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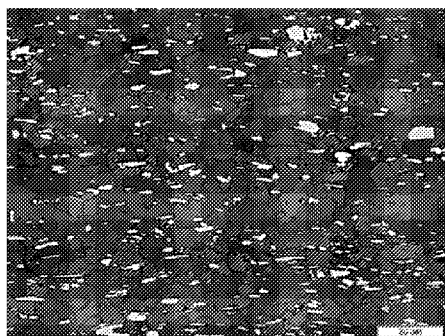
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(54) Title: HIGH FORMABILITY STEEL SHEET FOR THE MANUFACTURE OF LIGHTWEIGHT STRUCTURAL PARTS AND MANUFACTURING PROCESS

**FIG.9**

(57) Abstract: A steel sheet having a composition comprising, by weight: $0.010\% \leq C \leq 0.080\%$, $0.06\% \leq Mn \leq 3\%$, $Si \leq 1.5\%$, $0.005\% \leq Al \leq 1.5\%$, $S \leq 0.030\%$, $P \leq 0.040\%$, Ti and B such that: $3.2\% \leq Ti \leq 7.5\%$ and $(0.45x Ti) - 1.35 \leq B \leq (0.45x Ti) - 0.43$, optionally $Ni \leq 1\%$, $Mo \leq 1\%$, $Cr \leq 3\%$, $Nb \leq 0.1\%$, $V \leq 0.1\%$, the remainder being iron and unavoidable impurities resulting from the smelting. The steel sheet has a structure consisting of ferrite, at most 0% of austenite, and precipitates comprising eutectic precipitates of TiB_2 , the volume fraction of TiB_2 precipitates with respect to the whole structure being of at least 9%, the proportion of TiB_2 precipitates having a surface area lower than $8 \mu m^2$ being of at least 96%.



High formability steel sheet for the manufacture of lightweight structural parts and manufacturing process

The invention relates to the manufacture of steel sheets or structural parts combining a high elasticity modulus E in tension, a low density d and a high processability, especially a high castability and high formability and ductility.

The mechanical performance in stiffness of structural elements are known to vary as E^x/d , the coefficient x depending on the mode of external loading (for example in tension or in bending) and on the geometry of the elements (plates, bars). Thus, steels exhibiting both a high elasticity modulus and a low density have high mechanical performances.

This requirement applies most particularly in the automotive industry, where vehicle lightening and safety are constant preoccupations. In order to produce steel parts having increased elasticity modulus and reduced density, it was proposed to incorporate in the steel ceramic particles of various types, such as carbides, nitrides, oxides or borides. Such materials indeed have a higher elasticity modulus, ranging from about 250 to 550 GPa, than that of base steels, which is around 210 GPa, into which they are incorporated. Hardening is achieved by load transfer between the steel matrix and the ceramic particles under the influence of a stress. This hardening is further increased due to the matrix grain size refinement by the ceramic particles. To manufacture these materials comprising ceramic particles distributed uniformly in a steel matrix, processes are known that are based on powder metallurgy: firstly, ceramic powders of controlled geometry are produced, these being blended with steel powders, thereby corresponding, for the steel, to an extrinsic addition of ceramic particles. The powder blend is compacted in a mold and then heated to a temperature such that this blend undergoes sintering. In a variant of the process, metal powders are blended so as to create the ceramic particles during the sintering phase.

This type of process however suffers from several limitations. Especially, it requires careful smelting and processing conditions in order not to cause a reaction with the atmosphere, taking into account the high specific surface area of metal powders. Besides, even after the compacting and sintering operations, residual porosities may remain, such porosities acting as damage initiation sites during cyclic stressing. Furthermore, the chemical composition of the matrix/particle interfaces, and therefore their cohesion, is difficult to control given the surface contamination of the powders before sintering (presence of oxides and carbon). In addition, when ceramic particles are added in large quantity, or when certain large particles are present, the elongation properties decrease. Finally, this type of process is suitable for low-volume production but cannot meet the

requirements of mass production in the automotive industry, and the manufacturing costs associated with this type of manufacturing process are high.

Manufacturing processes based on the extrinsic addition of ceramic powders into the liquid metal were also proposed. However, these processes suffer from most of the abovementioned drawbacks. More particularly, the difficulty of homogeneously dispersing the particles may be mentioned, such particles having a tendency to agglomerate or to settle in or float on the liquid metal.

Among the known ceramics that could be used to increase the properties of steel is in particular titanium diboride TiB_2 , which has the following intrinsic characteristics:

Elasticity modulus: 583 GPa;

Relative density: 4.52.

In order to produce a steel sheet or part having increased elasticity modulus and reduced density, whilst avoiding the above mentioned problems, it was proposed to produce steel sheets having a composition with C, Ti and B contents such that TiB_2 , Fe_2B and/or TiC precipitates form upon casting.

For example, EP 2 703 510 discloses a method for manufacturing a steel sheet having a composition comprises 0.21% to 1.5% of C, 4% to 12% of Ti and 1.5% to 3% of B, with $2.22 \cdot B \leq \text{Ti}$, the steel comprising TiC and TiB_2 precipitates having an average size of below $10 \mu\text{m}$. The steel sheets are produced by casting the steel in the form of a semi-product, for example an ingot, then reheating, hot-rolling and optionally cold-rolling to obtain a steel sheet. With such a process, elasticity modulus in tension comprised between 230 and 255 GPa can be obtained.

However, this solution also suffers from several limitations, arising both from the composition and from the manufacturing method, and leading to castability issues, as well as formability issues during the manufacturing process and during the subsequent forming steps performed on the steel sheet to produce a part:

- First, such steels have a low liquidus temperature (around 1300°C , so that the solidification starts at a relatively low temperature. In addition, the TiB_2 , TiC and/or Fe_2B precipitate at an early stage of the casting process, at the beginning of the solidification. The presence of these precipitates and the low temperature result in a hardening of the steel and lead to rheological issues, not only during the casting process, but also during the further crop shearing and rolling operations. In particular, the precipitates increase the hot hardness of the solidified shell in contact with the mold, causing surface defects and increasing the risks of breakout. Consequently, surface defects, bleedings and cracks occur during the manufacturing process. In addition, owing to the high hardness, the range of achievable sizes for the hot-rolled or cold-rolled steel sheets is limited. As an

example, steel sheets 1 meter wide having a thickness lower than 3.5 mm cannot be produced in some hot strip mills due to rolling power limitation.

Second, despite the relatively small average size of the precipitates, the size distribution of the precipitates is wide. The steel thus comprises a substantial fraction of coarse precipitates, which negatively impact the formability, especially the ductility and the toughness of the steel, both during the manufacturing process of the sheet and during the subsequent forming operations to produce a part.

Besides, EP 1 897 963 discloses a method for manufacturing a steel sheet having a composition comprises 0.010% to 0.20% of C, 2.5% to 7.2% of Ti and $0.45 \times \text{Ti} - 0.35\% \leq \text{B} \leq 0.45 \times \text{Ti} + 0.70\%$, the steel comprising TiB_2 precipitates. However, this document does not address the problem of processability mentioned above.

Therefore, the invention aims at solving the above problems, in particular at providing a steel sheet having an increased specific elasticity modulus in tension together with a high formability, especially a high ductility and a high toughness. The invention also aims at providing a manufacturing process of such a steel sheet, in which the above issues are not encountered.

The elasticity modulus in tension here designates the Young's modulus in the transverse direction, measured by a dynamic Young's modulus measurement, for example by a resonant frequency method.

The specific elasticity modulus in tension here refers to the ratio between the elasticity modulus in tension and the density of the steel. The density is for example determined using a helium pycnometer.

To that end, the invention relates to a steel sheet made of a steel having a composition comprising, by weight percent:

$$0.010\% \leq \text{C} \leq 0.080\%$$

$$0.06\% \leq \text{Mn} \leq 3\%$$

$$\text{Si} \leq 1.5\%$$

$$0.005\% \leq \text{Al} \leq 1.5\%$$

$$\text{S} \leq 0.030\%$$

$$\text{P} \leq 0.040\%,$$

Ti and B such that:

$$3.2\% \leq \text{Ti} \leq 7.5\%$$

$$(0.45 \times \text{Ti}) - 1.35 \leq \text{B} \leq (0.45 \times \text{Ti}) - 0.43$$

optionally one or more elements chosen amongst:

$$\text{Ni} \leq 1\%$$

$$\text{Mo} \leq 1\%$$

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 $\text{Cr} \leq 3\%$ $\text{Nb} \leq 0.1\%$ $\text{V} \leq 0.1\%$

the remainder being iron and unavoidable impurities resulting from the smelting,

said steel sheet having a structure consisting of ferrite, at most 10% of austenite, and precipitates, said precipitates comprising eutectic precipitates of TiB_2 , the volume fraction of TiB_2 precipitates with respect to the whole structure being of at least 9%, the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ being of at least 96%.

Indeed, the inventors have found that with this composition, the content in free Ti of the steel is of at least 0.95%, and that owing to this content in free Ti, the structure of the steel remains mainly ferritic at any temperature below the liquidus temperature. As a result, the hot hardness of the steel is significantly reduced as compared to the steels of the state of the art, so that the castability and the hot formability are strongly increased.

In addition, the inventors have found that controlling the size distribution of the TiB_2 precipitates leads to a high formability, especially high ductility and toughness, at high and low temperatures, so that the hot and cold rollability of the steel is improved, and parts with complex shapes can be produced.

Preferably, the proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$ is of at least 80%.

Preferably, the proportion of TiB_2 precipitates having a surface area lower than $25 \mu\text{m}^2$ is of 100%.

Preferably, in the core region of the steel sheet, the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ is of at least 96%, the proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$ is preferably of at least 80% and the proportion of TiB_2 precipitates having a surface area lower than $25 \mu\text{m}^2$ is preferably of 100%.

Preferably, the steel sheet comprises no TiC precipitates, or TiC precipitates with a volume fraction lower than 0.5% (with respect to the whole structure).

Generally, the steel sheet comprises no Fe_2B precipitates.

According to an embodiment, the titanium, boron and manganese contents are such that: $(0.45 \times \text{Ti}) - 1.35 \leq \text{B} \leq (0.45 \times \text{Ti}) - (0.261 \times \text{Mn}) - 0.414$.

According to an embodiment, the titanium and boron contents are such that:

$$(0.45 \times \text{Ti}) - 1.35 \leq \text{B} \leq (0.45 \times \text{Ti}) - 0.50.$$

According to an embodiment, the composition is such that $\text{C} \leq 0.050\%$.

