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(54) Title: METHOD FOR PRODUCING A STEEL PRODUCT FROM STEEL BILLET, A STEEL PRODUCT AND A MICRO-
STRUCTURE OF A STEEL

(57) Abstract: The invention relates to a method for producing a steel product, such as a steel plate, having a thickness of 2-60 mm, from a steel billet, which is produced from steel comprising iron and residue contents as well as unavoidable impurities. The steel comprises, as percentages by weight, C: 0,3-0,6%, Al: 1,0-2,5%, and V: 0-0,4%. The method comprises a step, in which to the steel billet is performed annealing for austenitizing at a temperature of 1000-1300°C, more preferably 1050-1220°C. The invention also relates to a steel product, such as a steel plate, having a thickness of 2- 60 mm.



Method for producing a steel product from steel billet, a steel product and a microstructure of a steel

Background of the invention

5 The invention relates to a method according to the preamble of claim 1 for producing a steel product, such as a steel plate, having a thickness of 2–60 mm from a steel billet, which is produced from steel comprising iron and residue contents as well as unavoidable impurities.

10 The invention also relates to a steel product according to the preamble of claim 18, such as a steel plate, which is hot-rolled to a thickness of 2–60 mm, wherein the steel product is produced from steel comprising iron and residue contents as well as unavoidable impurities.

15 The invention also relates to a substantially martensitic microstructure of a steel product according to the preamble of claim 37, such as preferably a wear resistant steel plate, having a hardness of greater than 300 HB, especially a hardness of greater than 500 HB.

The invention relates to such steel products, such as plate-like steel products or steel plates having a hardness of greater than 300 HB, especially greater than 500 HB and having a thickness of 2–60 mm, preferably 5–60 mm and most preferably 5–20 mm.

20 Already known are several steel products having a hardness of greater than 300 HB, particularly greater than 500 HB. These extremely hard steel products have, however, certain disadvantages. One is that they are typically produced from steel, which contains significant amounts of exceptionally expensive alloying elements, such as nickel, Ni, and molybdenum, Mo. Nickel is alloyed so that the martensite remains tough and thus no hardening fractures are created. Further, as is known, molybdenum Mo is alloyed because, using it, hardenability can be increased and impact toughness can be improved and, as needed, upper temper brittleness can be prevented.

30 The problem of known art is thus that, in particular, steel products hardened to a hardness of greater than 500 HB require very expensive alloying. Alternatively, without expensive alloying according to known art, steel products fracture during hardening, as is illustrated in the examples of this description.

35 Also known are microstructures of steel, in which a substantially martensitic microstructure comprises ferrite, but also significant amounts of bainite. The excess formation of bainite is problematic because it impairs the mechanical properties of the steel product in question.

Brief description of the invention

The object of the invention is to provide a steel product having a low alloying element level and a hardness of, however, greater than 300 HB, preferably as the primary target greater than 500 HB, without creation of visually observable fractures particularly in hardening quenching.

The object of the invention is achieved by a method according to independent claim 1 for producing a steel product, such as a steel plate, having a thickness of 2–60 mm from steel comprising iron and residue contents as well as unavoidable impurities.

The invention also relates to a steel product according to independent claim 18, such as a steel plate, having a thickness of 2–60 mm, wherein the steel product is produced from steel comprising iron and residue contents as well as unavoidable impurities.

The invention also relates to a microstructure of a steel product according to independent claim 37.

The preferred embodiments of the invention are presented in the dependent claims.

The steel product has two possible mechanisms, which together or separately prevent problematic hardening fractures of the steel without the alloying of Ni which would make the martensite tougher:

1.) There is ferrite in the microstructure of the steel product. This is due to that the steel, from which the steel product is produced, contains aluminium 1,0–2,5%. Aluminium leads, for example, to that ferrite can form to the microstructure of the steel already at hot-rolling temperatures.

2.) There are vanadium carbides in the steel product, which gather hydrogen around them and provide an even distribution of hydrogen in the steel, in which case hydrogen gas does not necessarily cause a delayed fracture. Vanadium carbides can be created in the steel product because the steel, from which the steel product is produced, preferably contains vanadium. Additionally, the somewhat high carbon content of steel according to the invention contributes to formation of vanadium carbides. Vanadium also assures that the microstructure of the steel product develops substantially martensitic.

The vanadium used in the steel of the steel product increases the hardenability of the austenite and prevents formation of bainite in the microstructure of the steel product.

It was observed that ferrite formed as equal-axial to the microstructure of the steel product specifically at the boundaries of the austenite, in which case a structure

is achieved that prevents hardening fractures exceptionally well. The ferrite zone at the grain boundaries of the austenite grains can be seen as functioning as a type of a soft, formable buffer during the martensitic transformation and possibly also after the martensitic transformation, releasing the stresses caused by the changes in volume of the martensite. Ferrite releases stresses in thermal treatment steps such as in welding or flame cutting, due to which the tendency of the steel product to fracture decreases. However, it is recommended that pre-heating be performed before thermal treatments.

In one solution according to the invention, the steel billet, from which the steel product is produced, is hot-rolled to provide a hot-rolled steel billet and the hot-rolled steel billet is cooled in an accelerated manner to a low temperature, i.e. is direct-quenched immediately after hot-rolling. Alternatively, the hot-rolled steel billet, from which the steel product is produced, can be later post-hardened in a hardening furnace. Direct-hardening is, in this case, a more advantageous manner than post-hardening in a hardening furnace because the worked structure has, in comparison to the unworked structure, a wider ferrite area in the continuous cooling transformation curve diagram (in the CCT-curve diagram). Hot-rolling raises the temperature of ferrite formation and moves the ferrite area in the continuous cooling transformation curve diagram to the left.

The most significant advantage of the invention is the hardness to be attained in the steel product without significant problems relating to hardening fractures. This can be achieved by an exceptionally innovative alloying, which leads to the low alloying element costs of the steel. Further, a steel product according to the invention is, under certain conditions, weldable and suitable for thermal cutting, such as flame cutting.

One advantage of a steel product according to the invention is that it can be produced for very different intended uses at low alloying element costs. Thus, the invention provides mass tailoring into different products using the same chemical composition of the billet and even at the same heat treatment condition of the hot-rolled steel product. The steel product can be used in very many different applications depending on the manner of production. Most preferably, the steel product is used in the hardened condition as so-called wear resistant steel, from which is required great hardness and resistance to wear. Wear resistant steels are used, for example, in platform bodies and excavator buckets.

Alternatively, the steel can, after hardening, be tempered in a known manner, for example, at a temperature of 650°C, i.e. a tempered martensitic quenched and tempering steel with a completely new and preferred steel composition can be provided. In other words, mechanical engineering steel can be produced. This kind of steel is exceptionally suitable for use, for example, in the shaft of a machine, wherein

an elongated steel rod is a recommended form of the steel product. Further, the steel is exceptionally suitable as tempering steel, which as further machined machine parts, such as gear wheels, is surface hardened.

5 The diversity of the applications for use of the steel product when produced from the same steel with low alloying element costs is thus a significant technical advantage of the invention.

List of figures

In the following, some preferred embodiments of the invention are presented in more detail with reference to the accompanying figures, in which

10 Fig. 1 shows the steps of a first preferred embodiment of the method according to the invention,

Fig. 2 shows the steps of a second preferred embodiment of the method according to the invention,

15 Fig. 3 shows the steps of a third preferred embodiment of the method according to the invention,

Fig. 4 shows the steps of a fourth preferred embodiment of the method according to the invention,

Fig. 5 shows the effect of the hardening temperature relating to post-hardening in a hardening furnace on the hardness of the steel product with one steel composition,

20 Fig. 6 shows the continuous cooling transformation curves for an unmodified structure with one reference steel composition, which has a low Al-level (0,084% as percentage by weight),

Fig. 7 shows the continuous cooling transformation curves for a modified structure with the reference steel composition, which is the same as in Fig. 6,

25 Fig. 8 shows the continuous cooling transformation curves for an unmodified structure with a steel composition, which is according to the invention,

Fig. 9 shows the continuous cooling transformation curves for a modified structure with the steel composition, which is the same as in Fig. 8,

30 Fig. 10 shows a microstructure of a first steel product according to the invention,

Fig. 11 shows a microstructure of a second steel product according to the invention,

Fig. 12 shows a fractured steel plate.

Detailed description of the invention

35 The invention relates, first of all, to a method for producing a steel product, such as a steel plate, having a thickness of 2–60 mm, preferably 2–20 mm from a steel

billet, which is produced from steel comprising iron and residue contents as well as unavoidable impurities, such as phosphorus, P, and sulphur, S. The steel further comprises, as percentages by weight:

- Carbon, C, 0,3–0,6%,
- 5 Aluminium, Al, 1,0–2,5%, and
- Vanadium, V, 0–0,4%.

Steel according to one preferred embodiment further comprises, as percentages by weight:

- Silicon, Si, 0,15–1,0%,
- 10 Manganese, Mn, 0,4–1,5%,
- Titanium, Ti, 0–0,05%,
- Chromium, Cr, 0–1,0%, and
- Boron, B, 0–0,005%.

- Before beginning accelerated cooling, to the steel billet is performed annealing
- 15 for austenitizing above the A_3 temperature at a temperature of 1000–1300°C, more preferably at a temperature of 1050–1220°C.

The method comprises a step, in which the steel billet is hot-rolled to provide a hot-rolled steel billet.

- The somewhat high carbon content of the steel increases hardenability and promotes achieving hardness due to i.a. iron carbides. Due to this, the carbon content of the steel is at least 0,30%. However, greater than 0,6% limits the use of the steel due to weakening weldability. In the method, in the steel billet is used preferably steel comprising, as a percentage by weight, carbon, C, 0,35–0,50%, more preferably 0,4–0,5%.

- 25 The aluminium content of the steel is at least 1,0%, with which is assured the effect of aluminium to form ferrite. However, contents greater than 2,5% lead to too great a portion of ferrite and a decrease in hardness to below the target hardness. In the method, in the steel billet is used preferably steel comprising, as a percentage by weight, aluminium, Al, 1,2–2,0%, most preferably 1,5–1,9 %.

- 30 Vanadium, V, is an essential alloying element and it is alloyed at the most 0,4%. In the method, in the steel billet is used preferably steel comprising, as a percentage by weight, vanadium, V, 0,05–0,4%, more preferably 0,1–0,3%. Vanadium can precipitate with carbon and/or nitrogen into carbides, nitrides and/or carbonitrides. According to a preferred embodiment, these precipitations are
- 35 incoherencies, which are outlined from the matrix. In this case, it is possible that the interface of the precipitation and the matrix functions exceptionally well as a hydrogen trap further preventing fractures.

In a steel product according to the invention, which has a somewhat high carbon content, there is preferably, but not necessarily, manganese below 1,5% because, in this case, problems relating to strong segregation of manganese can be decreased. However, there is preferably, but not necessarily, at least 0,4% of manganese in order that hardenability remains at the required level. In the invention, it is observed, as is observed from Example 2, that a high Mn content weakens the hardenability of the steel at high carbon contents and the target hardness is achieved only at high hardening temperatures. Additionally, using i.a. a low alloying of Mn, the shape of the grain boundary ferrite can be affected such that the impact toughness of the steel product improves. In the method, in the steel billet is indeed thus used more preferably a steel comprising, as a percentage by weight, Manganese, Mn, 0,4–1,2%, most preferably 0,4–0,8%, wherein an excellent combination in relation to hardenability and segregation sensitivity is achieved, which leads to a fairly homogenous microstructure. Further, in this case, hardness can be achieved over a wide hardening temperature range.

In the method, in the steel billet is used preferably, but not necessarily, steel comprising, as a percentage by weight, silicon, Si, 0,15–1,0%, more preferably 0,25–0,8%, most preferably 0,3–0,7%.

Chromium, Cr, is alloyed preferably, but not necessarily, less than 1%. Chromium increases the hardenability of the steel and thus decreases the need for high alloying of Mn. In the method, in the steel billet is thus used preferably steel comprising, as a percentage by weight, chromium, Cr, 0–1,0%, more preferably 0,1–0,8%, most preferably 0,15–0,5%.

Titanium, Ti, prevents the growth of grains in thermal treatments, such as weldings and flame cutting when appearing as TiN titanium nitrides. Ti is alloyed particularly, when Boron B is along in the steel in order that boron nitrides BN, detrimental to the function of boron B, are not created. In the method, in the steel billet is thus used preferably steel comprising, as a percentage by weight, titanium, Ti, $\leq 0,02\%$, most preferably titanium Ti is alloyed, however, at least 0,005%, with which better weldability properties are provided.

