



(11)

**EP 4 019 654 A1**

(12)

**EUROPEAN PATENT APPLICATION**

- (43) Date of publication:  
**29.06.2022 Bulletin 2022/26**
- (21) Application number: **20383154.0**
- (22) Date of filing: **23.12.2020**

- (51) International Patent Classification (IPC):  
**C22C 37/10** <sup>(2006.01)</sup> **C22C 38/02** <sup>(2006.01)</sup>  
**C22C 38/04** <sup>(2006.01)</sup> **C22C 38/06** <sup>(2006.01)</sup>  
**C21D 1/28** <sup>(2006.01)</sup> **C21D 9/28** <sup>(2006.01)</sup>  
**C21D 9/30** <sup>(2006.01)</sup> **C21D 9/32** <sup>(2006.01)</sup>  
**C21D 9/46** <sup>(2006.01)</sup>
- (52) Cooperative Patent Classification (CPC):  
**C22C 37/10; C21D 1/28; C21D 9/28; C21D 9/30;**  
**C21D 9/32; C21D 9/46; C22C 38/02; C22C 38/04;**  
**C22C 38/06; C21C 7/10; C21D 2211/008**

- (84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB**  
**GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO**  
**PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**  
Designated Validation States:  
**KH MA MD TN**
- (71) Applicant: **Fundación Azterlan**  
**48200 Durango, Vizcaya (ES)**
- (72) Inventors:  
• **Santos, Fernando**  
**48200 Durango, Vizcaya (ES)**

- **García, David**  
**48200 Durango, Vizcaya (ES)**
  - **Niklas, Andrea**  
**48200 Durango, Vizcaya (ES)**
  - **Andonegi, Hegoi**  
**48200 Durango, Vizcaya (ES)**
- (74) Representative: **Balder IP Law, S.L.**  
**Paseo de la Castellana 93**  
**5ª planta**  
**28046 Madrid (ES)**

(54) **LOW DENSITY MEDIUM ALLOYED STEELS WITH ALUMINIUM AND MANGANESE**

(57) Medium alloyed steels comprising aluminum, manganese, carbon, silicon and iron, with low density and balanced mechanical properties. The alloys may be manufactured by a process including a normalizing and a tempering heat treatment, and machinery parts, such

as machine shafts, industrial machines and vehicles cog-wheels, spanners, cardan forks, crankshafts, camshafts, steering box forks, body and white components and engine mounts, may be manufactured with said alloys.

**EP 4 019 654 A1**

**Description****FIELD OF THE INVENTION**

**[0001]** The present invention is encompassed within the sector of metallurgical industry. Particularly, it relates to a new family of medium alloyed steels with a low density and balanced mechanical properties, such as yield strength, tensile strength and elongation, which avoids the inclusion of costly and scarce alloying elements, such as Cr, Mo, Ni and V. In general, medium alloyed steels are alloys incorporating scarce and costly alloying elements, such as Cr, Mo, Ni and V (chromium, molybdenum, nickel and vanadium, respectively), whereas the alloys according to the present invention comprise Mn and Al (manganese and aluminium, respectively), which are abundant in nature and therefore significantly more affordable.

**BACKGROUND OF THE INVENTION**

**[0002]** Medium alloyed steels are commonly used in different sectors, for example industrial machinery, such as machine tools or hand tools, and also in the transport sector, such as aeronautic, marine or automotive sectors. The use of these alloys is highly conditioned by the final cost and scarcity of chemical elements contained therein, as well as by the weight of the final alloy composition. The combination of these two aspects clearly affects the final sustainability, price and weight of the component, and also affects the use of resources in their fabrication and the energy consumption by transport equipment, such as cars, trucks and ships, wherein the alloys could be integrated.

**[0003]** Medium alloyed steels are reported in standard norm EN-101293 "*steel casting for general engineering uses*", including steels containing, as the main chemical alloying element, C, Si, Mn, Cr, Mo, V, Ni or W. These steels are manufactured using casting processes in chemically bonded sand molds, using open air induction furnaces, and in steel making processes, using arc furnaces, ladle furnaces and a vacuum degassing step, prior to continuous casting or ingot manufacturing.