Preferably, the steel sheet has a Charpy energy Kcv of at least 25 J/cm² at -40°C.

Generally, the steel sheet has a content in free Ti of at least 0.95%.

The invention also relates to a process for manufacturing a steel sheet, the process comprising the following successive steps:

- providing a steel having a composition comprising, by weight percent:

$$0.010\% \leq C \leq 0.080\%$$

$$0.06\% \leq Mn \leq 3\%$$

$$Si \leq 1.5\%$$

$$0.005\% \leq Al \leq 1.5\%$$

$$S \leq 0.030\%$$

$$P \leq 0.040\%,$$

Ti and B such that:

$$3.2\% \leq Ti \leq 7.5\%$$

$$(0.45 \times Ti) - 1.35 \leq B \leq (0.45 \times Ti) - 0.43$$

optionally one or more elements chosen amongst:

$$Ni \leq 1\%$$

$$Mo \leq 1\%$$

$$Cr \leq 3\%$$

$$Nb \leq 0.1\%$$

$$V \leq 0.1\%$$

the remainder being iron and unavoidable impurities,

- casting the steel in the form of a semi-product, the casting temperature being lower than or equal to $L_{\text{liquidus}} + 40^\circ\text{C}$, L_{liquidus} designating the liquidus temperature of the steel, the semi-product being cast in the form of a thin semi-product having a thickness of at most 110 mm, the steel being solidified during the casting with a solidification rate comprised between 0.03 cm/s and 5 cm/s at every location of the semi-product.

Indeed, the inventors have found that controlling cooling of the solidification such that the solidification rate is of at least 0.03 cm/s at every location of the product, especially at the core of the product, makes it possible to control the size distribution of the TiB₂ precipitates. In addition, the casting under the form of a thin semi-product, with the composition of the invention allows achieving such high solidification rates.

According to an embodiment, the semi-product is cast in the form of a thin slab having a thickness lower than or equal to 110 mm, preferably lower than or equal to 70 mm.

Preferably, the semi-product is cast by compact strip production.

According to another embodiment, the semi-product is cast in the form of a thin strip having a thickness lower than or equal to 6 mm, the solidification rate being comprised between 0.2 cm/s and 5 cm/s at every location of the semi-product.

Preferably, the semi-product is cast by direct strip casting between counter-rotating rolls.

Generally, after casting and solidification, the semi-product is hot rolled, to obtain a hot-rolled steel sheet.

Preferably, between casting and hot-rolling, the temperature of the semi-product remains higher than 700°C.

Preferably, before hot-rolling, the semi-product is de-scaled at a temperature of at least 1050°C.

According to an embodiment, after hot-rolling, the hot-rolled steel sheet is cold-rolled, to obtain a cold-rolled steel sheet having a thickness lower than or equal to 2 mm.

Preferably, the titanium, boron and manganese contents are such that:

$$(0.45 \times \text{Ti}) - 1.35 \leq \text{B} \leq (0.45 \times \text{Ti}) - (0.261 \times \text{Mn}) - 0.414.$$

The invention also relates to a method for manufacturing a structural part, the method comprising:

- cutting at least one blank from a steel sheet according to the invention or produced by a process according to the invention, and

- deforming said blank within a temperature range from 20°C to 900°C.

According to an embodiment, the method comprises, before deforming the blank, a step of welding the blank to another blank.

The invention also relates to a structural part comprising at least of portion made of a steel having a composition comprising, by weight percent:

$$0.010\% \leq \text{C} \leq 0.080\%$$

$$0.06\% \leq \text{Mn} \leq 3\%$$

$$\text{Si} \leq 1.5\%$$

$$0.005\% \leq \text{Al} \leq 1.5\%$$

$$\text{S} \leq 0.030\%$$

$$\text{P} \leq 0.040\%,$$

Ti and B such that:

$$3.2\% \leq \text{Ti} \leq 7.5\%$$

$$(0.45 \times \text{Ti}) - 1.35 \leq \text{B} \leq (0.45 \times \text{Ti}) - 0.43$$

optionally one or more elements chosen amongst:

$$\text{Ni} \leq 1\%$$

$$\text{Mo} \leq 1\%$$

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 $\text{Cr} \leq 3\%$ $\text{Nb} \leq 0.1\%$ $\text{V} \leq 0.1\%$

the remainder being iron and unavoidable impurities resulting from the smelting,

5 said portion having a structure consisting of ferrite, at most 10% of austenite, and precipitates, said precipitates comprising eutectic precipitates of TiB_2 , the volume fraction of TiB_2 precipitates with respect to the whole structure of said portion being of at least 9%, the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ being of at least 96%.

10 Preferably, the structural part is obtained by the method according to the invention.

Other features and advantages of the invention will become apparent over the course of the description below, given by way of non limiting example and with reference to the appended figures in which:

- Figure 1 is a micrograph illustrating the damage mechanism of individual coarse
15 TiB_2 precipitates,

- Figure 2 is a micrograph illustrating the damage mechanism of individual fine TiB_2 precipitates,

- Figure 3 is a micrograph illustrating fine TiB_2 precipitates after a collision of these precipitates,

20 - Figure 4 is a micrograph illustrating coarse TiB_2 precipitates after a collision of these precipitates,

- Figure 5 is a graph illustrating the reduction in area obtained through a tensile test at high temperatures for a steel of the invention and a comparative steel,

25 - Figure 6 is a micrograph illustrating the structure of a steel sheet according to the invention, along a longitudinal plane located at $\frac{1}{4}$ of the thickness of the steel sheet,

- Figures 7 and 8 are micrographs illustrating the structure of comparative steel sheets, along a longitudinal plane located at $\frac{1}{4}$ of the thickness of the steel sheets,

- Figure 9 is a micrograph illustrating the structure of the steel sheet of Figure 6, along a longitudinal plane located at half the thickness of the steel sheet,

30 - Figures 10 and 11 are micrographs illustrating the structure of the comparative steel sheets of figures 7 and 8, along a longitudinal plane located at half the thickness of the steel sheets,

- Figure 12 illustrates the forming limit curves for the steel sheets of Figures 6-11,

35 - Figures 13 and 14 are micrographs illustrating the damages of the steel sheet of Figures 7 and 10 after cold-rolling, along a longitudinal plane located at the surface of the

cold-rolled steel sheet and along a longitudinal plane located at half the thickness of the cold-rolled steel sheet respectively,

- Figure 15 is a graph illustrating the Charpy energy Kcv of the steel sheet of Figures 6 and 9 and of the steel sheet of figures 8 and 11.

As regards the chemical composition of the steel, the carbon content is adapted for achieving the desired level of strength. For this reason, the carbon content is of at least 0.010%.

However, the C content must be limited in order to avoid primary precipitation of TiC and/or Ti(C,N) in the liquid steel, and precipitation of TiC and/or Ti(C,N) during eutectic solidification and in the solid phase fraction, that could otherwise occur owing to the high Ti content of the steel. Indeed, TiC and Ti(C,N) precipitating in the liquid steel would deteriorate the castability by increasing the hot hardness of the solidified shell during the casting and lead to cracks in the cast product. In addition, the presence of TiC precipitates decreases the content in free Ti in the steel, and therefore inhibits the alphageneous role of Ti. For these reasons, the C content must be of at most 0.080%. Preferably, the C content is of at most 0.050%.

In a content of at least 0.06%, manganese increases the hardenability and contributes to the solid-solution hardening and therefore increases the tensile strength. It combines with any sulfur present, thus reducing the risk of hot cracking. However, if the Mn content is higher than 3%, the structure of the steel will not be mainly ferritic at all temperatures, so that the hot hardness of the steel will be too high, as explained in further details below.

Silicon effectively contributes to increasing the tensile strength by solid solution hardening. However, excessive addition of Si causes the formation of adherent oxides that are difficult to remove by pickling, and the possible formation of surface defects due in particular to a lack of wettability in hot-dip galvanizing operations. To ensure a good coatability, the Si content must not exceed 1.5%.

In a content of at least 0.005%, aluminum is a very effective element for deoxidizing the steel. However, in a content above 1.5%, excessive primary precipitation of alumina occurs, impairing the castability of the steel.

In a content higher than 0.030%, sulfur tends to precipitate in excessively large amounts in the form of manganese sulfides, which reduce to a large extent the hot and cold formability of the steel. Therefore, the S content is of at most 0.030%.

Phosphorus is an element that segregates at the grain boundaries. Its content must not exceed 0.040% so as to maintain sufficient hot ductility, thereby avoiding cracking, and to prevent hot cracking during welding operations.

Optionally, nickel and/or molybdenum may be added, these elements increasing the tensile strength of the steel. For cost reasons, the additions of Ni and Mo are each limited to 1%.

Optionally, chromium may be added to increase the tensile strength, the Cr content being limited to at most 3% for cost reasons. Cr also promotes the precipitation of borides. However, the addition of Cr above 0.080% may promote the precipitation of (Fe, Cr) borides, to the detriment of TiB_2 precipitates. Therefore, the Cr content is preferably of at most 0.080%.

Also optionally, niobium and vanadium may be added in an amount equal to or less than 0.1% so as to obtain complementary hardening in the form of fine precipitated carbonitrides.

Titanium and boron play an important role in the invention. Indeed, Ti and B precipitate under the form of TiB_2 precipitates which significantly increase the elasticity modulus in tension E of the steel. TiB_2 may precipitate at an early stage of the manufacturing process, especially under the form of primary TiB_2 precipitating in the liquid steel, and/or as eutectic precipitates.

However, the inventors have found that the TiB_2 precipitates may lead to an increase in the hot hardness of the solidified shell during the casting and thereby results in the formation of cracks in the cast product, in the appearance of surface defects and in a decrease in the hot rollability of the steel which limit the accessible thickness range for the hot-rolled steel sheet.

Surprisingly, the inventors have found that if the Ti and the B content are adjusted such that the content of free Ti (hereinafter Ti^*) is higher than or equal to 0.95%, the hot hardness of the steel is significantly reduced. Indeed, the inventors have found that under this condition, the steel remains mainly ferritic, i.e. comprises at most 10% of austenite, whatever the temperature (below the liquidus), especially during the solidification and the hot-rolling, which leads to a decrease of the hot hardness of the steel as compared to a steel undergoing an allotropic transformation of more than 10% on cooling. Thus, the castability and the hot ductility of the steel are improved to a large extent, despite the formation of TiB_2 in the steel during solidification.

The "free Ti" here designates the content of Ti not bound under the form of precipitates.

In addition, a Ti^* content of at least 0.95% greatly reduces, and even suppresses the formation of Fe_2B that would impair the ductility.