In a method according to the invention, it is not necessary to alloy boron, B because boron can hinder the formation of the desired soft buffer at the grain boundaries of the austenite. Due to this, boron is preferably limited B: 0–0,005%.

Particularly, when producing a steel product having a thickness of greater than 20 mm, in the method, in the steel billet can, however, be used preferably steel comprising, as a percentage by weight, boron, B, 0,0005–0,005%, more preferably 0,0008–0,003%, particularly when the thickness of a plate-like product exceeds 20

mm and the diameter of an elongated product exceeds 40 mm. In this case, using boron, the hardenability of the steel product is assured also with large thicknesses.

Of the alloying elements, C, Si, Mn, Cr, V and B can increase the depth of hardenability and prevent the transformation of austenite into bainite and perlite. Of these alloying elements, the use of boron B is avoided, if possible because it can hinder the nucleation of the ferrite at the grain boundaries of the austenite.

According to the basic idea of the invention, there is no need to substantially alloy nickel Ni or molybdenum Mo into a steel according to the invention, i.e. their contents, as percentages by weight, are, in principle, limited at least as follows $Mo < 0.5\%$ and $Ni < 1\%$. Molybdenum can be used particularly, if tempering treatment is performed to the steel product in the area of upper temper brittleness. Raising nickel content can be useless, needlessly increasing alloying element costs.

However, the contents of nickel Ni and molybdenum Mo are preferably limited to extremely small contents $Mo < 0.1\%$ and $Ni < 0.5\%$. In a method according to the invention, Mo is thus not actively alloyed into the steel, but it is, for example, possible that the steel has a low, $Mo < 0.1\%$, Mo residue content. At the most preferably, the contents of molybdenum Mo and nickel Ni are, at the most, residue contents.

One preferred embodiment of the method according the invention comprises a step, in which the steel billet is hot-rolled after annealing for austenitizing to provide a hot-rolled steel billet and preferably such that the temperature of the hot-rolled steel billet is at the last pass $800\text{--}1050^\circ\text{C}$, more preferably $820\text{--}960^\circ\text{C}$, most preferably $900\text{--}960^\circ\text{C}$, wherein a great hardness is achieved without the grain size of the austenite remaining large and that the rolling forces remain reasonably low. Additionally, the hardening temperature can advantageously affect impact toughness.

In one preferred embodiment of the method according to the invention, the hot-rolled steel billet is post-hardened in a hardening furnace after hot-rolling such that the hardening temperature of the hot-rolled steel billet in the annealing for hardening belonging to post-hardening in a hardening furnace is $800\text{--}1050^\circ\text{C}$, more preferably $850\text{--}1000^\circ\text{C}$, wherein a great hardness is achieved without the grain size of the austenite growing large.

From Fig. 5, it is observed that the hardening temperature relating to post-hardening in a hardening furnace has an essential effect on the hardness of a steel product post-hardened in a hardening furnace. From Fig. 5, it is also observed that a great hardness is achieved preferably by using hardening temperatures of $850\text{--}1000^\circ\text{C}$. By a hardening temperature is meant the temperature, at which the steel is annealed before the accelerated cooling belonging to hardening. Using a low

hardening temperature, primary target hardness may be difficult to achieve because, in this case, too much soft structure may be formed.

One preferred embodiment of the method according to the invention comprises a step, in which a steel billet, such as a hot-rolled steel billet or an annealed
5 for hardening hot-rolled steel billet, is cooled in an accelerated manner such that the temperature of the steel billet at the time cooling begins is 750–1050°C, more preferably 750–960°C, and such that the average speed of cooling in the temperature range of 700–400°C is greater than 5°C/s, more preferably greater than 12°C/s, most preferably 20–40°C/s, and such that the temperature of the steel billet at the time
10 cooling ends is below 400°C (i.e. approximately $M_s+100^\circ\text{C}$), preferably below 100°C. Accelerated cooling can also be performed to a room temperature of approximately 20°C.

Referring to Fig. 8, the optimal cooling speed for steel 1338 (see Table 1), which, in the case of Fig. 8, is unmodified before cooling, is 20–40°C/s in the
15 temperature range of 700–400°C. In this case, the bainite area (marked with the letter B in Fig. 8) is substantially avoided and the desired microstructure is provided in the steel.

Referring to Fig. 9, the optimal cooling speed for steel 1338 (see Table 1), which, in the case of Fig. 9, was further hot-rolled before immediate accelerated
20 cooling, is 20–40°C/s in the temperature range of 700–400°C. In this case, in a steel according to the invention, is avoided at least partially the shifted bainite area (marked with the letter B in Fig. 9) at the same time as in the microstructure forms as much ferrite as possible.

The continuous cooling transformation curves of Figs. 6–9 are defined using a
25 Gleeble-1500 thermal-mechanical simulator.

Fig. 10 shows an enlargement of the microstructure of steel 1338 (see Table 1) in a situation, in which accelerated cooling after hot-rolling is used and in which the average speed of cooling has been 12°C/s. As can be seen in the figure, at the edges of the prior austenite grains has formed soft ferrite standing out as dark. The soft ferrite
30 is so-called grain boundary ferrite, which is provided as equal-axial. This has a advantageous affect on the impact toughness of the steel product. Inside the grains, there is hard martensite and possibly, at the most, a very small amounts of bainite.

Fig. 11 shows an enlargement of the microstructure of steel 1338 (see Table 1) in a situation, in which accelerated cooling after hot-rolling is used and in which the
35 average speed of cooling has been 24°C/s. As can be seen in the figure, at the edges of the prior austenite grains has formed soft ferrite standing out as dark. In comparison to the situation shown in Fig. 10, the amounts of ferrite and bainite in the microstructure have decreased, which means a greater hardness.

One preferred embodiment of the method according to the invention comprises a step, in which to the hot-rolled steel billet is performed air-cooling after hot-rolling, and a step, in which the air-cooled hot-rolled steel billet is hardened by the method of post-hardening in a hardening furnace known as such.

5 One preferred embodiment of the method according to the invention comprises steps, in which to the steel billet is performed air-cooling and in which the steel billet is coiled onto a coil. In this case, the steel product can be delivered as a coil and later hardened to provide a hard final result. Before hardening, the steel product can preferably be machined while it is soft.

10 One preferred embodiment of the method according to the invention comprises a step, in which to the steel billet is performed tempering after accelerated cooling. In tempering, the temperature is at the highest 700°C, preferably 600–680°C, wherein the toughness and machineability of the steel can be further increased.

One preferred embodiment of the method according to the invention
15 comprises a step, in which to the steel billet is performed surface hardening after tempering.

In the method, most preferably, but not necessarily, a steel product, such as a steel plate, is produced having a thickness of 5–60 mm, most preferably 5–20 mm.

Figs. 1–4 show four different ways to produce a steel product.

20 Fig. 1 shows a first embodiment of the method. In this embodiment, the steel billet is annealed for austenitizing above the A_3 temperature at a temperature of 1000–1300°C, more preferably at a temperature of 1050–1220°C, after which the austenitized steel billet is hot-rolled to provide a hot-rolled steel billet such that the temperature of the steel billet at the last pass is 800–1050°C, more preferably 820–
25 960°C, most preferably 900–960°C. After this, the hot-rolled steel billet is cooled in an accelerated manner from hot-rolling, i.e. immediately after hot-rolling. The temperature of the hot-rolled steel billet at the time accelerated cooling begins is 750–1050°C, more preferably 750–960°C, most preferably 750–960°C, in order that the hot-rolled steel billet can be cooled quickly in the range of 700–400°C. In the
30 embodiment according to Fig. 1, accelerated cooling is performed preferably such that the average quenching speed in the range of 700–400°C is greater than 5°C/s, preferably greater than 12°C/s, and more preferably 20–40°C/s. The temperature of the steel billet at the time accelerated cooling ends is below 400°C, such as below 100°C. Cooling can be performed to a room temperature of approximately 20°C. Fast cooling
35 i.e. quenching prevents, in particular, the undesirable excess creation of bainite in the microstructure of the steel product. Fast cooling can also lead to a harder steel product. In this matter, we refer to Fig. 9, which shows the continuous cooling transformation curves of steel 1338 (see Table 1 and Example 4 in the passage

Examples), in which the bainite area is marked with the letter B. As can be observed from Fig. 9, hot-rolling also widens the ferrite area (marked with the letter F) in comparison to the situation of Fig. 8, in which the steel billet is not modified by hot-rolling immediately before accelerated cooling to a low temperature.

5 Preferably, hot-rolling is performed as plate- or strip rolling.

Fig. 2 shows a second embodiment of the method. In this embodiment, the steel billet is annealed for austenitizing above the A_3 temperature at a temperature of 1000–1300°C, more preferably at a temperature of 1050–1220°C, after which the austenitized steel billet is hot-rolled to provide a hot-rolled steel billet such that the
10 temperature of the hot-rolled steel billet at the last pass is 800–1050°C, more preferably 820–960°C, most preferably 900–960°C. After this, the hot-rolled steel billet is cooled in an accelerated manner from hot-rolling immediately after hot-rolling. The temperature of the hot-rolled steel billet at the time accelerated cooling begins is 750–1050°C, more preferably 750–960°C, most preferably 750–960°C. The
15 hot-rolled steel billet is cooled quickly in the range of 700–400°C. In the embodiment according to Fig. 2, accelerated cooling is performed preferably such that the average speed of quenching in the range of 700–400°C is greater than 5°C/s, preferably greater than 12°C/s, and most preferably 20–40°C/s. The temperature of the steel billet at the time accelerated cooling ends is below 400°C, preferably below 100°C. Most
20 preferably, cooling is performed to a room temperature of approximately 20°C. Fast cooling i.e. quenching prevents, in particular, undesirable excess formation of bainite in the microstructure of the steel product. After accelerated cooling, in this embodiment is also performed tempering. In tempering, the temperature of the steel product is at the highest 700°C, most preferably 600–680 °C

25 According to one embodiment of the invention, after the last pass of hot-rolling, the steel billet is cooled for a moment freely in the air before accelerated cooling (such as water cooling). This step might be possible because water cooling apparatus is seldom located immediately after the roller stand. Further, it can be preferred for increasing the amount of ferrite and/or for forming VC precipitations in
30 the desired amount, wherein it is also assured that in the steel product are not created fractures in connection with quenching.

Fig. 3 shows a third embodiment of the method. In this embodiment, the steel billet is annealed for austenitizing above the A_3 temperature at a temperature of 1000–1300°C, more preferably at a temperature of 1050–1220°C, after which the
35 austenitized steel billet is hot-rolled and cooled to provide a hot-rolled steel billet. In other words, in this embodiment, it is not direct-quenched. After this, the hot-rolled steel billet is annealed for the purpose of hardening such that the hardening temperature of the hot-rolled steel billet in annealing for hardening is 800–1050°C,

more preferably 850–1000°C. After annealing for hardening, the hot-rolled steel billet is cooled in an accelerated manner. The steel billet is cooled quickly in the range 700–400°C. In the embodiment according to Fig. 3, accelerated cooling is performed preferably such that the average speed of hardening in the range 700–400°C is greater than 5°C/s, preferably greater than 12°C/s, and most preferably 20–40°C/s. The temperature of the steel billet at the time accelerated cooling ends is below 400°C, preferably below 100°C. Most preferably, cooling is performed to a room temperature of approximately 20°C. Fast cooling i.e. hardening prevents, in particular, undesirable excess creation of bainite in the microstructure of the steel product.

Fig. 4 shows a fourth embodiment of the method. In this embodiment, the steel billet is annealed for austenitizing above the A_3 temperature at a temperature of 1000–1300°C, more preferably at a temperature of 1050–1220°C, after which the austenitized steel billet is hot-rolled to provide a hot-rolled steel billet. Cooling after hot-rolling can be implemented, for example, partially or completely freely in the air. After this, the hot-rolled steel billet is annealed for hardening such that the hardening temperature of the hot-rolled steel billet in annealing for hardening is 800–1050°C, more preferably 850–1000°C. After annealing for hardening, the hot-rolled steel billet is cooled in an accelerated manner. The steel billet is cooled quickly in the range of 700–400°C. In the embodiment according to Fig. 4, accelerated cooling is performed preferably such that the average speed of quenching in the range of 700–400°C is greater than 5°C/s, preferably greater than 12°C/s, and most preferably 20–40°C/s. The temperature of the steel billet at the time accelerated cooling ends is below 400°C, preferably below 100°C. Most preferably, cooling is performed to a room temperature of approximately 20°C. Fast cooling i.e. quenching prevents, in particular, undesirable excess creation of bainite in the microstructure of the steel product. After accelerated cooling, in this embodiment is also performed tempering. In tempering, the temperature is at the highest 700°C, more preferably 600–680 °C.