**[0004]** Generally used alloys are usually characterized by a carbon (C) content up to 0.6 wt. %, which increases yield strength and tensile strength, but reduces ductility; by a silicon content below 1 wt. %, which increases mechanical properties, such as tensile strength and yield strength, but reduces ductility and elongation, and increases brittle temperature transition; by a manganese (Mn) content below 1.80 wt.%, which increases hardenability, yield strength and tensile strength.

**[0005]** On the other hand, the chromium (Cr) content can be in a wide range, up to 1.80 wt.%, and it provides hardenability and increases yield strength and tensile strength, reducing the elongation values. Cr contents higher than 10 wt.% are linked with corrosion resistance. Molybden (Mo) added in concentrations up to 1.50 wt.% significantly increases hardenability, wear resistance, resistance to softening of the steel with temperature corrosion resistance to halogens, yield strength and tensile strength, but reduces ductility. Vanadium (V) contents are in the range of 0-0.35 wt. %; V is mainly linked with increasing wear resistance, tensile and yield strength, as well as ductility reduction. Cost of such alloys is significantly affected by the content of elements such as Mo and V, and in less degree of Cr, which are scarce elements, very high in cost. As an example, the cost by weight of Mo is generally even about 24 times the cost of Mn. The Al content in medium alloyed steel typically is a residual content, which is never higher than 0.10 wt.%.

**[0006]** The aforementioned medium alloyed steels are used in applications in which a combination of mechanical properties is required to perform cyclic routines, wherein they are subjected to significant loads and wear conditions; however, they have limited hardenability, which requires a hardening heat treatment, consisting in heating up to 900 °C, and cooling in oil at around 50°C; the alloys are prone to produce deformations and cracks, thus requiring additional machining operations. The density of medium alloyed steel such as G42CrMo4 and G26CrMo4 these alloys is in the range of 7.8-8.0 g/cm<sup>3</sup>; this means that, in the case of transport application, its weight will be elevated, and thus imply higher equipment energy consumption. In view of all these shortcomings, there is still the need in the state of the art to provide new alloys, not requiring scarce chemical elements, with higher hardenability properties, which will allow them to cool down in open air, and having a lower density, to provide new consumption reduction opportunities to the transport sector.

**[0007]** Xu et al. [ISIJ International (2015), 55(3), 662-669] performed a study to investigate the effect of aluminium addition on the microstructure and the mechanical properties in 0.2C - 5Mn steels; different conventional quenching and tempering heat treatments were used in their preparation of such steels. The chemical composition of the studied alloys comprised 0.2 wt. % C, 4.72 wt. % Mn, 1.5 wt. % Al, and some impurities in the thousandth wt.% range.

**[0008]** There is still a need in the art for medium alloy steels with reduced density while maintaining good mechanical properties.

## BRIEF DESCRIPTION OF THE FIGURES

[0009]

**Figure 1:** General dimensions of an exemplary keel-block

**Figure 2:** Area of extraction and dimensions of samples for metallographic and density analysis

**Figure 3:** Area of extraction and dimensions of samples for mechanical tests.

**Figure 4:** Metallographic images showing differentiated dark grey (martensite phase) and white phases (ferrite/austenite phase).

a) Magnification 5X\_6 alloy, with 0.4 wt. % C and 2.74 wt. % Al, heat treated

b) Magnification 50X\_6-alloy 0.4 wt. % C and 2.74 wt. % Al, heat treated

**Figure 5:** Metallographic images showing the increase of white phase when increasing the Al content.

a) Magnification 5X\_1-alloy with 0.18 wt. % C and 0.9 wt. % Al, heat treated

b) Magnification 5X\_3-alloy with 0.19 wt. % C and 2.84 wt. % Al, heat treated

**Figure 6:** Metallographic images showing the increase of the dark grey phase when increasing the carbon content.

a) Magnification 50X\_3-alloy with 0.19 wt. % C and 2.84 wt. % of Al after heat treatment

b) Magnification 50X\_9-alloy with 0.60 wt. % C and 3.12 wt. % Al after heat treatment

**Figure 7:** Graph showing the reduction in density when increasing the Al content, at a constant carbon content of 0.2 wt. %.