Preferably, the Ti^* content is higher than or equal to $0.92 + 0.58 \cdot \text{Mn}$, wherein Mn designates the Mn content in the steel. Indeed, Mn is a gammageneous element that may

favor the presence of austenite in the structure. Thus, the Ti^* is preferably adjusted depending on the Mn content so as to ensure that the steel remains mainly ferritic whatever the temperature.

However, the Ti^* content should remain lower than 3%, as no significant beneficial technical effect would be obtained from a Ti^* content higher than 3%, despite the higher cost of adding titanium.

In order to ensure a sufficient TiB_2 precipitation, and in the same time allow the content Ti^* to reach 0.95%, the Ti content must be of at least 3.2%. If the Ti content is lower than 3.2%, the TiB_2 precipitation is not sufficient, thereby precluding a significant increase in the elasticity modulus in tension, which remains lower than 220 GPa.

However, if the Ti content is higher than 7.5%, coarse primary TiB_2 precipitation may occur in the liquid steel and cause castability problems in the semi-product, as well as a reduction of the ductility of the steel leading to a poor hot and cold rollability.

Therefore, the Ti content is comprised between 3.2% and 7.5%.

Besides, in order to ensure a Ti^* content of at least 0.95%, the boron content should be of at most $(0.45 \times Ti) - 0.43$, Ti designating the Ti content by weight percent.

If $B > (0.45 \times Ti) - 0.43$, the Ti^* content will not reach 0.95%. Indeed, the Ti^* content can be evaluated as $Ti^* = Ti - 2.215 \times B$, B designating the B content in the steel. As a consequence, if $B > (0.45 \times Ti) - 0.43$, the structure of the steel will not be mainly ferritic during the casting and the hot rolling operations, so that its hot ductility will be reduced, which may lead to the formation of cracks and/or surface defects during the casting and hot rolling operations.

If a Ti^* content higher than or equal to $0.92 + 0.58 \times Mn$ is targeted, the boron content should be of at most $(0.45 \times Ti) - (0.261 \times Mn) - 0.414$, Ti and Mn designating the Ti and Mn content by weight percent.

If $B > (0.45 \times Ti) - (0.261 \times Mn) - 0.414$, the Ti^* content will not reach $0.92 + 0.58 \times Mn$.

The boron content should however be higher than or equal to $(0.45 \times Ti) - 1.35$ to ensure a sufficient precipitation of TiB_2 . In addition, a B content lower than $(0.45 \times Ti) - 1.35$ would corresponds to a Ti^* content higher than 3%.

The balance is iron and residual elements resulting from the steelmaking.

According to the invention, the structure of the steel is mainly ferritic whatever the temperature (below $T_{liquidus}$). By "mainly ferritic", it must be understood that the structure of the steel consists of ferrite, precipitates (especially TiB_2 precipitates) and at most 10% of austenite.

Thus, the steel sheet according to the invention has a structure which is mainly ferritic at all temperatures, especially at room temperature. The structure of the steel sheet at room temperature is generally ferritic, i.e. comprises no austenite.

The ferritic grain size is generally lower than 6 μm .

5 The volume fraction of TiB_2 precipitates is of at least 9%, so as to obtain an elasticity modulus in tension E of at least 230 GPa.

The volume fraction of TiB_2 precipitates is preferably of at least 12%, so as to obtain an elasticity modulus in tension E of at least 240 GPa.

10 The TiB_2 precipitates mainly result from very fine eutectic precipitation upon solidification, the mean surface area of the TiB_2 precipitates being preferably lower than $8.5 \mu\text{m}^2$, still preferably lower than $4.5 \mu\text{m}^2$, still preferably lower than $3 \mu\text{m}^2$.

15 The inventors have found that the size of the TiB_2 precipitates in the steel have an influence on the properties of the steel, in particular on the damage resistance of the product during its manufacture, especially its hot and cold rollability, on the damage resistance of the steel sheet, especially during the forming operation, its fatigue strength, its fracture stress and its toughness.

However, the inventors have found that the main factor for ensuring a high damage resistance and therefore a high formability is the size distribution of the TiB_2 precipitates.

20 Indeed, the inventors have found that in a steel comprising TiB_2 precipitates, the damages occurring during the manufacture, especially during the hot and/or cold rolling steps and the further forming operations, may result from damages undergone by individual precipitates, and from collisions between the precipitates.

25 Especially, damage initiation of the individual TiB_2 precipitates comes from pile-up of dislocations at the interface between the ferrite and the TiB_2 precipitates, and depends on the size of the TiB_2 precipitates. In particular, the fracture stress of the TiB_2 precipitates is a decreasing function of the TiB_2 precipitate size. If the size of some of the TiB_2 precipitates increases such that the fracture stress of these precipitates becomes lower than the interface disbonding stress, the damage mechanism changes from interface disbonding to fracture of the TiB_2 precipitates, leading to a significant decrease of the ductility, formability and toughness.

30 This change in damage mechanism is illustrated by Figures 1 and 2.

Figure 1 illustrates the damage of a coarse TiB_2 precipitate under compressive stress during cold-rolling: in that case, the TiB_2 precipitate is fractured along a direction parallel to the compressive stress, under a relatively low stress.

By contrast, Figure 2 illustrates the interface disbonding of smaller TiB_2 precipitates during cold-rolling, by the appearance of cavities at the interface between the ferritic matrix and the TiB_2 precipitates.

Consequently, if a steel sheet, though having TiB_2 precipitates with a reduced mean size, comprises large TiB_2 precipitates, these large TiB_2 precipitates will cause a change in the damage mechanism of the steel and a decrease of the steel mechanical properties.

Besides, the inventors have found that the damages resulting from collisions between TiB_2 precipitates are all the more important that the size of these precipitates is large. In particular, whereas a collision between coarse TiB_2 precipitates results in a fracture of these precipitates, a collision of small TiB_2 precipitates does not lead to such fracture.

Figures 3 and 4 illustrate precipitates of different sizes further to a collision.

Especially, Figures 3 and 4 illustrate fine precipitates and large TiB_2 precipitates after a collision respectively. These figures show that the collision of the large precipitates led to a fracture of one of the colliding precipitates, whereas the collision of the fine precipitates did not result in any damage.

In order to ensure high ductility, formability and toughness, the inventors have found that the distribution of the size of the TiB_2 precipitates must be such that the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ is of at least 96%.

Moreover, the proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$ should preferably be of at least 80%, and the proportion of TiB_2 precipitates having a surface area lower than $25 \mu\text{m}^2$ should preferably be of 100%.

The proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$, $8 \mu\text{m}^2$ or $25 \mu\text{m}^2$ is defined as the number of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$, $8 \mu\text{m}^2$ or $25 \mu\text{m}^2$, divided by the number of TiB_2 precipitates, and multiplied by a factor 100.

The proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$, $8 \mu\text{m}^2$ or $25 \mu\text{m}^2$ is preferably determined on a specimen prepared using standard metallographic technique for surface preparation and etched with nital reagent, by image analysis using a Scanning Electron Microscope (SEM).

Especially, at the core of the sheet, the distribution of the size of the TiB_2 precipitates must be such that the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ is of at least 96%, and preferably such that the proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$ is of at least 80%, still preferably such that the proportion of TiB_2 precipitates having a surface area lower than $25 \mu\text{m}^2$ is of 100%.

By considering a sheet having a generally rectangular shape having a length l in a longitudinal direction, a width w in the transversal direction and a thickness t in the thickness direction, the core of the sheet is defined as the portion of the sheet extending over the length l and over the width w , in the thickness direction of the sheet, from a first end located at 45% of the overall thickness t of the sheet to a second end located at 55% of the overall thickness t of the sheet.

Indeed, the inventors have found that under this condition, the damages occur by interface disbonding, so that the damage kinetics is delayed. Besides, under this condition, the damages that may result from collisions between TiB_2 precipitates are highly reduced.

As a consequence, the formability and the ductility of the steel sheet during its manufacture and in use are greatly improved.

In particular, the reduction ratio achievable through cold-rolling is increased, and the formability is increased, so that parts with complex shapes can be formed.

Having a proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ of at least 96% is critical. Indeed, the inventors have found that below this value, the coarse TiB_2 precipitates cause a change in damage mechanism, as explained above, which drastically reduces the damage resistance of the steel.

Besides, the steel sheet according to the invention comprises no or a small fraction of TiC precipitates, the volume fraction of TiC precipitates in the structure remaining lower than 0.5%, generally lower than 0.36%.

Indeed, as explained above, TiC precipitates, if present, would have formed in the liquid steel, and would have deteriorated the castability of the steel, so that a fraction of TiC precipitates in the structure higher than 0.5% would result in cracks and/or surface defects in the steel sheet. The presence of TiC precipitates further decreases the ductility of the steel.

In addition, owing to the high Ti^* content, the steel sheet does not comprise any Fe_2B precipitates, the volume fraction of Fe_2B precipitates in the structure being of 0%. The absence of Fe_2B precipitates increases the ductility of the steel sheet.

The steel sheet, whether hot-rolled or cold-rolled, has a very high toughness, even at low temperatures. Especially, the transition temperature from ductile mode to mixed mode is lower than -20°C , and the Charpy energy K_{cv} of the steel sheet is generally higher than or equal to 25 J/cm^2 at -40°C , and higher than or equal to 20 J/cm^2 at -60°C .

The steel sheet has an elasticity modulus in tension E of at least 230 GPa, generally of at least 240 GPa, a tensile strength TS of at least 640 MPa and a yield strength of at

least 250 MPa before any skin-pass. Thus, a non skin-passed sheet according to the invention generally has a yield strength of at least 250 MPa.

The high tensile strength, of at least 640 MPa, is especially achieved owing to the small size and the size distribution of the TiB_2 precipitates in the steel of the invention, due to the Hall-Petch effect and increased work-hardening.

The elasticity modulus in tension is an increasing function of the fraction of TiB_2 precipitates.

Especially, an elasticity modulus in tension E of at least 230 GPa is achieved with a fraction of TiB_2 precipitates of 9% or higher. In the preferred embodiment wherein the volume fraction of TiB_2 precipitates is of at least 12%, an elasticity modulus in tension E of at least 240 GPa is achieved.

Besides, the presence of TiB_2 precipitates leads to a decrease of the density of the steel.

As a consequence, the steel sheet of the invention has a very high specific elasticity modulus in tension.

A process for manufacturing a steel sheet according to the invention is implemented as follows.

A steel with the composition according to the invention is provided, and the steel is then cast into a semi-product.