The invention also relates to a steel product, such as a steel plate, which is hot-rolled to a thickness of 2–60 mm. The steel product can be such that it is hot-rolled to a thickness of 2–60 mm, which, at the same time, is the final thickness of the steel product. In other words, steel according to the invention is not substantially cold-rolled, except for possible skin pass rolling.

The thickness of the steel product is preferably in the range of 2–20 mm. Most preferably, the thickness of the steel product is in the range of 5–20 mm. Most preferably, the steel product is a so-called heavy steel plate product, i.e. it is not a steel strip product that is coiled onto a coil.

The steel product is produced from steel comprising iron and residue contents as well as unavoidable impurities, such as phosphorus, P, and sulphur, S, and comprising, as percentages by weight:

- Carbon, C, 0,3–0,6%,
5 Aluminium, Al, 1,0–2,5%, and
Vanadium, V, 0–0,4%.

The steel of the steel product comprises more preferably, but not necessarily, as a percentage by weight, carbon, C, 0,35–0,50%, most preferably C 0,40–0,50%.

- 10 The steel of the steel product comprises more preferably, but not necessarily, as a percentage by weight, aluminium, Al, 1,2–2,0%, most preferably 1,5–1,9%.

The steel of the steel product comprises more preferably, but not necessarily, as a percentage by weight, vanadium, V, 0,05–0,4%, more preferably 0,1–0,3%.

- 15 The steel of the steel product further comprises, preferably, but not necessarily, as a percentage by weight, silicon, Si, 0,15–1,0%, more preferably 0,25–0,8%, most preferably 0,3–0,7%,

The steel of the steel product further comprises, preferably, but not necessarily, as a percentage by weight, manganese, Mn, 0,4–1,5%, more preferably 0,4–1,2%, most preferably 0,4–0,8%.

- 20 The steel of the steel product further comprises, preferably, but not necessarily, as a percentage by weight, titanium, Ti, 0–0,05%, more preferably 0,005–0,02%.

The steel of the steel product further comprises, preferably, but not necessarily, as a percentage by weight, chromium, Cr, 0–1,0%, more preferably 0,1–0,8%, most preferably 0,15–0,5%, and

- 25 The steel of the steel product further comprises, preferably, but not necessarily, as a percentage by weight, boron, B, 0–0,005%, more preferably 0,0005–0,005%, most preferably 0,0008–0,003%.

- 30 The reasons for the chemical composition of the steel product are described above in connection with the description of the method. Additionally, they are further described in connection with the examples.

The percentage portions applying to the phases of the microstructure are given as percentages by volume.

- 35 According to one embodiment, the microstructure of the steel is substantially 2-phase, comprising ferrite and at least 90% martensite. The microstructure of the steel product comprises preferably 2–10% ferrite, most preferably 2–5% as well as possibly small amounts of residual austenite, however, less than 10%, most preferably less than 2% residual austenite.

Ferrite is formed at the grain boundaries of the prior austenite as so-called grain boundary ferrite. Most preferably, grain boundary ferrite is equal-axial, wherein the impact toughness of the steel product remains good. In other words, the invention has succeeded in avoiding lath like ferrite, which has a detrimental effect on i.a. impact toughness.

Bainite is an undesirable phase and the invention has succeeded in keeping its amount relatively quite small. However, the microstructure can comprise very small amounts of bainite, such as at the most 5%.

In one preferred embodiment of the steel product, a part of the microstructure of the steel product comprises at least 90% martensite. Thus, the predominant phase of the steel is preferably a carbon-rich and hard phase. Additionally, a part of the microstructure of the steel product comprises preferably 2–10% ferrite, most preferably 2–5% as well as possibly small amounts of residual austenite, however, less than 10%, most preferably less than 2% residual austenite.

Preferably, the microstructure of the steel product consists of the following structures, as percentages by volume,

90% martensite

2–10% ferrite formed at the grain boundaries of the prior austenite as well as

possibly the rest of residual austenite as well as possibly a very small amount of bainite.

By hardening, preferably also by hardening and tempering, the hardness of the steel product is preferably, but not necessarily, greater than 300 HB, preferably greater than 500 HB, most preferably of all 550–750 HB, when hardness is measured less than 5 mm, preferably 1,0–2 mm, from the surface of the steel product.

By hardening, the tensile strength of the steel product is preferably at least 1600 MPa, i.e. $R_m \geq 1600$ MPa. Most preferably, the tensile strength of the hardened steel product is at least 1800 MPa, i.e. $R_m \geq 1800$ MPa.

In one preferred embodiment of the steel product, the martensite of the microstructure of the steel product is tempered martensite. Preferably, in exactly this preferred embodiment, the hardness of the steel product is 300–500 HB, the yield ratio of the steel product ($R_{p0,2}/R_m$) is at least 0,85, the yield limit of the steel product $R_{p0,2}$ is 600–1050 MPa, and the tensile strength of the steel product R_m is 700–1100 MPa.

The steel product is preferably, but not necessarily, an elongated steel rod or a plate-like heavy plate or strip plate.

According to the most preferable embodiment, the steel product is a heavy steel plate, i.e. a steel plate, which is produced on a plate rolling line.

Examples

In the following, the invention is illustrated by means of examples.

- The tests are implemented on a laboratory scale as small-scale rolling by hot-rolling the steel billet to a final thickness of 12 mm. The examples apply to a steel cooled immediately from hot-rolling in an accelerated manner to a low temperature, i.e. direct-quenched steel.

Table 1: Test compositions. Steels 1294 and 1295 in Table 1 are reference steels.

steel code	C	Si	Mn	Al	V	Ti	Cr	R / I
1294	0,38	0,18	0,65	0,080	0,20	0,019	0,37	R
1295	0,39	0,22	1,49	0,084	0,21	0,017	-	R
1296	0,39	0,30	1,15	1,23	0,20	0,021	-	I
1310	0,43	0,26	1,50	2,10	0,20	0,019	-	I
1337L	0,36	0,6	0,7	2,14	0,002	0,02	0,2	I
1338L	0,47	0,56	0,77	1,9	0,192	0,02	0,2	I
R=reference								
I=invention								

Table 2: Hardening test results. Steels 1294 and 1295 in Table 2 are reference steels. HT=hardening temperature. The steels shown are cooled in an accelerated manner as water cooling.

method example R / pro	steel code - HT	hardness Brinell (HB)	Visually noticeably hardening cracks?
R1	1294-850WQ	610	yes
R1	1294-950WQ	614	yes
R2	1295-850WQ	632	yes
R2	1295-950WQ	633	yes
1	1296-850WQ	572	no
1	1296-950WQ	586	no
2	1310-850WQ	430	no
2	1310-950WQ	609	no
3	1337L-850WQ-1-Pi	447	no
3	1337L-900WQ-1-Pi	454	no
3	1337L-950WQ-1-Pi	514	no
3	1337L-1000WQ-1-Pi	563	no
4	1338L-850WQ-1-Pi	639	no
4	1338L-900WQ-1-Pi	691	no
4	1338L-950WQ-1-Pi	650	no
4	1338L-950WQ-3-Pi	655	no
4	1338L-950WQ-4-Pi	639	no
4	1338L-950WQ-5-Pi	663	no
4	1338L-1000WQ-1-Pi	686	no

Reference example (R1/R2)

In Reference example R1, in the steel products was used steel 1294 of Table 1, which is characterized by a significantly lower Al-content and Mn-content than the steel product according to the invention. As the hardening temperature was used 850°C at the point 1294-850WQ of Table 2 and 950°C at the point 1294-950WQ of Table 2. In both cases, the steel product was cooled in an accelerated manner to a low temperature after hot-rolling. As can be observed from Table 2, in both cases, the result was a steel product, the hardness of which exceeded the set primary target, 500 HB, but, in connection with quenching, a clearly visually observable fracture was formed in the steel product.

In Reference example R2, in the steel products was used steel 1295 of Table 1, which is characterized by a significantly lower Al-content as well as a somewhat high Mn-content than the steel product according to the invention. As the hardening temperature was used 850°C at the point 1295-850WQ of Table 2 and 950°C at the point 1295-950WQ of Table 2. In both cases, the steel product was cooled in an accelerated manner to a low temperature after hot-rolling. As can be seen from Table 2, in both cases, the result was a steel product, the hardness of which exceeded the set primary target, 500 HB, but, in connection with quenching, a clearly visually observable fracture was formed in the steel product making the steel unusable. Further, it is observed that increasing the amount of manganese can affect hardness.

Fig. 12 shows an example of test steel fractured in reference tests. In the following are presented examples according to the invention, with which i.a. the problem shown in Fig. 12 is solved:

Example 1

In the tests of Example 1, in the steel products was used steel 1296 of Table 1, which is characterized by an Al-content according to the invention, but a somewhat low other alloying element level.

As the hardening temperature was used 850°C at the point 1296-850WQ of Table 2 and 950°C at the point 1296-950WQ of Table 2. In both cases, the steel product was cooled in an accelerated manner to a low temperature after hot-rolling. As can be seen from Table 2, in both cases, as the result was a steel product, whose hardness exceeded the set primary target, 500 HB, without visually observable cracks or fractures.

Example 2

In the tests of Example 2, in the steel products was used steel 1310 of Table 1, which is characterized in that the steel comprises somewhat high Mn- and Al-contents.

5 As the hardening temperature was used 850°C at the point 1310-850WQ of Table 2 and 950°C at the point 1310-950WQ of Table 2. In both cases, the steel product was cooled in an accelerated manner to a low temperature after hot-rolling.

As can be seen from Table 2, in case 1310-950WQ, as the result was a steel product, the hardness of which exceeded the set primary target, 500 HB, whereas in
10 case of 1310-850WQ, as the result was a steel product, whose hardness fell below the set primary target, 500 HB. From the example, it is observed that a steel product comprising a somewhat high Mn-content combined with a somewhat low Si-content as well as a lack of chromium Cr, leads to low hardenability, i.e. somewhat low hardness at low starting temperatures of accelerated cooling of a hot-rolled steel billet.
15 From the example, it is thus learned that it is not preferable to increase the hardenability of a steel product according to the invention solely by raising Mn without alloying Cr and without somewhat high alloying of Si.

Example 3

20 In the tests of Example 3, in the steel products was used steel 1337L of Table 1, which is particularly characterized in that into it is not substantially alloyed vanadium V.

As the hardening temperature was used 850°C at the point 1337L-850WQ of Table 2, 900°C at the point 1337L-900WQ of Table 2, 950°C at the point 1337L-
25 950WQ of Table 2, and 1000°C at the point 1337L-1000WQ of Table 2. In all cases, the steel product was cooled in an accelerated manner to a low temperature after hot-rolling.

As can be seen from Table 2, in cases of 1337L-950WQ and 1337L-1000WQ was a steel product, whose hardness exceeded the set primary target, 500 HB, without
30 visually observable fractures or cracks, whereas in cases of 1337L-850WQ and 1337L-900WQ was a steel product, whose hardness fell below the set primary target, 500 HB.

From the example, it is observed that, without vanadium V, the primary targets of the invention are achieved only using high (over 900°C) starting temperatures of
35 accelerated cooling of the hot-rolled steel billet. Thus, into steel according to the invention, it is preferable to alloy vanadium V 0,05-0,4%, most preferably 0,1-0,3%.

Example 4

In the tests of Example 4, in the steel products was used steel 1338L of Table 1, which is characterized by the high alloying level of preferred embodiments of steel according to the invention, in particular, in relation to carbon C, silicon Si, aluminium Al and chromium Cr.

As the hardening temperature was used 850°C at the point 1338L-850WQ of Table 2, 900°C at the point 1338L-900WQ of Table 2, 950°C at the point 1338L-950WQ of Table 2, and 1000°C at the point 1338L-1000WQ of Table 2. In all cases, the steel product was cooled in an accelerated manner to a low temperature after hot-rolling.

As can be seen from Table 2, in all cases, as the result was a steel product, the hardness of which exceeded the set primary target, 500 HB, at all hardening temperatures of 850°C, 900°C, 950°C, and 1000°C. Further, the embodiment fulfils the preferred primary target of the invention 550–750 HB at all hardening temperatures of 850°C, 900°C, 950°C, and 1000°C, when hardness is measured less than 5 mm, more preferably 1,0–2 mm, from the surface of the steel product.