**Figure 8:** Graph showing the reduction in density when increasing the Al content, at a constant carbon content of 0.4 wt. %.

**Figure 9:** Graph showing the reduction in density when increasing the Al content, at a constant carbon content of 0.6 wt. %.

**Figure 10:** Graph showing the evolution of the density value when increasing the carbon content, at a constant aluminium content of 1 wt. %.

**Figure 11:** Graph showing the evolution of the density value when increasing the carbon content, at a constant aluminium content of 2 wt. %.

**Figure 12:** Graph showing the evolution of the density value when increasing the carbon content, at a constant aluminium content of 3 wt. %.

**Figure 13:** Graph showing a significant increase in Rp0.2 and Rm when carbon content arrives at 0.6 wt. %, at a constant aluminium content of 1 wt. %.

**Figure 14:** Graph showing a significant increase in Rp0.2 and Rm when carbon content arrives at 0.6 wt. %, at a constant aluminium content of 2 wt. %.

**Figure 15:** Graph showing a significant increase in Rp0.2 and Rm when carbon content arrives at 0.6 wt. %, at a constant aluminium content of 3 wt. %.

**Figure 16:** Graph showing the stable values of Rp0.2 and Rm in 0.6 wt. % carbon containing alloys (7, 8 and 9), with independence of the increase of the Al value.

**Figure 17:** Metallographic images of Alloy 9 -0.60 wt. % C, 3.12 wt. % Al: evolution of martensite from coarse acicular form in as-cast alloy, to finer martensite once normalized, to finer and slightly globulized after tempering.

a) Magnification 50X as cast

b) Magnification 50X after normalizing heat treatment

c) Magnification 50X after normalizing and tempering heat treatments

## DESCRIPTION OF THE INVENTION

**[0010]** Medium alloyed steels are well-known by their balance of mechanical properties for a given density, at an affordable production cost, to be used in mass production of industrial components.

**[0011]** The present invention provides new low density medium alloyed steels; the steels of the present invention comprise aluminium and manganese, which are alloying elements abundant in nature, and thus with an affordable price. The invention further provides methods for their melting and pouring, and their final conditioning through a non-critical heat treatment.

**[0012]** In a first aspect, the present invention refers to an alloy steel comprising:

Aluminium (Al):	1.8 - 6.0 wt. %;
Manganese (Mn):	1.0 - 4.0 wt. %;
Carbon (C):	0.1 - 0.8 wt. %;
Silicon (Si):	0.1 - 1.0 wt. %;
Impurities:	0.1 wt. % or less;

the rest of the alloy, until reaching 100 wt. %, being Fe.

**[0013]** As impurities, which are unavoidable, especially phosphorus (P) and sulphur (S) may be mentioned, which, when present, are each comprised in an amount of 0.03 wt. % or less.

**[0014]** The alloys according to the invention avoid the inclusion of costly and scarce alloying elements, such as Cr, Mo, Ni and V. Therefore, according to a particular embodiment the alloys of the invention are free of at least one of Cr, Mo, Ni and V, preferably free of Cr, Mo, Ni and V.

**[0015]** According to particular embodiments of the invention, aluminium is comprised in an amount of at least 2.0 wt. %, of at least 2.5 wt. %, or of at least 2.7 wt. %; and in an amount of at most 5.5 wt. %, of at most 5.0 wt. %, of at most 4.0 wt. %, of at most 3.5 wt. % or of at most 3.1 wt. %. Any of the lower values may be combined with any of the higher values to provide preferred ranges for the aluminium amount in the steel alloys of the invention, e.g. from 2.0 wt. % to 4.0 wt. %, from 1.8 to 6 wt. %, or from 1.8 to 3.1 wt. %.

**[0016]** According to further particular embodiments of the invention, manganese is comprised in an amount of at least 2.0 wt. %, of at least 2.3 wt. %, of at least 2.5 wt. %, of at least 2.8 or of at least 3.1 wt. %; and in an amount of at most 3.9 wt. %, of at most 3.8 wt. %, of at most 3.6 wt. %, of at most 3.4 wt. %, or of at most 3.2 wt. %. Any of the lower values may be combined with any of the higher values to provide preferred ranges for the manganese amount in the steel alloys of the invention, e.g. from 2.0 wt. % to 3.9 wt. %, from 2.5 to 4 wt. %, or from 3.1 wt. % to 3.8 wt. %.