The casting is performed at a temperature lower than or equal to $T_{\text{liquidus}} + 40^\circ\text{C}$, T_{liquidus} designating the liquidus temperature of the steel.

Indeed, a casting temperature higher than $T_{\text{liquidus}} + 40^\circ\text{C}$ could lead to the formation of coarse TiB_2 precipitates.

The liquidus temperature T_{liquidus} of the steel of the invention is generally comprised between 1290°C and 1310°C . Therefore, the casting temperature should generally be of at most 1350°C .

The casting is carried out so as to form upon casting a thin product, having a thickness of at most 110 mm, especially a thin slab or a thin strip.

To that end, the casting is preferably performed by compact strip production, to form a thin slab having a thickness lower than or equal to 110 mm, preferably of at most 70 mm, or by direct strip casting between counter-rotating rolls, to form a thin strip having a thickness lower than or equal to 6 mm.

In any case, the thickness of the semi-product must be of at most 110 mm, and preferably of at most 70 mm.

Casting the semi-product under the form of a thin semi-product, for example a thin slab or strip, improves the processability of the steel by limiting the damage of the steel during rolling and forming operations.

Indeed, casting the semi-product under the form of a thin semi-product, for example a thin slab or strip allows using during the subsequent rolling steps a lower reduction rate to achieve the desired thickness.

A decrease in the reduction rate limits the damage of the steel that may result from collisions of the TiB_2 precipitates during hot and cold rolling operations.

Most of all, the casting under the form of a thin semi-product allows achieving very fine TiB_2 precipitates, so that the damage that may result from collisions of TiB_2 precipitates and the damage of individual TiB_2 precipitates are reduced, as explained above.

Especially, the casting under the form of a thin semi-product allows a fine control of the solidification rate upon cooling across the thickness of the sheet, ensures a solidification rate fast enough in the whole product and minimizes the difference in solidification rate between the surface of the product and the core of the product.

Indeed, achieving a sufficient and homogeneous solidification rate is necessary to obtaining very fine TiB_2 precipitates, not only at the surface of the product, but also at the core of the semi-product. By considering a semi-product having a generally rectangular shape having a length l_2 in a longitudinal direction, a width w_2 in the transversal direction and a thickness t_2 in the thickness direction, the core (or core region) of the semi-product is defined as the portion of the semi-product extending over the length l_2 and over the width w_2 , in the thickness direction of the semi-product, from a first end located at 45% of the overall thickness t_2 of the semi-product, to a second end located at 55% of the overall thickness of the semi-product.

The inventors have further found that in order to obtain very fine TiB_2 precipitates such that the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ is of at least 96%, the cooling conditions during the solidification must be such that the steel is solidified with a solidification rate equal to or greater than 0.03 cm/s, up to 5 cm/s, at every location of the semi-product.

Owing to the decrease of the solidification rate from the surface to the core of the product, a solidification rate of at least 0.03 cm/s at every location implies that the solidification rate at the core of the product is of at least 0.03 cm/s, up to 5 cm/s.

Besides, if the semi-product is cast under the form of a thin strip, especially by direct strip casting between counter-rotating rolls, to form a thin strip having a thickness lower

than or equal to 6 mm, the solidification rate is comprised between 0.2 cm/s and 5 cm/s at every location of the semi-product.

Indeed, the inventors have found that a solidification rate of at least 0.03 cm/s at every location, especially at the core of the product, allows obtaining very fine TiB_2 precipitates, not only at the surface of the product but also throughout the whole thickness of the product, such that the mean area surface is lower than $8.5 \mu\text{m}^2$ and the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ is of at least 96%. In addition, the proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$ is of at least 80%, and the proportion of TiB_2 precipitates having a surface area lower than $25 \mu\text{m}^2$ is of 100%.

Especially, a solidification rate of at least 0.03 cm/s in the core region of the product allows obtaining very fine TiB_2 precipitates in the core region of the semi-product, such that the mean area surface is lower than $8.5 \mu\text{m}^2$ and the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ is of at least 96%. In addition, the proportion of TiB_2 precipitates having a surface area lower than $3 \mu\text{m}^2$ is of at least 80%, and the proportion of TiB_2 precipitates having a surface area lower than $25 \mu\text{m}^2$ is of 100%.

By contrast, if the solidification rate at least some parts of the product is lower than 0.03 cm/s, TiC precipitates and/or coarse TiB_2 precipitates will form during solidification.

The control of the cooling and solidification rates to the above values is achieved owing to the casting of the steel in the form of a thin semi-product with a thickness lower than 110 mm, and to the composition of the steel.

Especially, the casting in the form of a thin semi-product results in a high cooling rate across the product thickness and in an improved homogeneity of the solidification rate from the surface to the core of the product.

In addition, owing to the high Ti^* content of the steel, the steel solidifies mainly as ferrite. Especially, the solidified steel has a mainly ferritic structure from the start of solidification and during the whole solidification process, the austenite fraction in the steel remaining of at most 10%. Thus, no or very limited phase transformation occurs during the cooling.

As a result the steel can be cooled by rewetting, rather than by film boiling, which allows reaching very high solidification rates.

Film boiling is a cooling mode in which a thin layer of vapor of cooling fluid, having a low thermal conductivity, is interposed between the surface of the steel and the liquid cooling fluid. In film boiling, the heat transfer coefficient is low. By contrast, cooling by rewetting occurs when the vapor layer is fractured, and the cooling fluid becomes in contact with the steel. This cooling mode occurs when the temperature of the surface of

the steel is lower than the Leidenfrost temperature. The heat transfer coefficient achieved through rewetting is higher than the heat transfer coefficient achievable through film boiling, so that the solidification rate is increased. However, if phase transformations occur during cooling by rewetting, the coupling between rewetting and phase transformation induces high strains in the steel resulting in cracks and surface defects.

Therefore, steels enduring a significant allotropic transformation during solidification cannot be cooled by rewetting.

By contrast, in the steels of the invention, which comprise at most 10% of austenite at any temperature, little or no phase transformation occurs upon solidification, and the steel can therefore be cooled by rewetting.

Thus, very high solidification rates can be achieved.

At the end of the solidification, the structure of the steel is mainly ferritic and comprises very fine eutectic TiB_2 precipitates.

In addition, owing to the mainly ferritic structure of the steel as soon as the solidification starts, no or little transformation of δ ferrite into austenite occurs during solidification (i.e. at most 10% of δ ferrite transforms into austenite during solidification), so that the local contractions that would result from this transformation, which could lead to cracks in the semi-product, are avoided.

In particular, in the absence of significant transformation of δ ferrite into austenite, no peritectic induced precipitation occurs during solidification. Such peritectic induced precipitation, occurring in the dendrites, could lead to a decrease of the hot ductility and induce cracks, especially during the further hot rolling.

Therefore, the solidified semi-product has a very good surface quality and comprises no or very few cracks.

Moreover, the solidification of the steel as mainly ferrite, as compared to a structure comprising more than 10% of austenite at the solidification, reduces to a large extent the hardness of the solidified steel, in particular the hardness of the solidified shell.

Especially, the hardness of the steel is about 40% lower than a comparable steel that would have an structure comprising more than 10% of austenite during solidification.

The low hot hardness of the solidified steel results in a reduction of the rheological issues involving the solidified shell, especially avoids the occurrence of surface defects, depression and bleedings in the cast product.

In addition, the low hot hardness of the solidified steel also guarantees a high hot ductility of the steel, as compared to allotropic grades.

Owing to the high hot ductility of the product, the formation of cracks, that would otherwise appear during the bending and straightening operations of the casting process, and/or during the subsequent hot rolling, is avoided.

After solidification, the semi-product is cooled to an end of cooling temperature which is preferably of not less than 700°C. At the end of the cooling, the structure of the semi-product remains mainly ferritic.

The semi-product is then heated, from the end of cooling temperature to about 1200°C, de-scaled then hot-rolled.

During de-scaling, the temperature of the surface of the steel is preferably of at least 1050°C. Indeed, below 1050°C, liquid oxides will solidify on the surface of the semi-product, which may cause surface defects.

Preferably, the semi-product is directly hot-rolled, i.e. is not cooled to a temperature below 700°C before hot-rolling, such that the temperature of the semi-product remains at any time higher than or equal to 700°C between the casting and the hot-rolling. The direct hot-rolling of the semi-product allows reducing the time necessary for homogenizing the temperature of the semi-product before hot-rolling, and therefore limiting the formation of liquid oxides at the surface of the semi-product.

In addition, the as cast semi-product is generally brittle at low temperatures, so that directly hot-rolling the semi-product allows avoiding cracks that may otherwise occur at low temperatures due to the brittleness of the as cast semi-product.

The hot-rolling is for example performed in a temperature range comprised between 1100°C and 900°C, preferably between 1050°C and 900°C.

As explained above, the hot ductility of the semi-product is very high, owing to the mainly ferritic structure of the steel. Indeed, no or little phase transformation, which would reduce the ductility, occurs in the steel during hot-rolling.

As a consequence, the hot rollability of the semi-product is satisfactory, even with a hot-rolling finish temperature of 900°C, and the appearance of cracks in the steel sheet during hot-rolling is avoided.

For example, hot-rolled steel sheets having a thickness comprised between 1.5 mm and 4 mm, for example comprised between 1.5 mm and 2 mm, are obtained.

After hot-rolling, the steel sheet is preferably coiled. The hot-rolled steel sheet is then preferably pickled, for example in an HCl bath, to guarantee a good surface quality

Optionally, if a lower thickness is desired, the hot-rolled steel sheet is subjected to cold-rolling, so as to obtain a cold-rolled steel sheet having a thickness of less than 2 mm, for example comprised between 0.9 mm and 1.2 mm.

Such thicknesses are achieved without producing any significant internal damage. This absence of significant damage is especially due to the casting under the form of a thin semi-product and to the composition of the steel.

Indeed, since the cold-rolled sheet is produced from a thin product, the hot and cold reduction ratios necessary to achieve a given thickness is reduced. Therefore, the occurrence of collisions between the TiB_2 precipitates, which could lead to damage, is reduced.

Furthermore, owing to the size distribution of the TiB_2 precipitates, achieved thanks to the low thickness of the semi-product and to the composition, cold reduction ratios of up to 40%, and even of up to 50% can be achieved without producing any significant internal damage.

Indeed, since the steel comprises no coarse TiB_2 precipitates, the damages occur by interface disbonding, so that the damage kinetics is delayed. Besides, the collision of the TiB_2 precipitates, owing to their small sizes, does not lead to any significant damage.

As a consequence, the occurrence of damages during cold-rolling is highly reduced.