Surprisingly, it is observed that using steel 1338 having substantially almost the same calculatory hardenability as that of steel 1310 can be provided excellent hardenability and hardness also using low starting temperatures of accelerated cooling of the hot-rolled steel billet, however, such that soft ferrite is along in the microstructure of the steel.

To the person skilled in the art it is obvious that, as technology develops, the fundamental idea of the invention can be implemented in many different ways. The invention and its embodiments are thus not limited to only the examples presented above, rather many variations are possible within the scope of the claims.

Claims

1. A method for producing a steel product, such as a steel plate, having a thickness of 2–60 mm, from a steel billet, which is produced from steel comprising iron and residue contents as well as unavoidable impurities, **characterized** in that the steel comprises, as percentages by weight,
- 5 C: 0,3–0,6%,
Al: 1,0–2,5%,
V: 0–0,4%,
- 10 wherein the method comprises steps, in which
to the steel billet is performed annealing for austenitizing at a temperature of 1000–1300°C, more preferably 1050–1220°C, and
the steel billet is hot-rolled to provide a hot-rolled steel billet.
- 15 2. A method according to claim 1, **characterized** in that in the method, in the steel billet is used steel comprising, as a percentage by weight, C 0,35–0,50%, more preferably 0,40–0,50%.
- 20 3. A method according to claim 1 or 2, **characterized** in that in the method, in the steel billet is used steel comprising, as a percentage by weight, Al 1,2–2,0%, more preferably 1,5–1,9%.
4. A method according to any one of claims 1–3, **characterized** in that in the method, in the steel billet is used steel comprising, as a percentage by weight, V 0,05–
- 25 0,4%, more preferably 0,1–0,3%,
5. A method according to any one of claims 1–4, **characterized** in that in the method, in the steel billet is used steel further comprising, as a percentage by weight, Si: 0,15–1,0%, more preferably 0,25–0,8%, most preferably 0,3–0,7%.
- 30 6. A method according to any one of claims 1–5, **characterized** in that in the method, in the steel billet is used steel further comprising, as a percentage by weight, Mn: 0,4–1,5%, more preferably 0,4–0,8%.
- 35 7. A method according to any one of claims 1–6, **characterized** in that in the method, in the steel billet is used steel further comprising, as a percentage by weight, Ti: 0–0,05%, more preferably 0,005–0,02%.

8. A method according to any one of claims 1–7, **characterized** in that in the method, in the steel billet is used steel further comprising, as a percentage by weight, Cr: 0–1,0%, more preferably 0,1–0,8%, most preferably 0,15–0,5%.

5

9. A method according to any one of claims 1–8, **characterized** in that in the method, in the steel billet is used steel further comprising, as a percentage by weight, B: 0–0,005%, more preferably 0,0005–0,005%, most preferably 0,0008–0,003%.

10

10. A method according to any one of claims 1–9, **characterized** in that in the method, in the steel billet is used steel comprising, as a percentage by weight, Mo < 0,1%, more preferably molybdenum content is, at the most, a residue content.

15

11. A method according to any one of claims 1–10, **characterized** in that in the method, in the steel billet is used steel comprising, as a percentage by weight, Ni < 0,5%, more preferably nickel content is, at the most, a residue content.

20

12. A method according to any one of claims 1–11, **characterized** in that the method comprises a step, in which the steel billet is cooled in an accelerated manner from a temperature of 750–1050°C such that the average speed of cooling in the temperature range of 700–400°C is greater than 5°C/s, more preferably greater than 12°C/s, most preferably 20–40°C/s and such that the temperature of the steel billet at the time accelerated cooling ends is below 400°C, more preferably below 100°C.

25

13. A method according to any one of claims 1–12, **characterized** in that the steel billet is hot-rolled after annealing for austenitizing to provide a hot-rolled steel billet such that the temperature of the hot-rolled steel billet at the last pass of the hot-rolling step is 800–1050°C, more preferably 820–960°C, most preferably 900–960°C,

30

that the hot-rolled steel billet is cooled in an accelerated manner immediately after hot-rolling such that the temperature of the hot-rolled steel billet at the time accelerated cooling begins is 750–1050°C, more preferably 750–960°C, most preferably 750–960°C,

35

that the average speed of cooling in the temperature range of 700–400°C is greater than 5°C/s, more preferably greater than 12°C/s, most preferably 20–40°C/s, and

that the temperature of the hot-rolled steel billet at the time accelerated cooling ends is below 400°C, more preferably below 100°C.

14. A method according to any one of claims 1–12, **characterized** in that the steel billet is hot-rolled after annealing for austenitizing to provide a hot-rolled steel billet,

5 that the hot-rolled steel billet is post-hardened in a hardening furnace such that the hardening temperature of the hot-rolled steel billet in the annealing for hardening step belonging to post-hardening in a hardening furnace is 800–1050°C, more preferably 850–1000°C,

10 that the hot-rolled steel billet is cooled after annealing for hardening step in an accelerated manner such that the temperature of the hot-rolled steel billet at the time accelerated cooling begins is 750–1050°C, more preferably 850–1000°C.

that the average speed of cooling in the temperature range of 700–400°C is greater than 5°C/s, more preferably greater than 12°C/s, most preferably 20–40°C/s, and

15 that the temperature of the hot-rolled steel billet at the time accelerated cooling ends is below 400°C, more preferably below 100°C.

15. A method according to any one of claims 10–14, **characterized** in that to the hot-rolled steel billet is performed tempering.

20

16. A method according to any one of claims 1–11, **characterized** in that the steel billet is hot-rolled after annealing for austenitizing to provide a hot-rolled steel billet,

25 that to the hot-rolled steel billet is performed air-cooling, and that the air-cooled hot-rolled steel billet is hardened.

17. A method according to any one of claims 1–16, **characterized** in that in the method is produced a steel product having a thickness of 5–20 mm.

30 18. A steel product, such as a steel plate, which is hot-rolled to a thickness of 2–60 mm, wherein the steel product is produced from steel comprising iron and residue contents as well as unavoidable impurities, **characterized** in that the steel comprises, as percentages by weight,

35 C: 0,3–0,6%,
Al: 1,0–2,5%, and
V: 0–0,4%.

19. A steel product according to claim 18, **characterized** in that the steel comprises, as a percentage by weight, C: 0,35–0,50%, more preferably 0,40–0,50%.

20. A steel product according to claim 18 or 19, **characterized** in that the steel comprises, as a percentage by weight, Al: 1,2–2,0%, more preferably 1,5–1,9%.

21. A steel product according to any one of claims 18–20, **characterized** in that the steel comprises, as a percentage by weight, V: 0,05–0,4%, more preferably 0,1–0,3%.

22. A steel product according to any one of claims 18–21, **characterized** in that the steel further comprises, as a percentage by weight, Si: 0,15–1,0%, more preferably 0,25–0,8%, most preferably 0,3–0,7%.

23. A steel product according to any one of claims 18–22, **characterized** in that the steel further comprises, as a percentage by weight, Mn: 0,4–1,5%, more preferably 0,4–0,8%.

24. A steel product according to any one of claims 18–23, **characterized** in that the steel further comprises, as a percentage by weight, Ti: 0–0,05%, more preferably 0,005–0,02%.

25. A steel product according to any one of claims 18–24, **characterized** in that the steel further comprises, as a percentage by weight, Cr: 0–1,0%, more preferably 0,1–0,8%, most preferably 0,15–0,5%.

26. A steel product according to any one of claims 18–25, **characterized** in that the steel further comprises, as a percentage by weight, B 0–0,005%, more preferably 0,0005–0,005%, most preferably 0,0008–0,003%.

27. A steel product according to any one of claims 18–26, **characterized** in that the steel comprises, as a percentage by weight, Mo < 0,1%, more preferably molybdenum content is, at the most, a residue content.

28. A steel product according to any one of claims 18–27, **characterized** in that the steel comprises, as a percentage by weight, Ni < 0,5%, more preferably nickel content is, at the most, a residue content.

29. A steel product according to any one of claims 18–28, **characterized** in that the thickness of the steel product is in the range of 5–20 mm.

5 30. A steel product according to any one of claims 18–29, **characterized** in that the microstructure of the steel is substantially 2-phase, comprising ferrite and at least 90% martensite.

10 31. A steel product according to any one of claims 18–30, **characterized** in that the microstructure of the steel comprises at least 90% pure martensite, 2–10% ferrite as well as possibly small amounts of residual austenite, however, less than 10%, most preferably less than 2% residual austenite.

15 32. A steel product according to claim 30 or 31, **characterized** in that the microstructure of the steel comprises ferrite, which is formed at the grain boundaries of the prior austenite as grain boundary ferrite.

20 33. A steel product according to any one of claims 18–32, **characterized** in that the hardness of the steel product is greater than 300 HB, more preferably greater than 500 HB, most preferably 550–750 HB, when hardness is measured less than 5 mm, more preferably 1–2 mm, from the surface of the steel product.

25 34. A steel product according to any one of claims 18–33, **characterized** in that the yield strength of the steel product is at least 1600MPa, i.e. $R_m \geq 1600\text{MPa}$, most preferably at least 1800MPa, i.e. $R_m \geq 1800\text{MPa}$.

35. A steel product according to any one of claims 18–29, **characterized** in that the martensite of the microstructure of the steel product is tempered martensite.

30 36. A steel product according to claim 35, **characterized** in that the hardness of the steel product is 300–500 HB, that the yield ratio of the steel product ($R_{p0,2}/R_m$) is at least 0,85, that the yield limit of the steel product $R_{p0,2}$ is 600–1050 MPa, and that the tensile strength of the steel product R_m is 700–1100 MPa.

35 37. A microstructure of a steel product, such as a wear resistant steel plate, having a hardness of greater than 300 HB, more preferably greater than 500 HB, characterized in that the microstructure is composed of, as percentages by volume, at least 90% martensite,

2–10% ferrite formed at the grain boundaries of the prior austenite, and
0–10% residue austenite.

38. A microstructure according to claim 37, **characterized** in that the grain boundary
5 ferrite is equal-axial.

39. A microstructure according to claim 37, **characterized** in that there is ferrite, as a
percentage by volume, 2–5%.

10 40. A microstructure according to claim 37, 38 or 39, **characterized** in that there is
residual austenite, as a percentage by volume, 0–2%.

41. A microstructure according to any one of claims 37–39, **characterized** in that there is
bainite, as a percentage by volume, 0–2%.