**[0017]** According to particular embodiments of the invention, carbon is comprised in an amount of at least 0.12 wt. %, of at least 0.15 wt. %, or of at least 0.18 wt. %; and in an amount of at most 0.74 wt. %, of at most 0.68 wt. %, or of at most 0.62 wt. %. Any of the lower values may be combined with any of the higher values to provide preferred ranges for the carbon amount in the steel alloys of the invention, e.g. from 0.18 wt. % to 0.62 wt. %.

**[0018]** According to particular embodiments of the invention, silicon is comprised in an amount of at least 0.15 wt. %, of at least 0.15 wt. %, or of at least 0.21 wt. %; and in an amount of at most 0.79 wt. %, of at most 0.58 wt. %, or of at most 0.37 wt. %. Any of the lower values may be combined with any of the higher values to provide preferred ranges for the silicon amount in the steel alloys of the invention, e.g. from 0.21 wt. % to 0.37 wt. %.

**[0019]** According to one embodiment, the invention refers to an alloy steel as defined above, comprising:

from 1.8 to 3.1 wt. % Aluminium (Al);

from 3.0 to 4.0 wt. % Manganese (Mn);

from 0.18 to 0.62 wt. % Carbon (C);

from 0.21 to 0.37 wt. % Silicon (Si);

0.1 wt. % or less of impurities;

iron (Fe) until reaching 100 wt. %.

**[0020]** As will be further detailed in the Examples, the alloy steel of the invention, having a medium manganese and aluminium content, presents a structure consisting of a main matrix of martensite, with variable quantities of ferrite/austenite. Changes in the chemical composition of the alloy steel have a direct effect on the final microstructure, and thus on its mechanical properties. For example, it has been observed that the increment in aluminium quantity increases the quantity of ferrite for a fixed value of carbon, manganese and silicon. On the other hand, it has been observed that the increment in carbon content increases the quantity of martensite for a fixed value of manganese, aluminium and silicon.

**[0021]** The alloys of the present invention can be used for manufacturing complex components integrated in machines or in transport equipment. They can be used when cyclic or static loads in the range of 30-60 Kg/mm<sup>2</sup> are present. If they are going to be used outdoors, conveniently they may be provided with protection against environmental conditions for their use, e.g. by applying specific coatings; if they are going to be used indoors, they may be used in as-cast or machined condition.

**[0022]** In an additional aspect, the invention provides a process for the preparation of alloyed steels with medium manganese and aluminium content as defined above, which comprises the following steps:

(i) Introducing into a furnace the pure elements (at a purity of 99-100 wt. % each) or ferroalloys of the alloy to be prepared;

(ii) Introducing the charge obtained in step (i) into a vacuum chamber and generating vacuum in the range of 0.2 - 20 mbars;

(iii) Initiating the heating of the charge;

(iv) Introducing high purity argon at room temperature at a flow rate of between 0.5 l/min to 5 l/min until arriving at between 2.5-50 mbars;

(v) Increasing the temperature of the charge up to between 1550 and 1700°C;

(vi) Maintain the charge in its molten condition for at least 4 minutes for homogenization;

(vii) Pouring the charge into a mold, allow it to solidify and to cool down below 200 °C, thus obtaining an alloy;

(viii) Submitting the alloy to a normalizing heat treatment, wherein the alloy steel is heated up to a temperature of between 780 and 1250 °C during 1 to 30 hours; and cooling down in calm air until reaching room temperature;

(ix) Submitting the normalized alloy to a subsequent tempering heat treatment, wherein the alloy steel is heated up to between 500 and 780 °C, during 1 to 10 hours, and finally cooled down in calm air until reaching room temperature.

**[0023]** According to a particular embodiment, the furnace is a conventional furnace, such as a Vacuum Induction Melting (VIM) furnace.