After cold-rolling, the cold-rolled steel sheet may be subjected to an annealing. The annealing is for example performed by heating the cold-rolled steel sheet at a mean heating rate preferably comprised between 2 and 4°C/s, to an annealing temperature comprised between 800°C and 900°C, and holding the cold-rolled steel sheet at this annealing temperature for an annealing time generally comprised between 45 s and 90s.

The steel sheet thus obtained, which may be hot-rolled or cold rolled, has a mainly ferritic structure, i.e. consists of ferrite, at most 10% of austenite, and precipitates. Generally, the steel sheet thus obtained has a ferritic structure at room temperature, i.e. a structure consisting of ferrite and precipitates, without austenite.

The steel sheet thus obtained comprises TiB_2 precipitates, which are eutectic TiB_2 precipitates, the volume fraction of TiB_2 precipitates being of at least 9%.

The proportion of TiB_2 precipitates in the steel sheet having a surface area lower than 8 μm^2 is of at least 96%. In addition, the proportion of TiB_2 precipitates having a surface area lower than 3 μm^2 is preferably of at least 80%, and the proportion of TiB_2 precipitates having a surface area lower than 25 μm^2 is preferably of 100%.

This is especially the case in the core region of the sheet.

The steel sheet thus obtained comprises a very small amount of TiC precipitates, owing to the low C content of the steel and to the manufacturing process, and to the absence of peritectic induced precipitation during solidification. The volume fraction of TiC precipitates in the structure is in particular lower than 0.5%, generally lower than 0.36%.

The steel sheet thus obtained comprises no Fe_2B precipitates.

With this manufacturing process, the formation of surface defects and cracks in the cast product and the steel sheet is avoided.

Especially, the reduction in hardness achieved owing to the high Ti* content allows avoiding the occurrence of surface defects, depression and bleedings in the cast product.

In addition, the steel sheet thus obtained has very high formability, toughness and fatigue strength, so that the parts with complex geometry can be produced from such sheets.

Especially, the damages in the steel sheet that may result from hot and/or cold-rolling are minimized, so that steel has an improved ductility during the subsequent forming operations and an improved toughness.

Furthermore, the high elasticity modulus in tension of the steel according to the invention reduces the springback after the forming operations and thereby increases the dimensional precision on the finished parts.

To produce a part, the steel sheet is cut to produce a blank, and the blank is deformed, for example by drawing or bending, in a temperature range comprised between 20 and 900° C.

Advantageously, structural elements are manufactured by welding a steel sheet or blank according to the invention to another steel sheet or blank, having an identical or a different composition, and having an identical or a different thickness, so as to obtain a welded assembly with varying mechanical properties, which can be further deformed to produce a part.

For example, the steel sheet according to the invention may be welded to a steel sheet made of a steel having a composition comprising, by weight percent:

$$0.01\% \leq C \leq 0.25\%$$

$$0.05\% \leq Mn \leq 2\%$$

$$Si \leq 0.4\%$$

$$Al \leq 0.1\%$$

$$Ti \leq 0.1\%$$

$$Nb \leq 0.1\%$$

$$V \leq 0.1\%$$

$$Cr \leq 3\%$$

$$Mo \leq 1\%$$

$$Ni \leq 1\%$$

$$B \leq 0.003\%$$

the remainder being iron and unavoidable impurities resulting from the smelting.

Examples:

As examples and comparison, sheets made of steel compositions according to table I, have been manufactured, the elements being expressed in weight percent.

	C	Mn	Si	Al	S	P	Ti	B	Cr	Ti*=Ti- 2.215*B
A	0.0227	0.061	0.168	0.039	0.0067	0.008	5.32	1.67	0.12	1.6
B	0.04	0.09	0.14	0.146	0.0015	0.009	6.34	2.34	0.075	1.16
C	0.036	0.07	0.15	0.065	0.001	0.01	5.3	<u>2.05</u>	0.05	<u>0.75</u>

Table 1

In Table 1, the underline value is not according to the invention.

These steels were cast in the form of semi-products:

- steel A was continuously cast in the form of a slab having a thickness of 65 mm (sample I1),

- steel B was cast in the form of a ingot of 300 kg, having a section of 130 mm x 130 mm (sample R1),

- steel C was cast in the form of a thin slab having a thickness of 45 mm (sample R2).

The solidification rates during solidification of the cast products were assessed at the surface and at the core of the products, and are reported in Table 2 below.

Sample reference	Steel composition	At the surface (cm/s)	At the core (cm/s)
I1	A	0.3	0.06
R1	B	<u>0.001</u>	<u>0.0001</u>
R2	C	0.3	<u>0.01</u>

Table 2

In Table 2, the underlined values are not according to the invention.

Sample I1 was cast under the form of a thin slab, having a thickness lower than 110 mm.

In addition, the composition (A) of sample I1 is in accordance with the invention, and has therefore a content in free Ti of at least 0.95%, so that during the solidification, no or little phase transformation occurred, allowing cooling by rewetting.

Owing to the low thickness of the cast product and to the cooling by rewetting, the solidification rate for sample I1 could be higher than 0.03 cm/s, even at the core of the semi-product.

By contrast, sample R1 has a composition (B) according to the invention, but was not cast as a thin semi-product, its thickness being higher than 110 mm.

As a consequence, the solidification rate could not reach the targeted values, neither at the core nor at the surface of the semi-product.

Sample R2 does not have a composition (C) in accordance with the invention, its B content being higher than $(0.45 \times \text{Ti}) - 0.43$. Thus, sample R2 has a content in free Ti lower than 0.95% (0.75%).

Thus, even if the steel was cast under the form of a thin strip, an important phase transformation occurring during solidification, so that the cooling could not be performed by rewetting. As a result, the solidification rate did not reach 0.03 cm/s at the core of the product.

The inventors have investigated the hot formability of samples I1 and R2.

Especially, the hot formability of as cast samples I1 and R2 was assessed by performing hot plane strain compression tests with various strain rates as temperatures ranging from 950°C to 1200°C.

To that end, Rastegaiev specimens were sampled from as cast samples I1 and R2. The specimens were heated to a temperature of 950°C, 1000°C, 1100°C or 1200°C, and then compressed by two punches, located of opposite sides of the specimen, with various strain rates of 0.1 s^{-1} , 1 s^{-1} , 10 s^{-1} or 50 s^{-1} . The stresses were determined, and for each test, the maximum stress was assessed.

Table 3 below reports at each temperature and for each of the samples I1 and R2 the fraction of austenite in the structure at this temperature, and the maximal stress determined at each temperature for each strain rate.

	950°C		1000°C		1100°C		1200°C	
	I1	R2	I1	R2	I1	R2	I1	R2
% of austenite	< 10%	100%	< 10%	100%	< 10%	100%	< 10%	100%
Strain rate (s^{-1})	Stress max (MPa)							
0.1	93	196	70	169.5	47	127	27	81
1	138	230	108	209	75	164	53	112
10	199	270	169	253	125	212	90	153
50	236	316	204	294	155	250	126	191

Table 3

These results show that the maximum stress reached for sample I1 is much lower than for sample R2, whatever the temperature comprised between 950°C and 1200°C and whatever the strain rate, the maximum stress for steel I1 being of up to 67% lower than the maximum stress reached for steel R2.

This reduction of the maximum stress results especially from the difference between the structure of sample I1, which is mainly ferritic at all temperatures, and the structure of sample R2, which endures phase transformation and becomes austenitic at high temperatures. This reduction implies that at high temperatures, the hardness of the steel of the invention is reduced to a large extent as compared to a steel having a Ti* content lower than 0.95%, the hot formability being thereby improved.

The hot formability of as cast samples I1 and R2 was further assessed by performing high temperature tensile test on a thermomechanical simulator Gleeble.

Especially, the reduction of area was determined at temperatures ranging from 600°C to 1100°C.

The results of these tests, illustrated on Figure 5, show that the hot ductility of sample I1 remains high even at decreasing temperatures, especially at temperatures comprised between 800°C and 900°C, whereas the ductility of sample R2 drastically decreases with the temperature.

As a consequence, sample I1 can be processed at lower temperatures than sample R2. Conversely, during the manufacturing process, the occurrence of cracks or bleedings in sample I1 will be largely reduced as compared to sample R2.

The inventors have further characterized the TiB₂ precipitates of the as cast products on samples taken from ¼ the thickness from samples I1, R1 and R2, and a sample taken from half the thickness of sample I1 by image analysis using a Scanning Electron Microscope (SEM). The specimens for microscopic examination were prepared using standard metallographic technique for surface preparation and etched with nital reagent.

The size distributions are reported in Table 4 below

As shown in Table 4, sample R1 comprise a high percentage of coarse precipitates, having a surface area higher than 8 µm².

Sample R2 comprises a higher fraction of small TiB₂ precipitates than sample R1. However, the percentage of TiB₂ precipitates having a surface area lower than 8 µm² for sample R1 does not reach 96%.

By contrast, sample I1 has a very high fraction of TiB₂ precipitates with an area of at most 8 µm², especially higher than 96% In addition, the fraction of TiB₂ precipitates with an area of at most 3 µm² is higher than 80%, and all the TiB₂ precipitates have an area lower than or equal to 25 µm².

Sample reference	Percentage of TiB ₂ with an area of at most 3 μm^2	Percentage of TiB ₂ with an area of at most 8 μm^2	Percentage of TiB ₂ with an area of at most 25 μm^2
I1	83.9	96.7	100
R1	46.6	<u>70.3</u>	86.7
R2	81.2	<u>94.5</u>	98.5

Table 4

In Table 4, the underlined values are not according to the invention.

Besides, after solidification, sample I1 was heated to a temperature of 1200°C, then hot-rolled with a final rolling temperature of 920°C, to produce a hot-rolled sheet having a thickness of 2.4 mm.

The hot-rolled steel sheet I1 was further cold-rolled with a reduction ratio of 40% to obtain a cold-rolled sheet having a thickness of 1.4 mm.

After cold-rolling, the steel sheet I1 was heated with an average heating rate of 3°C/s to an annealing temperature of 800°C and held at this temperature for 60 s.

After solidification, samples R1 and R2 were cooled to room temperature, then reheated to a temperature of 1150°C and hot-rolled with a final rolling temperature of 920°C to produce a hot-rolled sheet having a thickness of 2.2 mm and 2.8 mm respectively.

The microstructures of the hot-rolled sheets produced from samples I1, R1 and R2 were investigated by collecting samples at locations situated at ¼ the thickness of the sheets and at half the thickness of the sheets, so as to observe the structure along longitudinal plane at half distance between the core and the surface of the sheets and at the core of the sheets respectively.