15

1 / 13

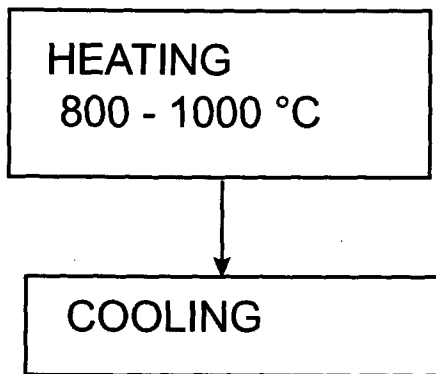


FIG 1

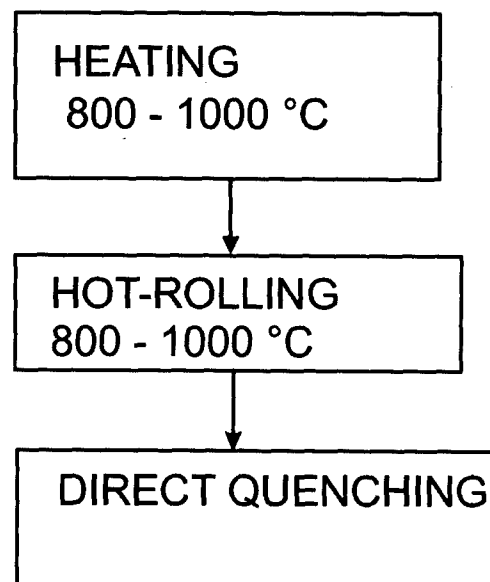


FIG 2

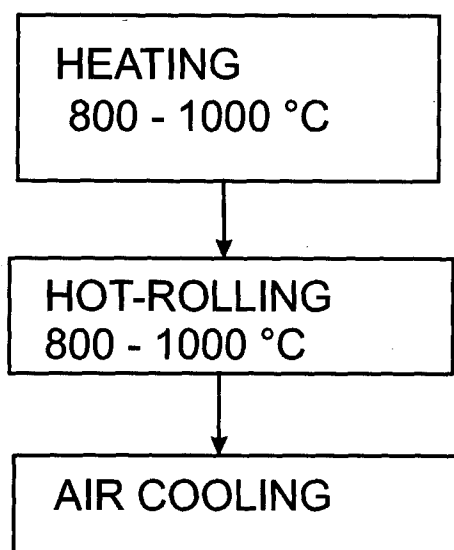


FIG 3

2 / 13

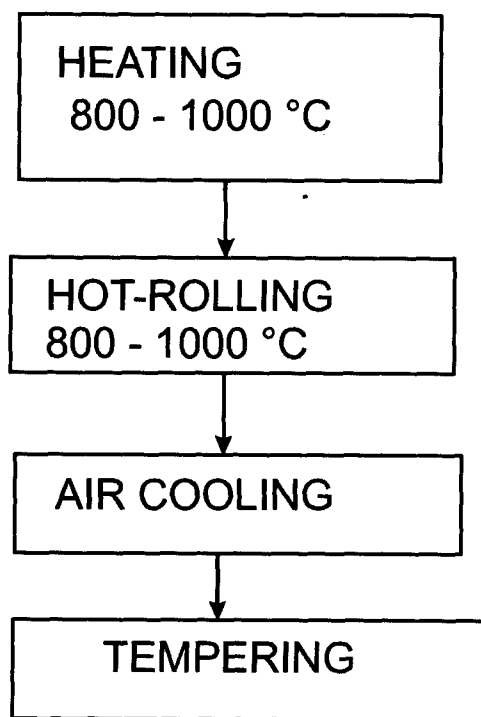


FIG 5

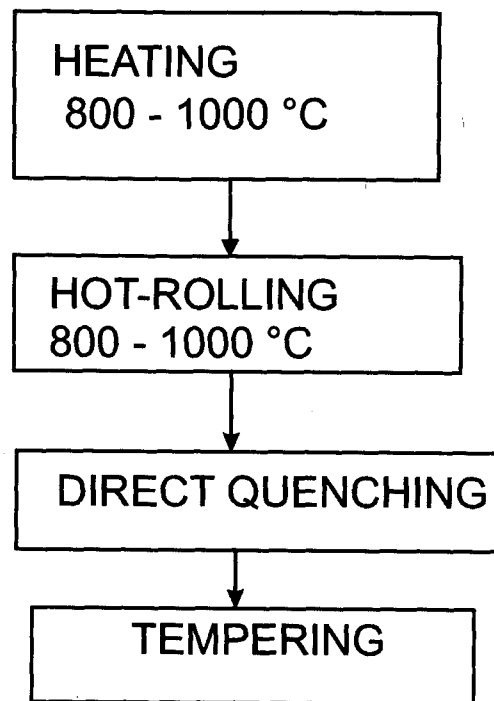


FIG 4

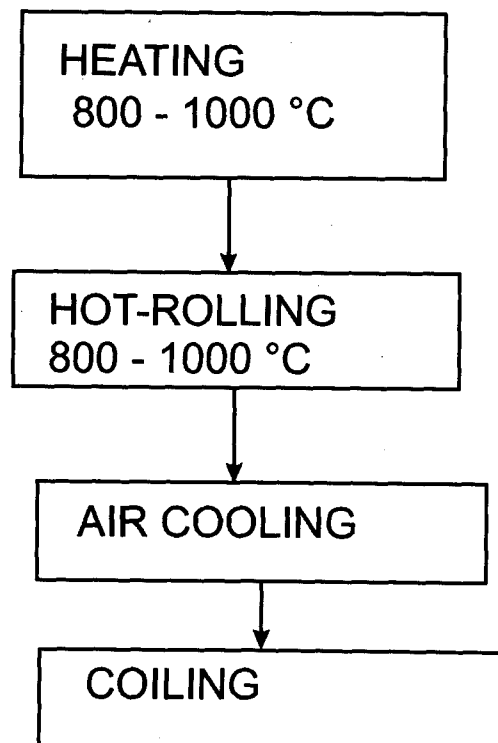


FIG 6

3 / 13

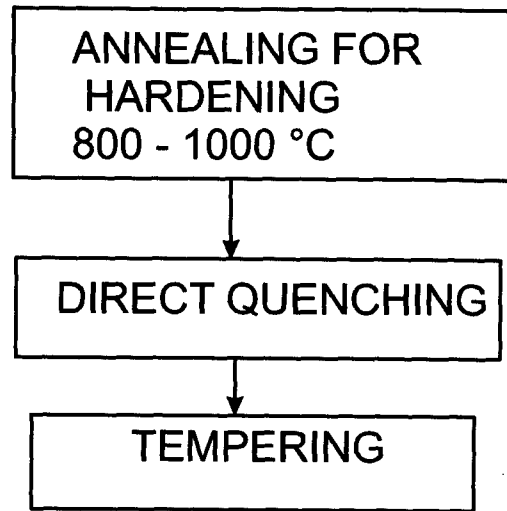


FIG 7

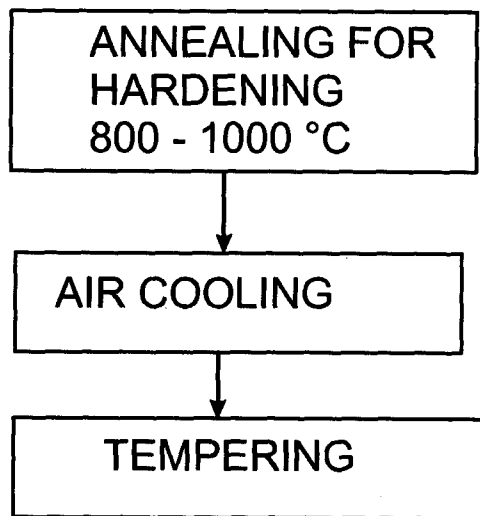


FIG 8

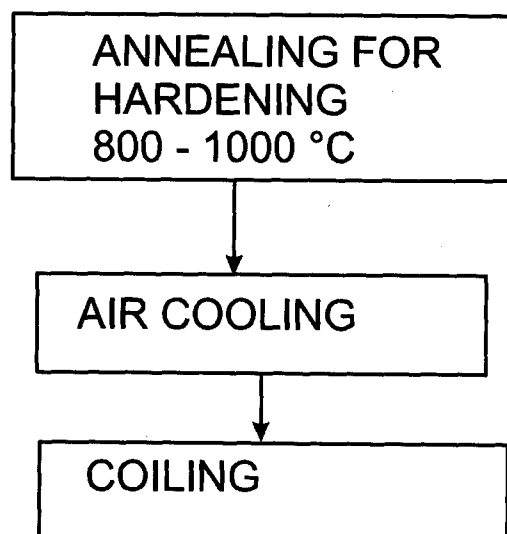


FIG 9

4 / 13

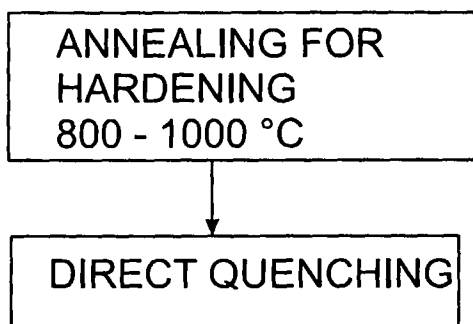


FIG 10

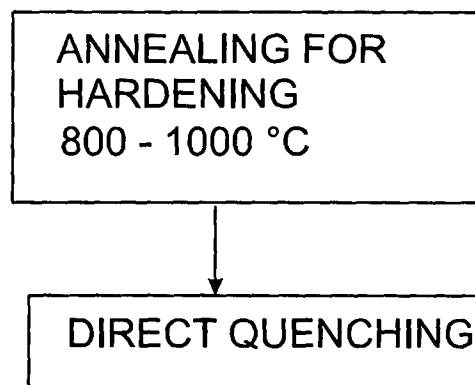


FIG 11