**[0024]** In the frame of the present invention, the term "calm air" refers to an environment in absence or nearly absence of air currents or wind, i.e. wind or air currents moving at less than 1 knot, or "cero" (0) on the international scale of wind force known as "Beaufort scale".

**[0025]** In order to obtain the desired composition of the alloy of the invention and prevent oxidation of aluminium and manganese in open air, the alloying elements Mn, Al, Si, Fe and C are added to the furnace in step (i) in the following forms:

◦ Pure manganese (99-100 wt. % Mn)

◦ Pure aluminium (99-100 wt. % Al)

◦ Pure silicon (99-100 wt. % Si),

◦ Pure iron (99-100 wt. % Fe)

◦ Pure graphite (99-100 wt. % C)

**[0026]** The adjustment of the additions and the desired composition are within the skills of a person skilled in the art.

**[0027]** During the process according to the present invention it is necessary to generate vacuum due to the high oxidation of manganese and aluminium in open air. A VIM furnace that has a vacuum chamber may be used for this purpose. The heating is carried out by increasing the power of the furnace progressively to higher power in 20 - 30 minutes to assure no refractory cracking takes place during heating up.

**[0028]** The vacuum during the heating up time is maintained in a value of around 0,2 mbars by pumping out air; when the metal starts melting a argon flow of 5 l/min at 2.5 bar and room temperature is introduced, to assure that a correct degasification of the charge takes place (i.e., removal of oxygen, nitrogen and hydrogen in the charge), without splitting out material. Argon gas is an inert gas that is not dissolved in molten metal, nor reacts with chemical elements in molten condition. The argon flow is maintained a constant pressure of 1.5 mbar.

**[0029]** The metal is heated up until 1650°C is reached, so that sufficient homogenization of the charge takes place.

**[0030]** Before pouring the melt into the mould, the metal must remain molten for a period of time, to allow a correct homogenization of the elements. Typically, time is not less than between 4 and 6 minutes. The melt is poured directly into a keel-block mold, manufactured with chemically bonded sand.

**[0031]** The process for manufacturing further comprises submitting the alloy of the invention to a heat treatment process. This heat treatment process can be carried out in any conventional manner known to the skilled person, and comprises the steps of: submitting the alloyed steel with medium manganese and aluminium content of the invention as-cast to a high temperature, and subsequently cooling; the first step is known as normalizing, and the lower temperature heat treatment and subsequent cooling is known as tempering. In a particular embodiment, the two stages heat treatment is done in a furnace, such as an electrical resistance non-controlled atmosphere heat treatment furnace.

**[0032]** The normalizing heat treatment homogenizes the microstructure of the alloy steel, and a subsequent tempering reduces internal stresses and modifies the microstructure, thus increasing ductility and achieving superior mechanical properties than in the as cast condition.

**[0033]** The normalizing treatment applied consists in heating up the metallic sample, preferably a keel-block sample (see Figure 1), to a temperature of between 780-1250°C; preferred temperature ranges are between 820 and 1100 °C, between 835 and 1100 °C, between 850 and 1000 °C, between 865 and 950 °C, between 880 and 920 °C, for example at about 900°C. The time the alloy as cast is submitted to heat treatment varies depending on factors like the size of the part, the selected temperature, and is typically from 1 to 30 hours, for example during between 1 and 20 hours, between 1 and 10 hours, between 1 and 5 hours, between 1.5 and 2.5 hours, for example during about 2 hours, in a 11kW power Termolab furnace with open air atmosphere. The metallic sample is extracted from the furnace and cooled down in calm air until reaching room temperature.

**[0034]** During the tempering step, which is performed subsequently to the normalizing step, the sample is heated up again up to between 500 and 780°C, during between 1 and 10 hours, and finally cooled down in calm air until room temperature is reached. Thanks to this tempering step, the microstructure is transformed from an acicular martensite phase, to a finer acicular martensite after the normalizing heat treatment, and subsequently to a slight globulized martensite after the tempering heat treatment, which is more ductile (see Figure 17). This heat treatment presents significant advantages over conventional oil quenching and tempering heat treatments carried out to equivalent medium alloyed steels known in the state of the art, such as G42CrMo4 and G26CrMo4. The cooling rate being slower in this case than quenching in oil, provides significant benefits for avoiding deformations in components and potential presence of cracks due to higher accumulated stress.