The microstructures were observed with a Scanning Electron Microscope (SEM) after etching with the Klemm reagent.

The microstructure of steels I1, R1 and R2 at ¼ of the thickness are shown on Figures 6, 7 and 8 respectively.

The microstructure of steel sheets I1, R1 and R2 at half the thickness are shown on Figures 9, 10 and 11 respectively.

These figures show that the structure of steel I1 is very fine, both at ¼ thickness and at the core of the product.

By contrast the structure of steel R1, which was cooled with lower solidification rates, comprises coarse grains.

The structure of steel R2, though comprising fine grains at $\frac{1}{4}$ thickness, also comprises coarse grains, especially at the core of the semi-product.

Overall, the structure of steel I1 is very homogeneous, whereas the structures of steels R1 and R2 each comprise grains with very different sizes.

The inventors have further investigated the cold formability of steels I1, R1 and R2.

The cold formability of the steels was assessed on steels sheets produced from as cast steels I1, R1 and R2 with plane strain tests.

Especially, samples were collected from the sheets made of steels I1, R1 and R2, and the forming limit curves for steels I1, R1 and R2 were determined. These forming limit curves are illustrated on Figure 12, and the measurements reported in Table 5 below.

Steel	ϵ_2	ϵ_1
I1	-0.061	0.292
	-0.052	0.275
	0.007	0.224
	0.02	0.229
	0.031	0.2
	0.034	0.247
	0.047	0.205
	0.058	0.212
	0.062	0.24
R1	0.00718	0.165
	0.00821	0.161
	0.0103	0.136
R2	0.016	0.104
	0.017	0.107
	0.021	0.111
	0.023	0.144

Table 5

As shown by Figure 12 and Table 5, steel I1 has an improved formability as compared to steels R1 and R2.

Without being bound to a theory, it is thought that the presence of coarse TiB_2 precipitates in steels R1 and R2, even in a small quantity, promotes localization of the strain during the forming operations, in the present case during the bending, which leads to a poorer formability than steel I1. It is further thought that the localization may result from the early damage of the coarse TiB_2 precipitates colliding.

By contrast, steel I1 comprise no coarse precipitates, which minimizes the collision of the TiB_2 precipitates and therefore improves the formability.

To confirm the influence of the size of the TiB_2 precipitates on the formability, the inventors subjected a hot-rolled steel sheet R1, obtained through the process disclosed above, to cold-rolling, with a cold reduction ratio of 50%. After cold-rolling, the steel sheet R1 was heated with an average heating rate of 3°C/s to an annealing temperature of 800°C and held at this temperature for 60 s.

The inventors then collected specimens from the surface and from the core of the cold-rolled steel sheet R1 (after annealing), and observed these specimens by Scanning Electron Microscopy.

The structures observed at the surface and at the core are illustrated on Figures 13 and 14 respectively.

As visible on these figures, the specimen collected from the surface of the sheet comprises few damages, unlike the specimen collected from the core, in which an important damaging is observed.

These observations confirm that the coarse TiB_2 precipitates, which are mainly located at the core of the sheet owing to the lower solidification rate in this portion, cause damage during deformation and therefore degrade the formability of the steel.

The bending ability of steels I1, R1 and R2 was assessed by performing an edge bending test (also named 90° flanging test) on samples collected from the hot-rolled steel sheets made of steels I1, R1 and R2, and from the cold-rolled steel sheet (after annealing) made of steel I1.

The samples were held between a pressure pad and a die, and a sliding die was slid to bend the portion of the sample protruding from the pad and the die. The bending test was performed in the rolling direction (RD) and in the transverse direction (TD), according to the standard EN ISO 7438:2005.

The bending ability was characterized by the ratio R/t between the radius of curvature R of the bent sheet (in mm) and the thickness t of the sample (in mm).

The results as summarized in Table 6 below.

Sample	t (mm)	R/t (RD)	R/t (TD)
I1	2.4	0.8	0.3
I1	1.4	0.4	0.3
R1	2.2	2.7	2.7
R2	2.8	2.1	1.4

Table 6

In this table, t designates the thickness of the sample, and R/t designates the measured ratio between the radius of curvature of the bent sheet and the thickness.

These results demonstrate that the steel according to the invention has an improved bending ability as compared to steels R1 and R2.

The Charpy energy of steels I1 and R2 was further determined on samples collected from the hot-rolled sheets, at temperatures ranging from -80°C to 20°C.

Especially, sub-size Charpy impact specimen (10 mm x55 mm x thickness of the sheet) with V notches 2mm deep, with an angle of 45° and 0.25 mm root radius were collected from hot-rolled steel sheets made of steels I1 and R2.

At each temperature, the surface density Kcv of impact energy was measured. At each temperature, the test was performed on two samples, and the average value of the two tests calculated.

The results are illustrated on Figure 15, and reported in Table 7 below.

T (°C)	Steel I1 (thickness=1.45 mm)		Steel R2 (thickness=1.8 mm)	
	Kcv (J/cm ²)	Fracture mode	Kcv (J/cm ²)	Fracture mode
-80	33	mixed	3	brittle
-60	33	mixed	6	brittle
-40	35	mixed	15	mixed
-20	38	ductile	25	mixed
0	39	ductile	29	mixed
20	41	ductile	33	ductile

Table 7

In this table, T designates the temperature in degrees Celsius and Kcv designates the surface density of impact energy in J/cm². In addition, the fracture mode (ductile fracture, mixed mode of ductile and brittle fracture or brittle fracture) is reported.

As shown in Table 7 and Figure 15, the Charpy energy of steel I1 of the invention is much higher than the Charpy energy of steel R2. Moreover, the transition temperature from ductile to mixed fracture mode for steel I1 is lowered as compared to steel R2. Especially, in the steel of the invention, the fracture remains 100% ductile at -20°C.

These tests therefore demonstrate that the steel of the invention as an improved formability, ductility and toughness as compared to:

- steel R1, which has a Ti* content higher than 0.95% but was not cast under the form a thin product, and thus having TiC and coarse TiB₂ precipitates,

- steel R2, which was cast in the form of a thin product but has a Ti* content lower than 0.95%, and thus having TiC and comprising may TiB₂ precipitates with a surface area higher than 8 μm².

Finally, the mechanical properties of steels sheets I1, R1 and R2 were determined. Table 8 below reports the yield strength YS, the tensile strength TS, the uniform elongation UE, the total elongation TE and the elasticity modulus in tension E, the work hardening coefficient n and the Lankford coefficient r. Table 8 also reports the volumic percentage of TiB₂ (f_{TiB2}) precipitates for each steel.

Sample	YS (MPa)	TS (MPa)	UE (%)	TE (%)	n	r	f _{TiB2} (%)	E (GPa)
I1	300	653	15.4	23.3	0.214	0.7	9	232
R1	245	530	14.2	19.7	0.192	0.8	12	240
R2	291	567	15.2	20.8	0.2	0.7	10.9	240

Table 8

These results demonstrate that the mechanical properties of steel I1 are improved as compared to the mechanical properties of steels R1 and R2. This improvement is in particular due to the high proportion of very small size precipitates in steel I1, as compared to steels R1 and R2.

The invention therefore provides a steel sheet and a manufacturing method thereof having at the same time a high elasticity modulus in tension, a low density, and improved castability and formability. The steel sheet of the invention can therefore be used to produce parts with complex shapes, without inducing damages or surface defects.

CLAIMS

1.- Steel sheet made of a steel having a composition comprising, by weight percent:

$$0.010\% \leq C \leq 0.080\%$$

$$0.06\% \leq Mn \leq 3\%$$

$$Si \leq 1.5\%$$

$$0.005\% \leq Al \leq 1.5\%$$

$$S \leq 0.030\%$$

$$P \leq 0.040\%,$$

Ti and B such that:

$$3.2\% \leq Ti \leq 7.5\%$$

$$(0.45 \times Ti) - 1.35 \leq B \leq (0.45 \times Ti) - 0.43$$

optionally one or more elements chosen amongst:

$$Ni \leq 1\%$$

$$Mo \leq 1\%$$

$$Cr \leq 3\%$$

$$Nb \leq 0.1\%$$

$$V \leq 0.1\%$$

the remainder being iron and unavoidable impurities resulting from the smelting,

said steel sheet having a structure consisting of ferrite, at most 10% of austenite, and precipitates, said precipitates comprising eutectic precipitates of TiB_2 , the volume fraction of TiB_2 precipitates with respect to the whole structure being of at least 9%, the proportion of TiB_2 precipitates having a surface area lower than $8 \mu m^2$ being of at least 96%.

2.- The steel sheet according to claim 1, wherein the proportion of TiB_2 precipitates having a surface area lower than $3 \mu m^2$ is of at least 80%.

3.- The steel sheet according to any one of claims 1 or 2, wherein the proportion of TiB_2 precipitates having a surface area lower than $25 \mu m^2$ is of 100%.

4.- The steel sheet according to any one of claims 1 to 3, wherein in the core region of the steel sheet, the proportion of TiB_2 precipitates having a surface area lower than $8 \mu m^2$ is of at least 96%, the proportion of TiB_2 precipitates having a surface area lower than $3 \mu m^2$ is preferably of at least 80% and the proportion of TiB_2 precipitates having a surface area lower than $25 \mu m^2$ is preferably of 100%.

5.- The steel sheet according to any one of claims 1 to 4, wherein said steel sheet comprises no TiC precipitates, or TiC precipitates with a volume fraction lower than 0.5%.

6.- The steel sheet according to any one of claims 1 to 5, wherein the steel sheet comprises no Fe₂B precipitates.

7.- The steel sheet according to any one of claims 1 to 6, wherein the titanium, boron and manganese contents are such that:

$$(0.45 \times \text{Ti}) - 1.35 \leq B \leq (0.45 \times \text{Ti}) - (0.261 \times \text{Mn}) - 0.414.$$

8. The steel sheet according to any one of claims 1 to 7, wherein the titanium and boron contents are such that:

$$(0.45 \times \text{Ti}) - 1.35 \leq B \leq (0.45 \times \text{Ti}) - 0.50.$$

9.- The steel sheet according to any one of claims 1 to 8, wherein the composition is such that C ≤ 0.050%.

10.- The steel sheet according to any one of claims 1 to 9, wherein the steel sheet has a Charpy energy Kcv of at least 25 J/cm² at -40°C.

11.- The steel sheet according to any one of claims 1 to 10, wherein the steel sheet has a content in free Ti of at least 0.95%.

