, with a total content of Ti, Nb and B of \leq 0.106%.

31. The steel of claim **19**, with a total content of Ti, Nb, B and Mo of $\leq 0.256\%$.

32. A method for producing a cold or hot rolled steel strip from the high strength multiphase steel of claim **19**, comprising:

heating the cold-rolled strip in a continuous annealing furnace to an annealing temperature in the range from 700 to 950° C.;

cooling the annealed steel strip to an intermediate temperature of from 200 to 250° C. at a cooling speed between 15 and 100° C./s; and

cooling the steel strip from the intermediate temperature to room temperature with a cooling speed of 2 to 30° C./s or with a cooling speed between 15 and 100° C./s, wherein for the cooling speed of 2 and 30 C/s the steel strip is cooled on air, wherein a multiphase microstructure is established in the steel strip by the annealing and cooling steps.

33. The method of claim **32**, further comprising after the heating step and prior to the cooling steps, hot dip coating the steel strip by inserting the steel strip into a melting bath.

34. The method of claim **32**, further comprising after cooling to the intermediate temperature,

holding the steel strip at the intermediate temperature for 1 to 20 seconds;

reheating the steel strip to a temperature of 420 to 470° C.; hot dip coating the steel strip by inserting the steel strip into a melting bath; and

cooling the steel strip to the intermediate temperature of 200 to 250° C. with a cooling speed between 15 and 100° C./s, wherein the cooling to room temperature is performed with the cooling speed of from 2 and 30° C./s.

35. The method of claim **32**, further comprising dressing the steel strip.

36. The method of claim **32**, further comprising straightening the steel strip by stretching and bending.

* * * * *