**[0035]** It has been shown that the normalizing heat treatment, in combination with cooling down in calm air, are very effective to transform the microstructure from coarse needle like martensite into austenite in the heating process, and to reprecipitate into a finer martensite.

**[0036]** As indicated above, the tempering heat treatment step is carried out at temperatures between 500 and 780 °C, preferably between 600 and 700 °C, more preferably at about 650 °C. This process may vary in its duration, and particularly may be between 1 and 20 hours, preferably between 1 and 10 hours, more preferably between 1 and 5 hours, most preferably between 1.5 and 2.5 hours. It has been shown that tempering treatment with cooling in calm air is very effective to transform microstructure from the fine needle like martensite into a globulized martensite.

**[0037]** According to a further aspect the present invention relates to a heat-treated alloy steel obtained by the above method.

**[0038]** The as-cast and the heat-treated low density medium alloy steels with aluminium and manganese of the invention can be used for manufacturing parts for use in diverse sectors like industrial machinery such as machine tool, hand tool and transport sector as aeronautic, marine sector, automotive. According to some embodiments the heat-treated alloyed steels with medium manganese and aluminum content according to the present invention are preferably used for their manufacturing.

**[0039]** Therefore, the present invention is also related to a machinery part comprising the alloy as-cast steel or the

heat-treated alloy steel of the invention.

**[0040]** Illustrative, the heat-treated alloyed steels with medium manganese and aluminum are preferably but non-limiting to examples of parts such as machine shafts, industrial machines and vehicles cogwheels, spanners, cardan forks, crankshafts, camshafts, steering box forks, body and white components and engine mounts.

**[0041]** The following examples are merely illustrative and should not be considered as limiting the invention.

## EXAMPLES

**[0042]** Examples of the alloys according to the present invention are gathered in Table 1; a range of alloys was prepared comprising the components in different weight percentages, presenting different levels of mechanical properties and densities, which allows them to be used in different industrial scenarios.

Table 1 Tensile properties, density and chemical composition of comparative alloys and alloys according to the invention (wt. %)

Alloy	Tensile properties			Density [g/cm <sup>3</sup> ]	Chemical composition (wt. %)				
	Rp0.2 [MPa]	Rm [MPa]	E [%]		Mn	Al	Si	C	Fe*
1 (Comparative)	545	745	22.0	7.74	3.64	0.9	0.25	0.18	bal.
2	433	651	22.1	7.55	3.24	2.0	0.25	0.21	bal.
3	486	684	21.9	7.43	3.78	2.8	0.23	0.19	bal.
4 (Comparative)	472	674	18.1	7.72	3.13	0.9	0.31	0.40	bal.
5	594	806	16.8	7.65	3.46	1.8	0.21	0.40	bal.
6	455	645	18.9	7.40	3.08	2.7	0.37	0.40	bal.
7 (Comparative)	680	935	8.3	7.65	3.66	1.0	0.28	0.61	bal.
8	676	925	7.3	7.62	3.56	1.8	0.24	0.62	bal.
9	664	907	7.5	7.39	3.93	3.1	0.26	0.60	bal.
* This wt. % includes unavoidable impurities, being the total sum lower than 0.1 wt. %.									

**[0043]** The alloys of Table 1 were prepared according to the following examples:

### Preparation of low density medium alloy steels with aluminium and manganese of the invention

#### Example 1: preparation of alloy 1

**[0044]** Different pure elements up to 8 kgs selected to achieve the chemical composition shown below in Table 2 were introduced in adequate amounts into a VIM furnace of 22 kg capacity. To facilitate the dissolution and adjustment of different alloys, certified alloys of purity higher than 99.0 wt. % were used.

**[0045]** Melting was performed, until a temperature of 1650°C was reached. Once the metal started heating, Argon was introduced into the vacuum chamber, up to a vacuum pressure of 1.3 mbar, to avoid splitting.