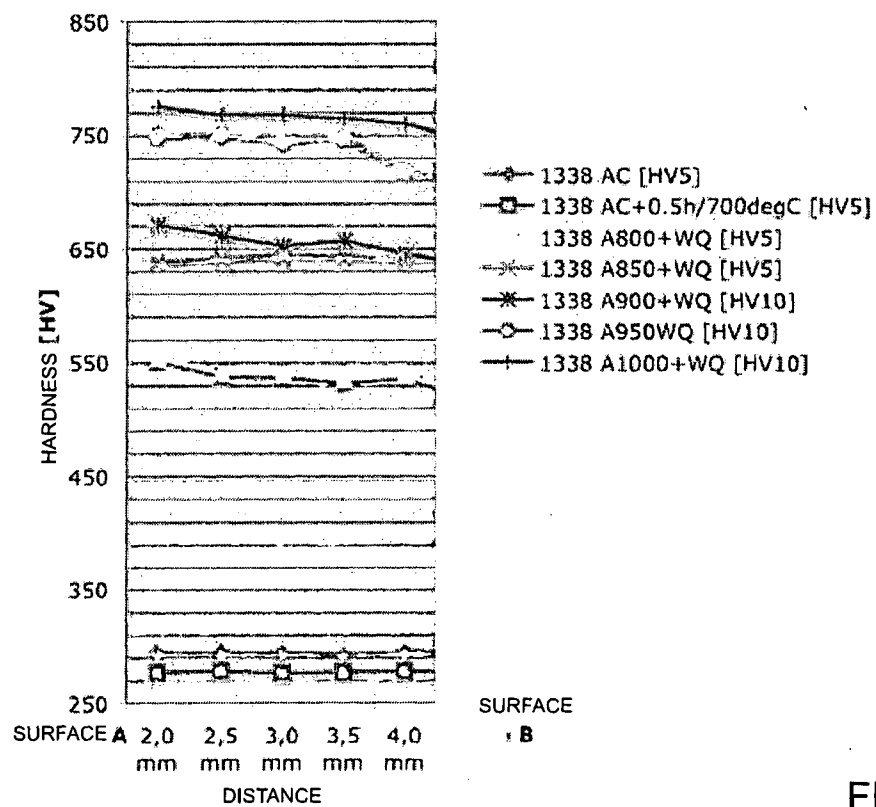


FIG 12

5 / 13

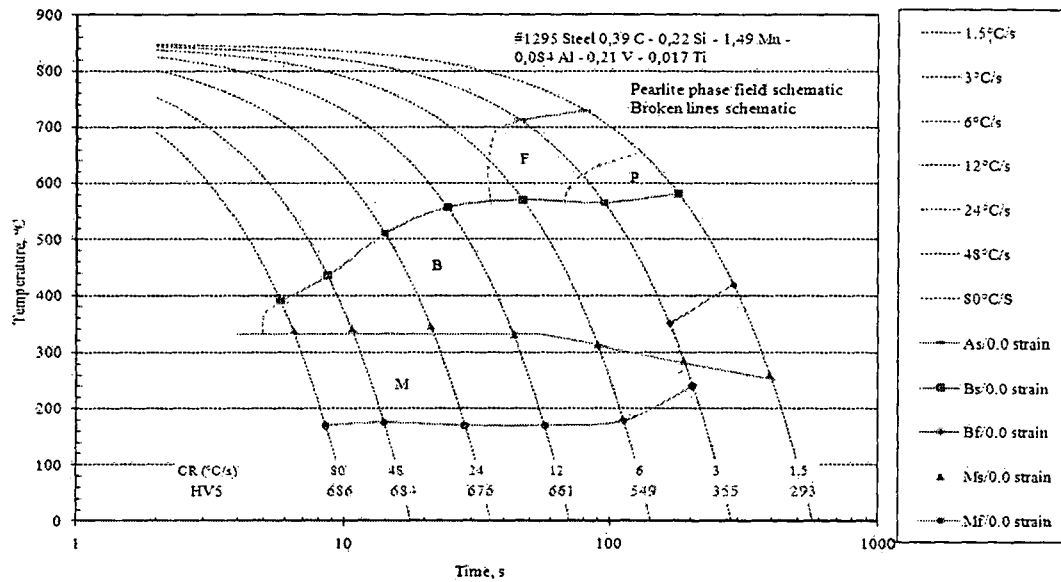


FIG 13

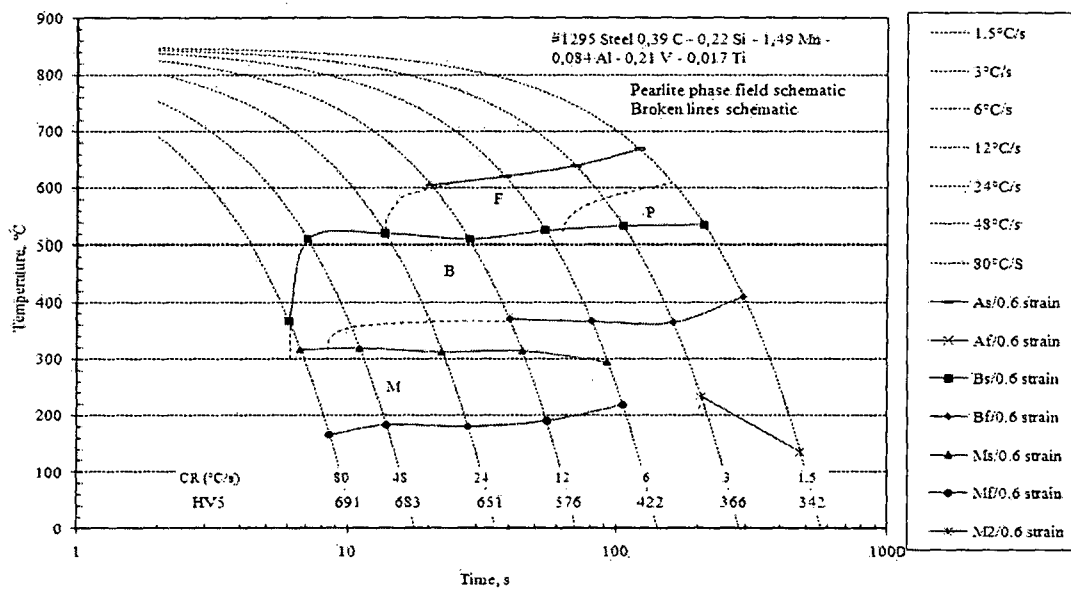


FIG 14

6 / 13

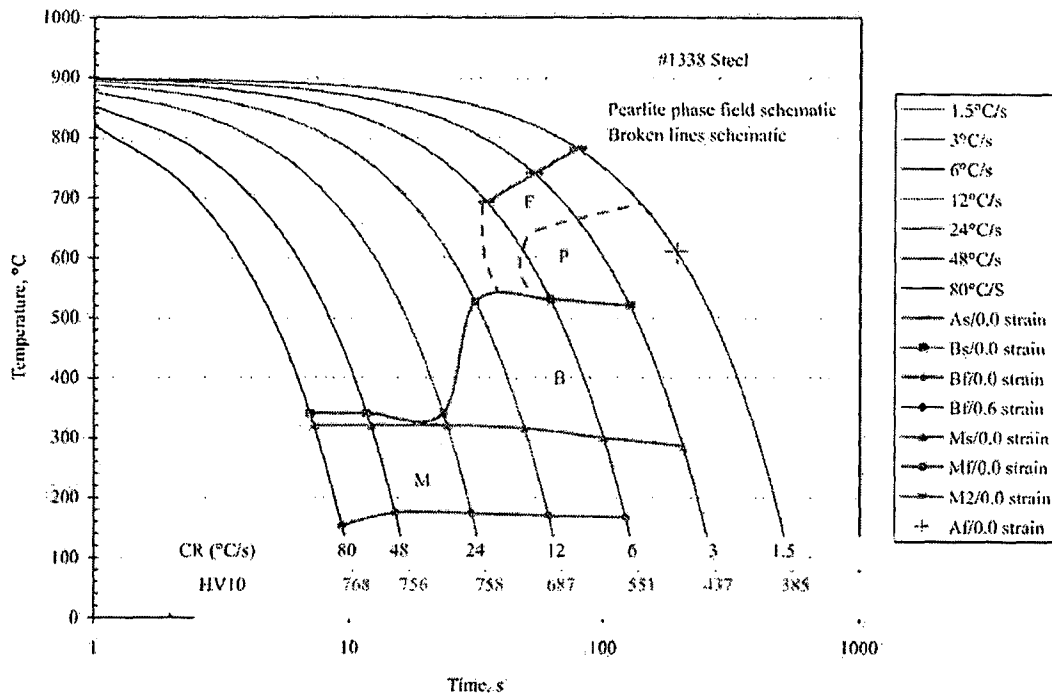


FIG 15

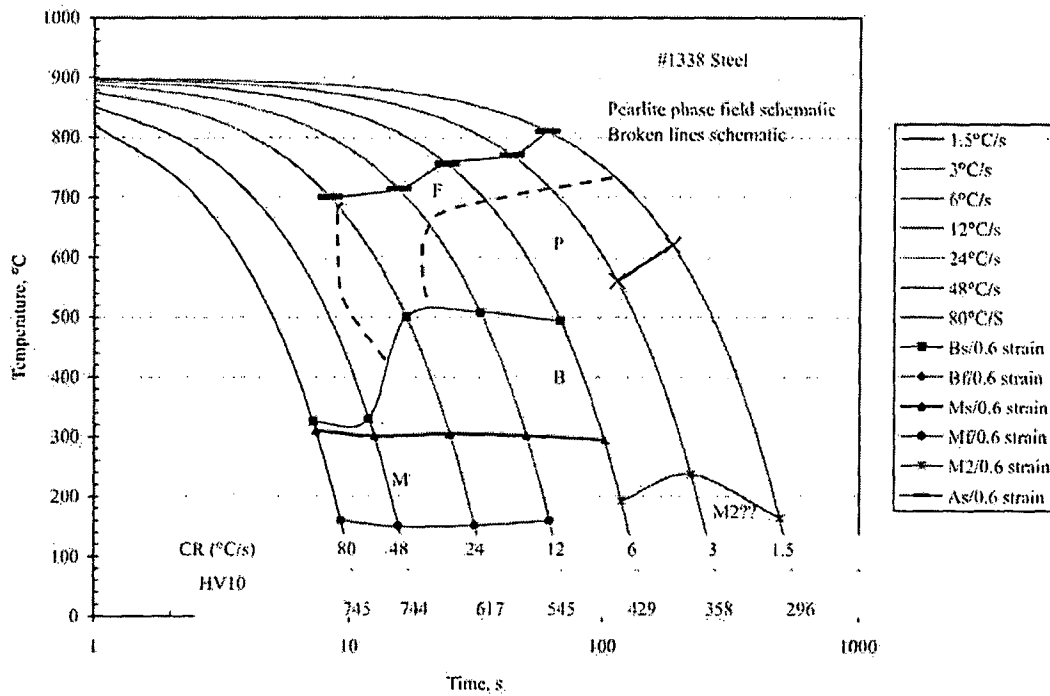


FIG 16

7 / 13

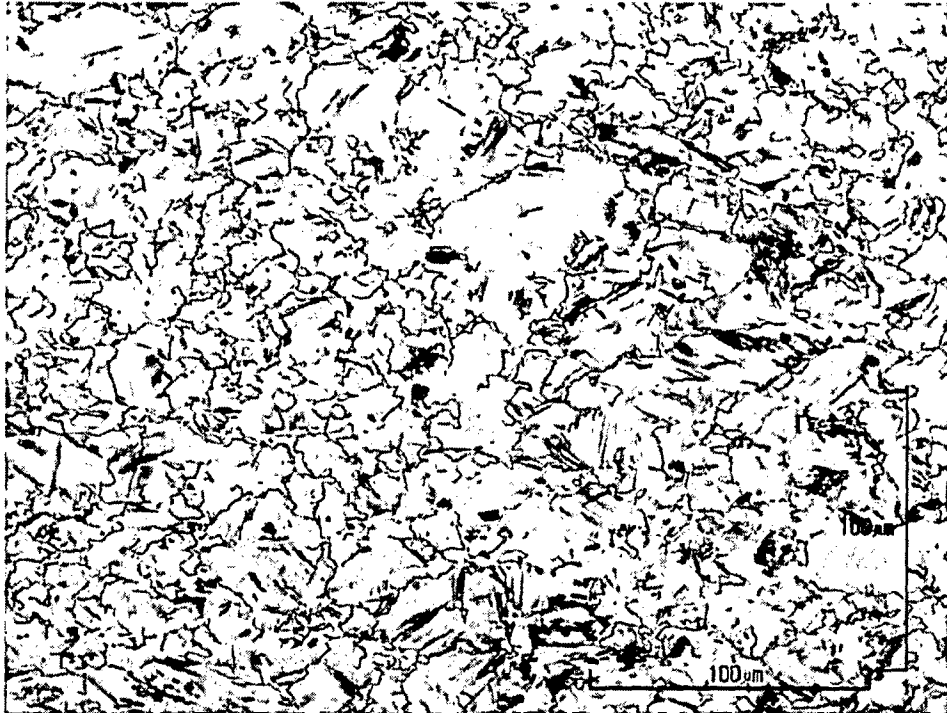


FIG 17

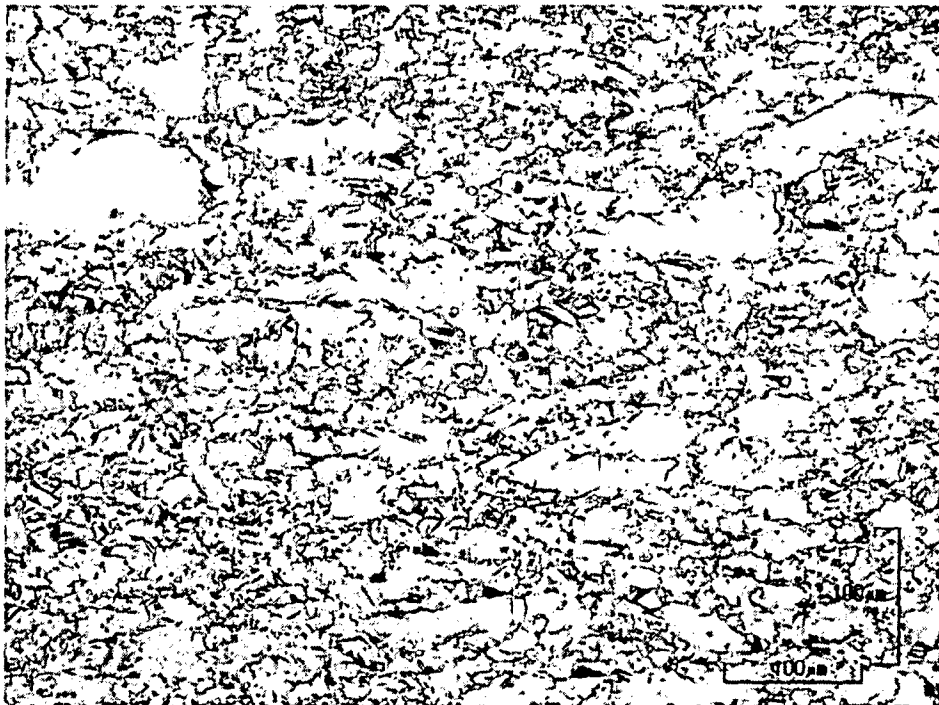


FIG 18

8 / 13

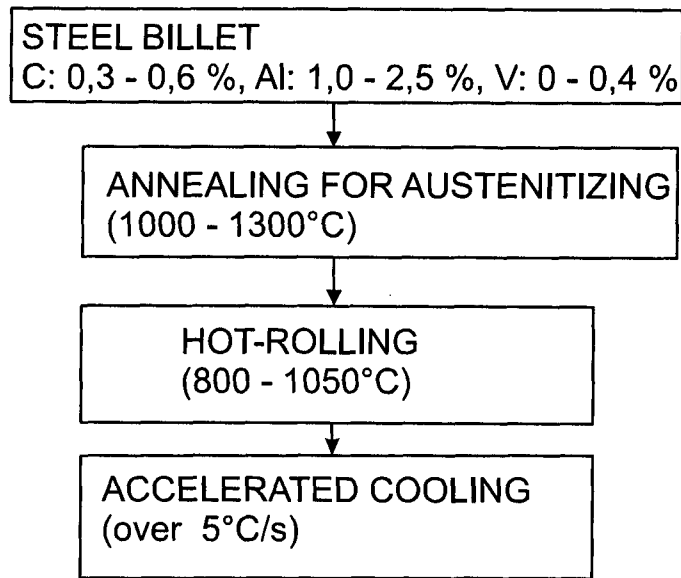


FIG 19

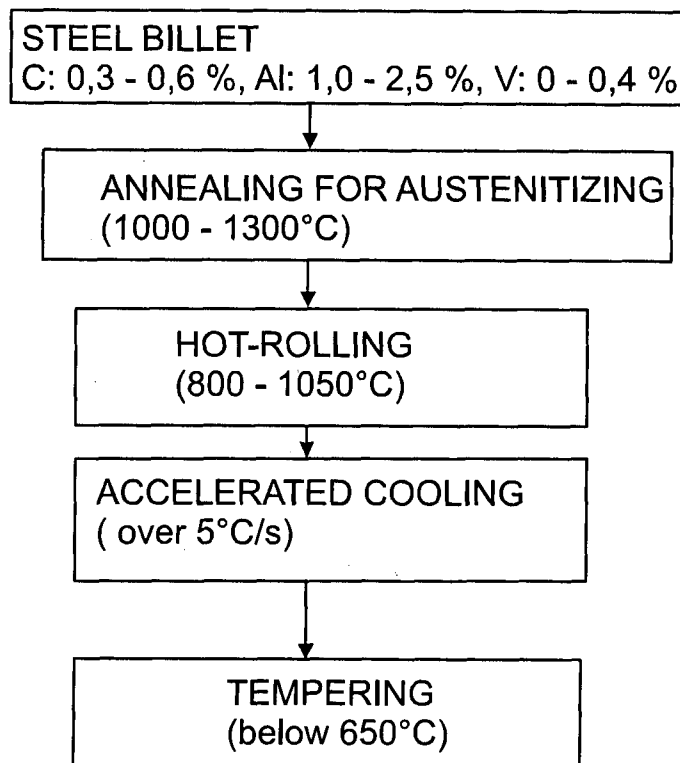


FIG 20

9 / 13

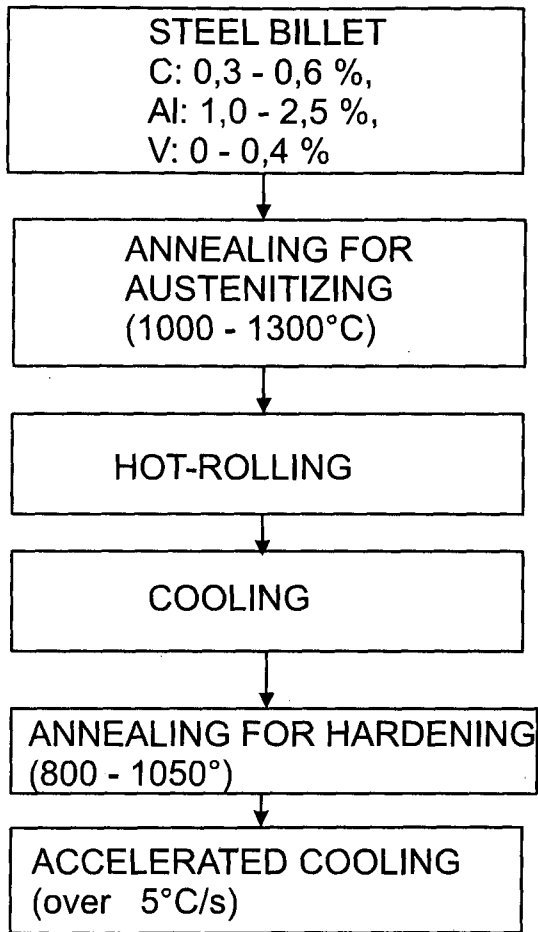
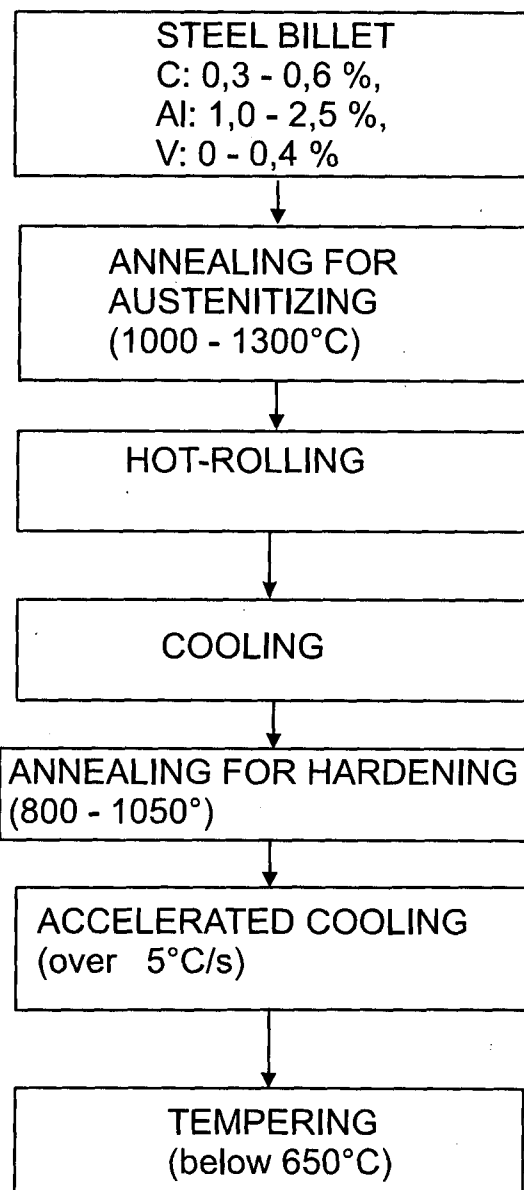