12.- Process for manufacturing a steel sheet, the process comprising the following successive steps:

- providing a steel having a composition comprising, by weight percent:

$$0.010\% \leq C \leq 0.080\%$$

$$0.06\% \leq \text{Mn} \leq 3\%$$

$$\text{Si} \leq 1.5\%$$

$$0.005\% \leq \text{Al} \leq 1.5\%$$

$$\text{S} \leq 0.030\%$$

$$\text{P} \leq 0.040\%,$$

Ti and B such that:

$$3.2\% \leq \text{Ti} \leq 7.5\%$$

$$(0.45 \times \text{Ti}) - 1.35 \leq B \leq (0.45 \times \text{Ti}) - 0.43$$

optionally one or more elements chosen amongst:

$$\text{Ni} \leq 1\%$$

$$\text{Mo} \leq 1\%$$

$$\text{Cr} \leq 3\%$$

$$\text{Nb} \leq 0.1\%$$

$$\text{V} \leq 0.1\%$$

the remainder being iron and unavoidable impurities,

- casting the steel in the form of a semi-product, the casting temperature being lower than or equal to $L_{\text{liquidus}} + 40^{\circ}\text{C}$, L_{liquidus} designating the liquidus temperature of the steel, the semi-product being cast in the form of a thin semi-product having a thickness of at most 110 mm, the steel being solidified during the casting with a solidification rate comprised between 0.03 cm/s and 5 cm/s at every location of the semi-product.

13.- The process according to claim 12, wherein the semi-product is cast in the form of a thin slab having a thickness lower than or equal to 110 mm, preferably lower than or equal to 70 mm.

14.- The process according to claim 13, wherein the semi-product is cast by compact strip production.

15.- The process according to claim 12, wherein the semi-product is cast in the form of a thin strip having a thickness lower than or equal to 6 mm, the solidification rate being comprised between 0.2 cm/s and 5 cm/s at every location of the semi-product.

16.- The process according to claim 15, wherein the semi-product is cast by direct strip casting between counter-rotating rolls.

17.- The process according to any one of claims 12 to 16, wherein, after casting and solidification, the semi-product is hot rolled, to obtain a hot-rolled steel sheet.

18.- The process according to claim 17, wherein between casting and hot-rolling, the temperature of the semi-product remains higher than 700°C .

19.- The process according to any one of claims 17 or 18, wherein before hot-rolling, the semi-product is de-scaled at a temperature of at least 1050°C .

20.- The process according to any one of claims 17 to 19, wherein after hot-rolling, the hot-rolled steel sheet is cold-rolled, to obtain a cold-rolled steel sheet having a thickness lower than or equal to 2 mm.

21.- The process according to any one of claims 12 to 20, wherein the titanium, boron and manganese contents are such that:

$$(0.45 \times \text{Ti}) - 1.35 \leq B \leq (0.45 \times \text{Ti}) - (0.261 \times \text{Mn}) - 0.414.$$

22. A method for manufacturing a structural part, the method comprising:

- cutting at least one blank from a steel sheet according to any one of claims 1 to 11 or produced by a process according to any one of claims 12 to 21, and
- deforming said blank within a temperature range from 20°C to 900°C.

23.- The method according to claim 22, comprising, before deforming the blank, a step of welding the blank to another blank.

24.- A structural part comprising at least of portion made of a steel having a composition comprising, by weight percent:

$$0.010\% \leq C \leq 0.080\%$$

$$0.06\% \leq \text{Mn} \leq 3\%$$

$$\text{Si} \leq 1.5\%$$

$$0.005\% \leq \text{Al} \leq 1.5\%$$

$$\text{S} \leq 0.030\%$$

$$\text{P} \leq 0.040\%,$$

$$\text{Ti and B such that:}$$

$$3.2\% \leq \text{Ti} \leq 7.5\%$$

$$(0.45 \times \text{Ti}) - 1.35 \leq B \leq (0.45 \times \text{Ti}) - 0.43$$

optionally one or more elements chosen amongst:

$$\text{Ni} \leq 1\%$$

$$\text{Mo} \leq 1\%$$

$$\text{Cr} \leq 3\%$$

$$\text{Nb} \leq 0.1\%$$

$$\text{V} \leq 0.1\%$$

the remainder being iron and unavoidable impurities resulting from the smelting, said portion having a structure consisting of ferrite, at most 10% of austenite, and precipitates, said precipitates comprising eutectic precipitates of TiB_2 , the volume fraction

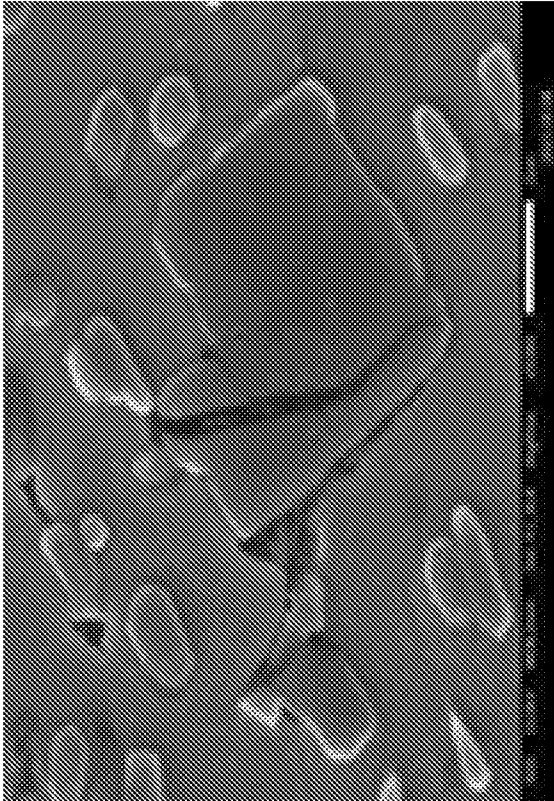
of TiB_2 precipitates with respect to the whole structure of said portion being of at least 9%, the proportion of TiB_2 precipitates having a surface area lower than $8 \mu\text{m}^2$ being of at least 96%.

- 5 25.- A structural part according to claim 24, wherein the structural part is obtained by the method according to any one of claims 22 or 23.



2 μm

FIG.2



2 μm

FIG.1

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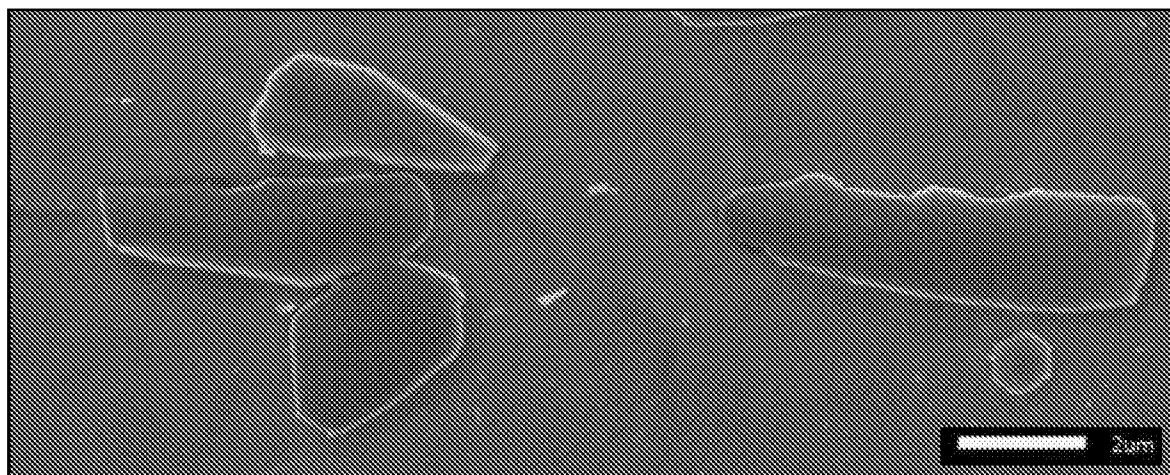