FIG 22

FIG 21



10 / 13

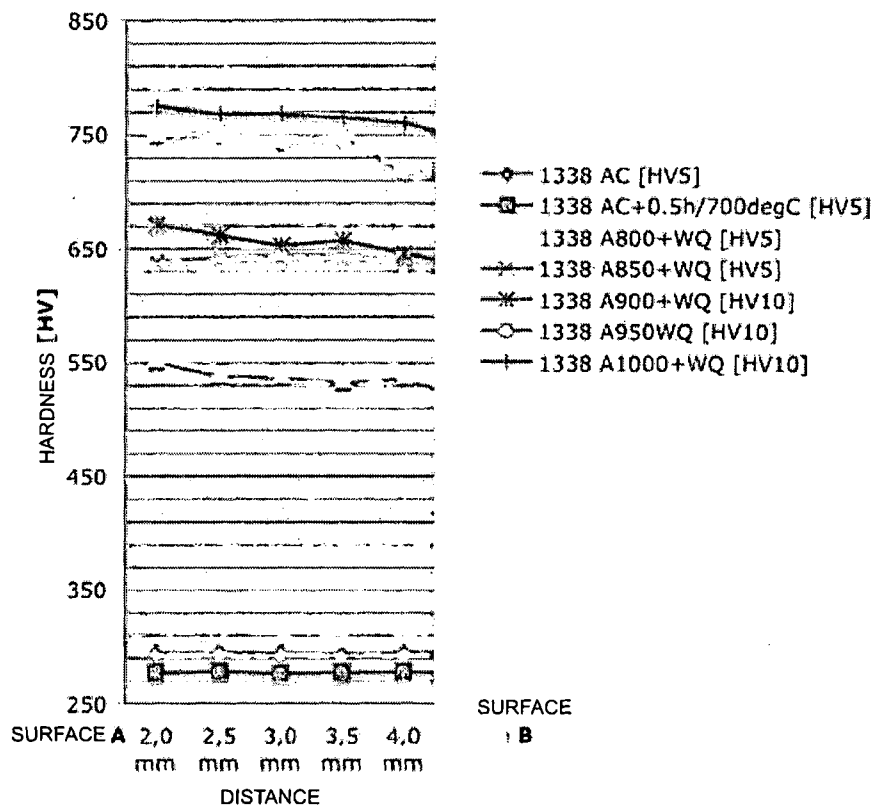


FIG 23

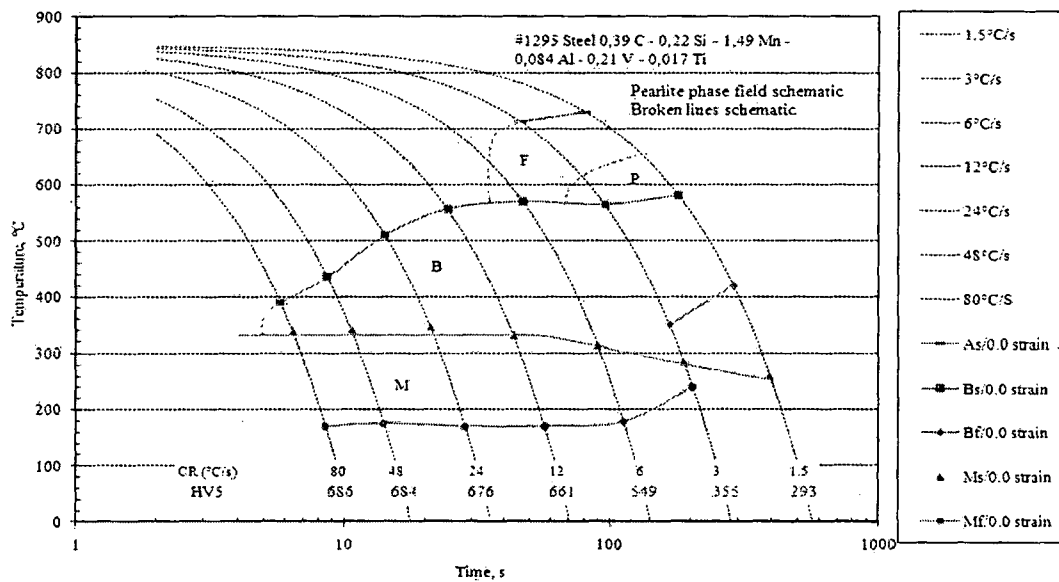


FIG 24

11 / 13

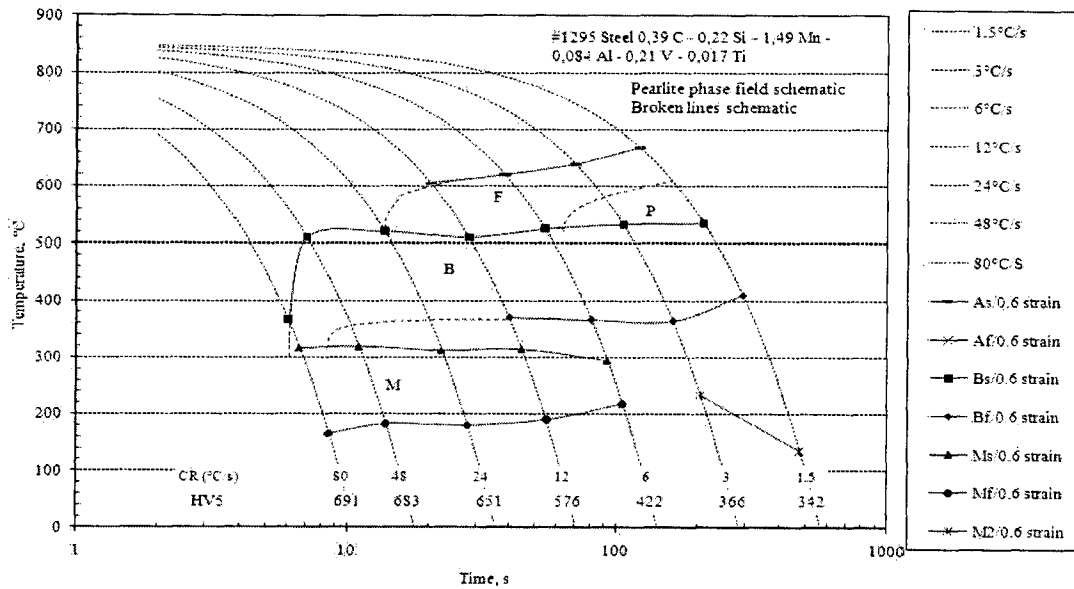


FIG 25

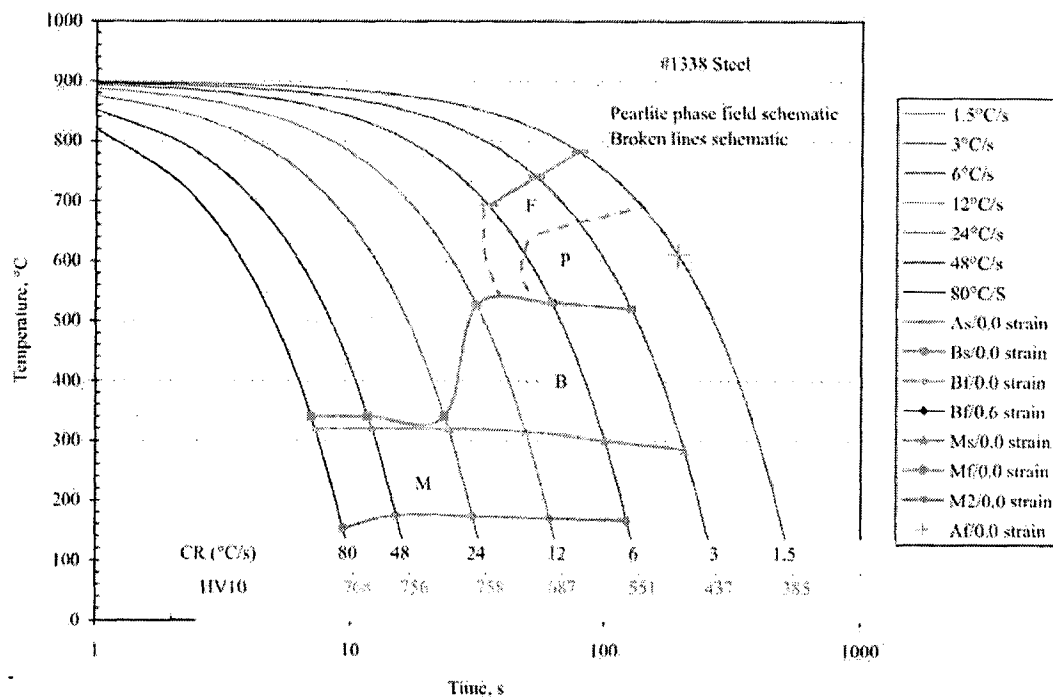


FIG 26

12 / 13

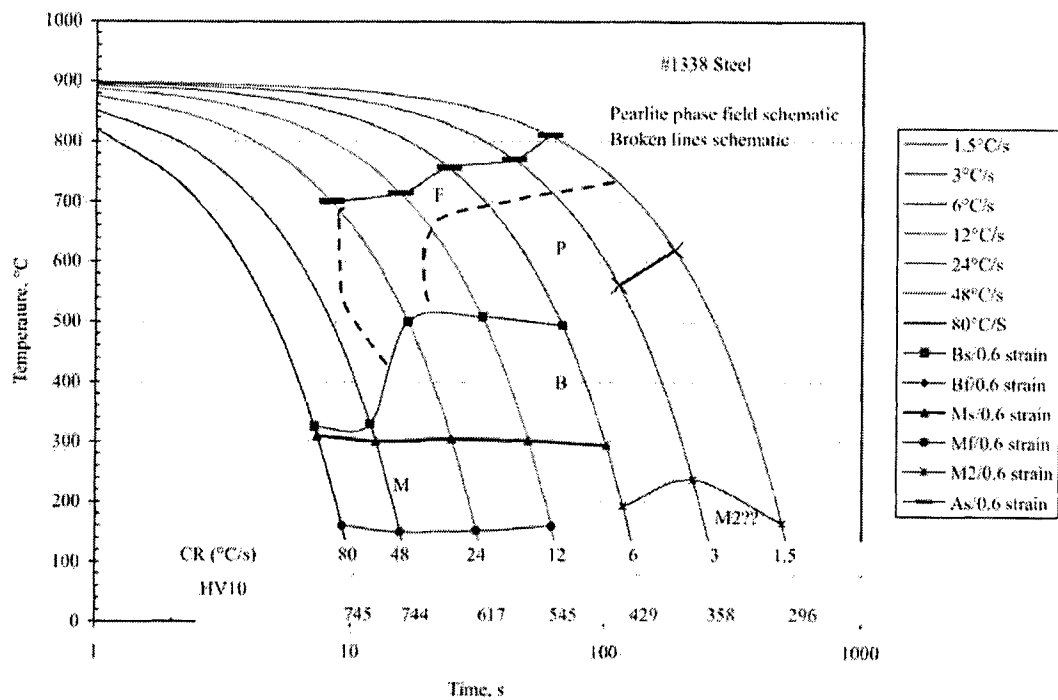


FIG 27

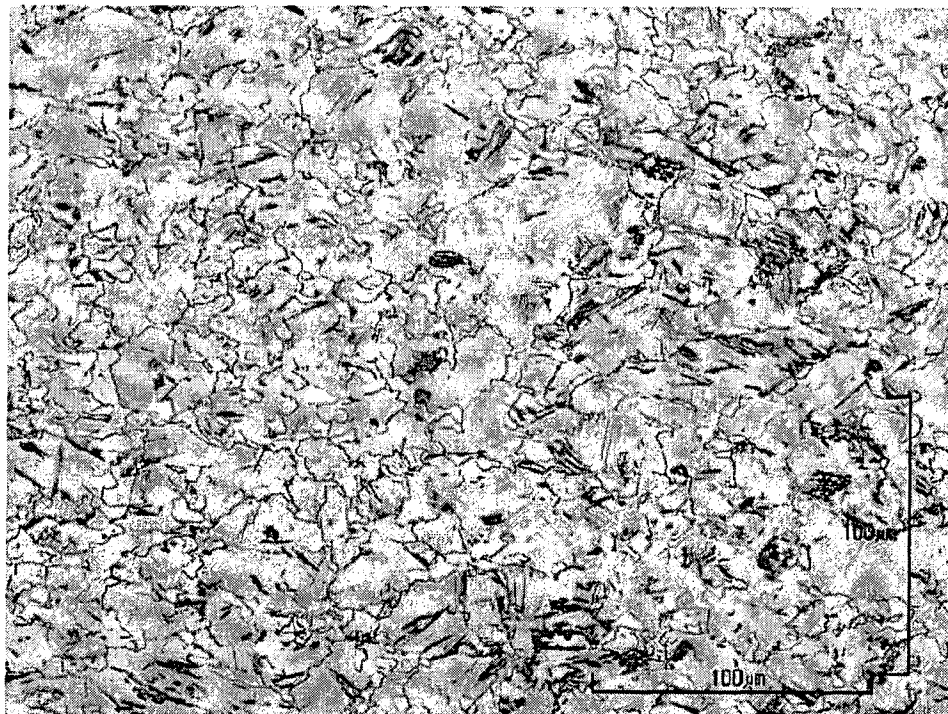


FIG 28

13 / 13

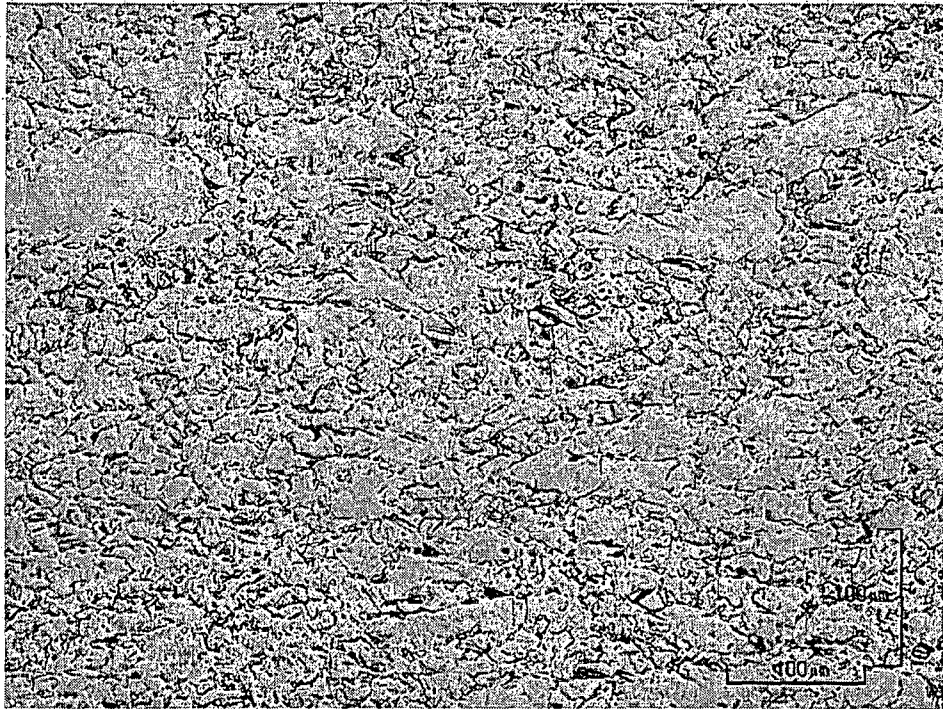


FIG 29

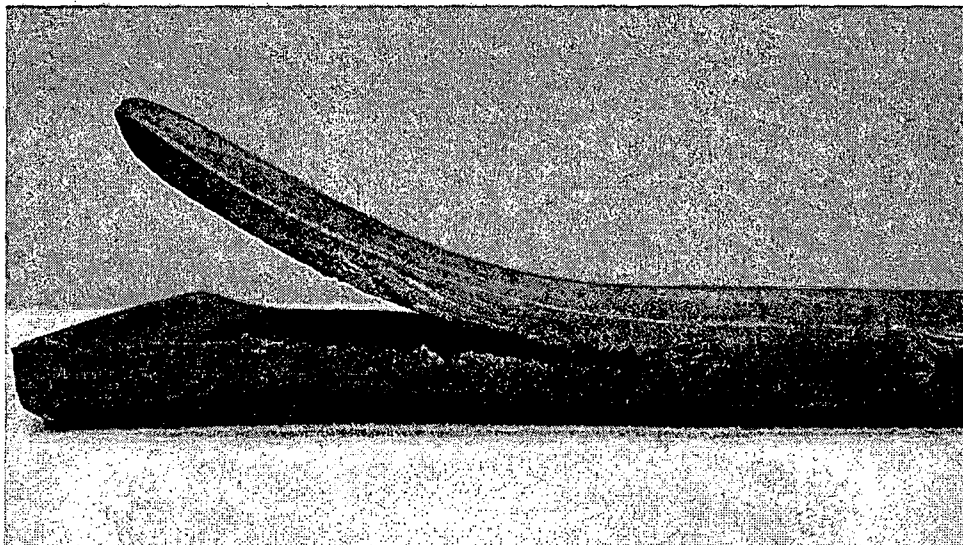


FIG 30

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2012/050353

A. CLASSIFICATION OF SUBJECT MATTER INV. C21D1/18 C21D1/25 C21D6/00 C21D8/02 C21D9/46 C22C38/06 C22C38/12 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) C21D C22C 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 <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> DATABASE WPI Week 199442 Thomson Scientific, London, GB; AN 1994-338629 XP002681441, & JP 6 264183 A (SUMITOMO METAL IND LTD) 20 September 1994 (1994-09-20) abstract ----- </td> <td style="vertical-align: top; text-align: center;"> 1,3-14, 16-18, 20-36 </td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> JP 2002 302734 A (KOBE STEEL LTD) 18 October 2002 (2002-10-18) paragraphs [0092] - [0093]; example 6; tables 4,7 figures 8,10 claims 1,4,5,7 ----- -/-- </td> <td style="vertical-align: top; text-align: center;"> 1,2, 5-13,15, 18,19, 22,23, 37-40 </td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	DATABASE WPI Week 199442 Thomson Scientific, London, GB; AN 1994-338629 XP002681441, & JP 6 264183 A (SUMITOMO METAL IND LTD) 20 September 1994 (1994-09-20) abstract -----	1,3-14, 16-18, 20-36	X	JP 2002 302734 A (KOBE STEEL LTD) 18 October 2002 (2002-10-18) paragraphs [0092] - [0093]; example 6; tables 4,7 figures 8,10 claims 1,4,5,7 ----- -/--	1,2, 5-13,15, 18,19, 22,23, 37-40
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
X	DATABASE WPI Week 199442 Thomson Scientific, London, GB; AN 1994-338629 XP002681441, & JP 6 264183 A (SUMITOMO METAL IND LTD) 20 September 1994 (1994-09-20) abstract -----	1,3-14, 16-18, 20-36									
X	JP 2002 302734 A (KOBE STEEL LTD) 18 October 2002 (2002-10-18) paragraphs [0092] - [0093]; example 6; tables 4,7 figures 8,10 claims 1,4,5,7 ----- -/--	1,2, 5-13,15, 18,19, 22,23, 37-40									
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.											
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Date of the actual completion of the international search 7 August 2012		Date of mailing of the international search report 23/08/2012									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Ugarte, Eva									

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International application No

PCT/FI2012/050353

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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X,P	the whole document -& EP 2 325 346 A1 (JFE STEEL CORP [JP]) 25 May 2011 (2011-05-25) abstract paragraph [0070]; examples T,30; tables 1,2 -----	1,2, 7-16,18, 19,24-40
X	US 2002/112786 A1 (ABE YUKIO [JP] ET AL) 22 August 2002 (2002-08-22) abstract example 17; table 1 -----	1-4,6,7, 9,11, 18-21, 23,24, 26,28, 30-40

INTERNATIONAL SEARCH REPORT

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International application No

PCT/FI2012/050353

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