FIG.3

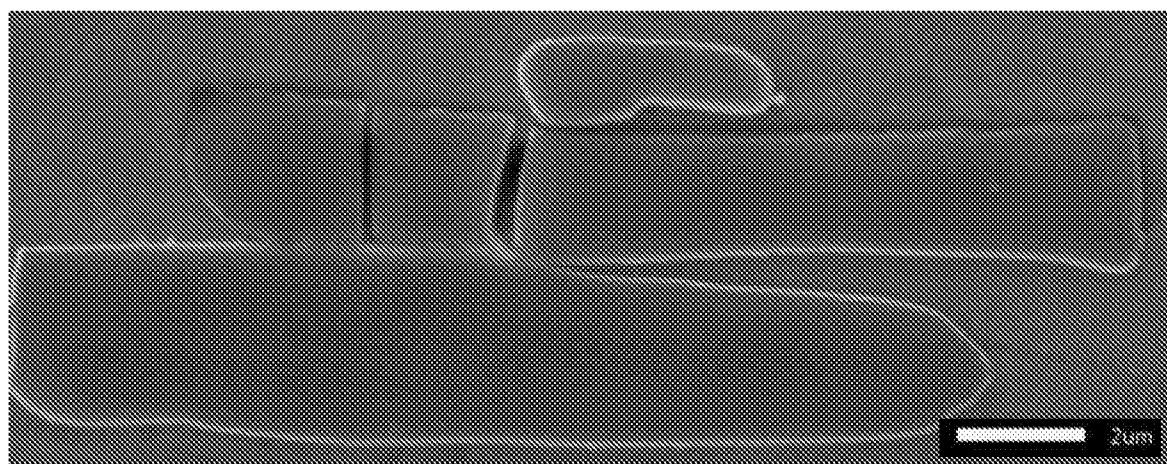


FIG.4

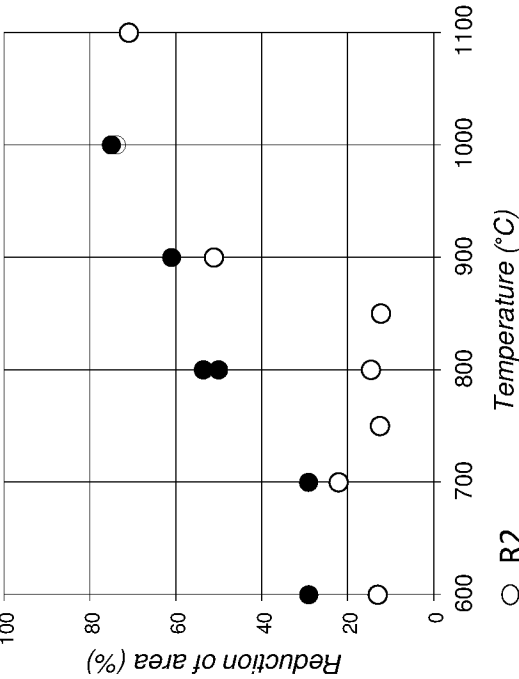


FIG.5

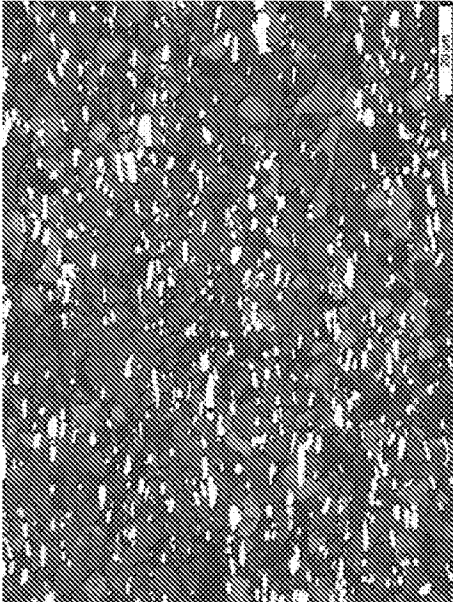


FIG.6



FIG.7

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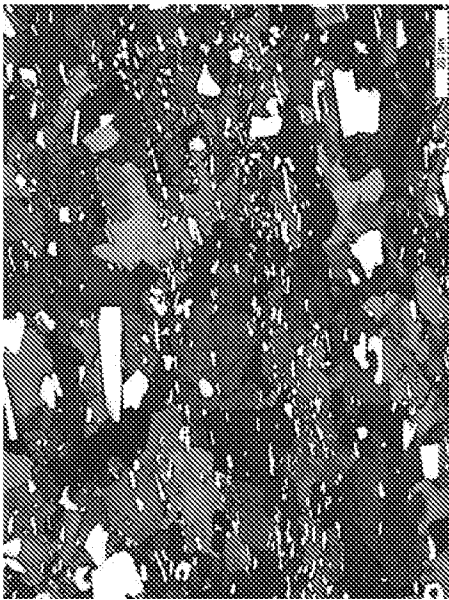


FIG.8

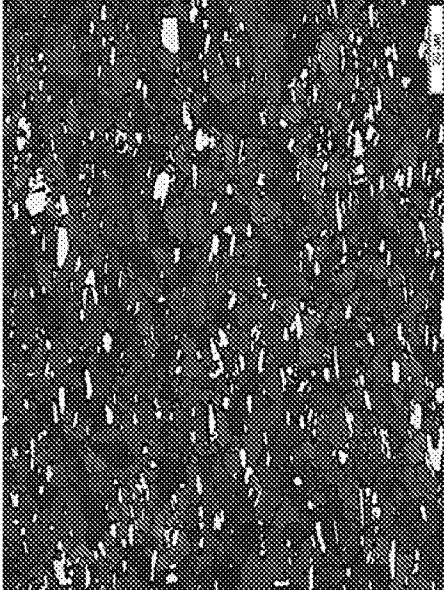


FIG.9

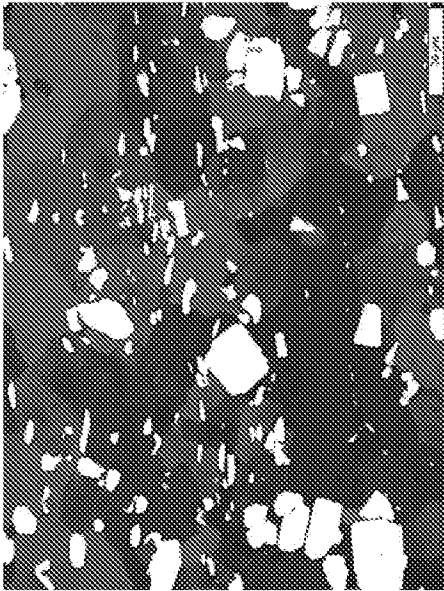


FIG.10

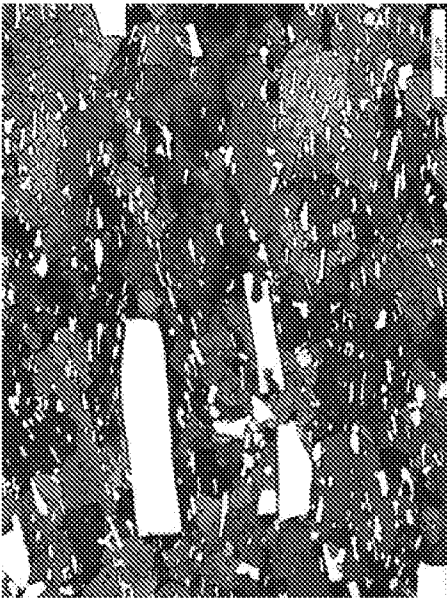


FIG.11

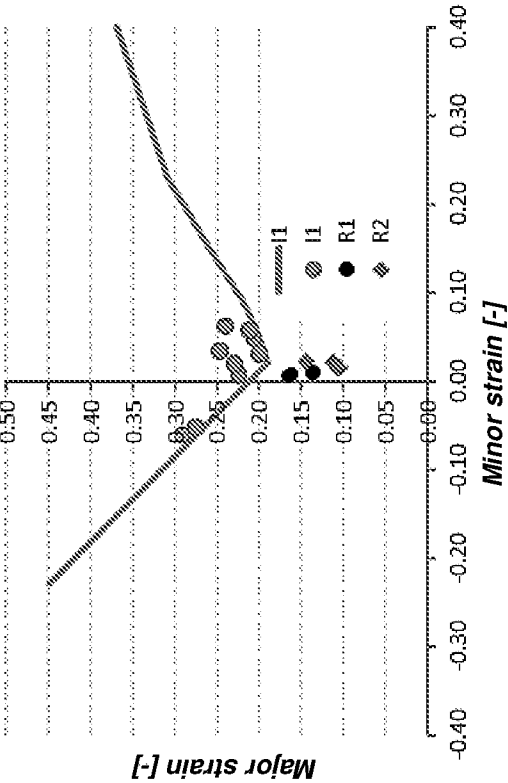


FIG.12

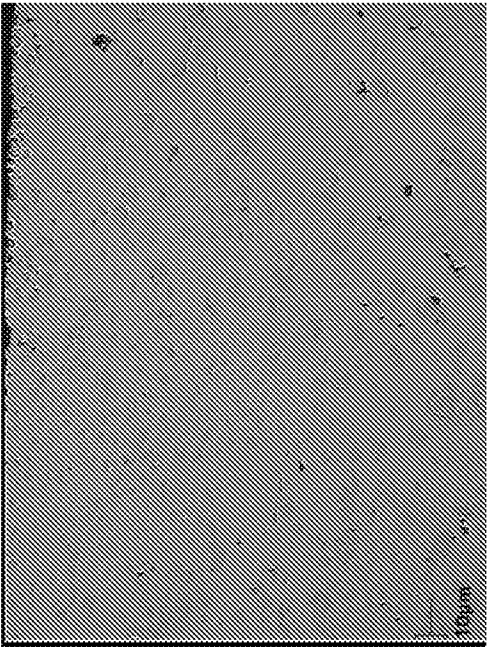


FIG.13



FIG.14

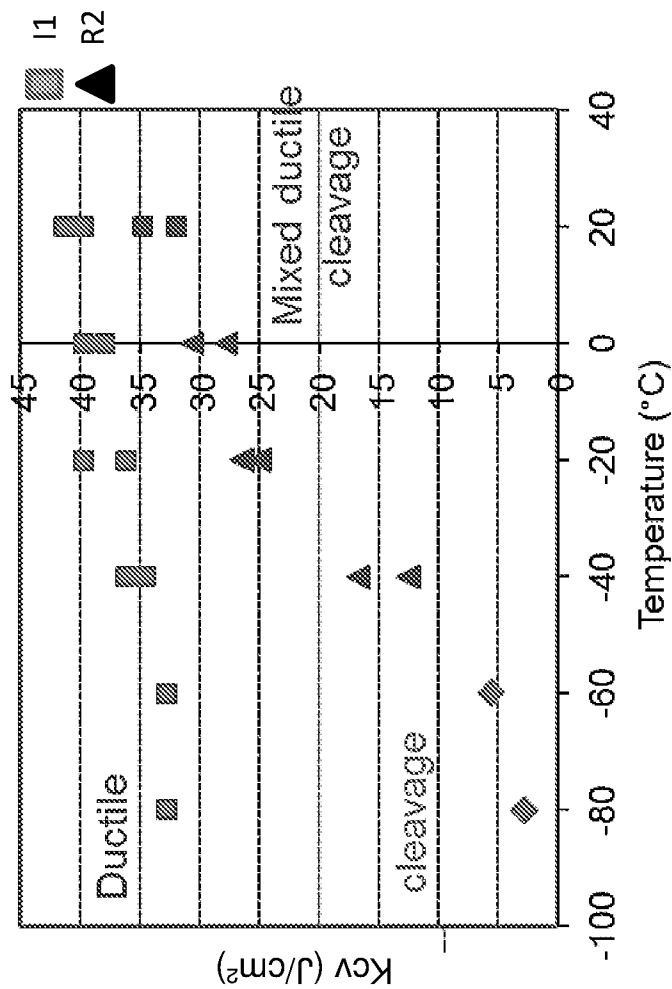


FIG.15

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/052312

A. CLASSIFICATION OF SUBJECT MATTER

INV. C22C38/00 C22C38/02 C22C38/04 C22C38/06 C22C38/14
C22C38/28 C22C38/32 B22D11/00 B22D11/06 B22D11/12

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C C21D B22D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 897 963 A1 (ARCELOR FRANCE [FR]) 12 March 2008 (2008-03-12) cited in the application abstract paragraph [0001] paragraphs [0007] - [0008] paragraph [0010] - paragraph [0031] paragraph [0044] - paragraph [0046] paragraph [0069] - paragraph [0092]; examples 1-3; tables 1-6 claims 1-27 the whole document	1-25
A	JP 2002 105588 A (KOBE STEEL LTD) 10 April 2002 (2002-04-10) abstract page 4; table 2	1-25
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

1 December 2017

Date of mailing of the international search report

08/12/2017

Name and mailing address of the ISA/

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Authorized officer

Ugarte, Eva

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/052312

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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			WO 2017173950 A1 12-10-2017