**[0046]** Once the metal was molten, the metal remained molten for 4 minutes. Pouring was performed into one keel blocks Y2 in order to obtain test specimens for later testing.

**[0047]** The composition of the obtained alloy 1 as cast can be seen in Table 2

Table 2: Chemical composition of alloy 1 (wt. %)\*

	Mn	Al	Si	C	Fe
Composition	3.64 wt. %	0.9 wt. %	0.25 wt. %	0.18 wt. %	balance.
* This wt. % includes unavoidable impurities, being the total sum lower than 0.1 wt. %.					

**Example 2: preparation of alloy 6**

[0048] Different pure elements up to 8 kgs selected to achieve the chemical composition shown below in Table 3 were introduced, in adequate amounts, into a VIM furnace of 22 kg capacity. To facilitate the dissolution and adjustment of different alloys, certified alloys of purity higher than 99.0 wt. % were used.

[0049] Melting was performed, until a temperature of 1650°C was reached. Argon was introduced into the vacuum chamber once the charge started heating until a final pressure vacuum pressure of 1.3 mbars.

[0050] Once the metal was molten, the metal remained molten for 4 minutes. Pouring was performed into one keel blocks Y2 in order to obtain test specimens for later on testing.

[0051] The final composition of the obtained alloy 6 as cast can be seen in Table 3

**Table 3:** Chemical composition of alloy 6 (wt. %)\*

	Mn	Al	Si	C	Fe
Composition	3.08 wt. %	2.7 wt. %	0.37 wt. %	0.40 wt. %	balance
* This wt. % includes unavoidable impurities, being the total sum lower that 0.1 wt. %.					

**Example 3: preparation of alloy 9**

[0052] Different pure elements up to 8 kgs selected to achieve the chemical composition shown below in Table 4, were introduced, in adequate amounts, into a VIM furnace of 22 kg capacity. To facilitate the dissolution and adjustment of different alloys, certified alloys of purity higher than 99.0 wt. % were used.

[0053] Melting was performed until a temperature of 1650°C was reached. Argon was introduced into the vacuum chamber once the charge started melting, until a final pressure of 1.5 mbars.

[0054] Once the metal was molten, the metal remained molten for 4 minutes. Pouring was performed into one keel blocks Y2 in order to obtain test specimens for later on testing.

[0055] The final composition of the alloy 9 as cast obtained can be seen in Table 4.

**Table 4:** Chemical composition of alloy 9 (wt. %)\*

	Mn	Al	Si	C	Fe
Composition	3.93 wt. %	3.1 wt. %	0.26 wt. %	0.60 wt. %	balance
*This wt. % includes unavoidable impurities. , being the total sum lower that 0.1 wt. %.					

**Example 4: Mechanical properties and heat treatment process**

[0056] In the context of the present invention, and unless otherwise stated, the indicated mechanical properties correspond to a test keel block sample. The dimensions and the part of the sample used for metallographic, density and mechanical tests are shown in Figures 1 to 3. unless otherwise stated, the chemical composition is expressed in weight percent with respect to the total weight of the alloy.

[0057] For the tests carried out in relation to the present invention keel blocks Y2 were prepared using chemically bonded sand moulds, following the standard norm UNE-EN 1563:1998. Casted Keel blocks Y2 were then extracted from the moulds and cleaned by shot blasting. These test bars were tested according to UNE-EN ISO 6892-1:2017 standard.

[0058] Keel blocks were then cut and test samples for micrographic inspection of rectangular dimensions of approximately 25 x 20 x 20 mm were prepared by surface polishing and their microstructures were then analysed with a field emission gun scanning electron microscope (SEM) (Model ULTRA PLUS, Zeiss).

[0059] Density was determined using test samples of rectangular dimensions of approximately 25 x 20 x 20 mm using a calibrated scale equipment for weight calculation and a graduated test tube for measuring the volume of the sample for final density calculation.

[0060] Two tensile metal samples coming from keel-blocks have been extracted of a diameter of 6 mm and threaded heads of M8 for tensile testing. These test bars were tested according to UNE-EN ISO 6892-1:2017 standard.

[0061] The alloy 9 once casted as detailed in example 3 was heat treated to obtain a modified microstructure.

[0062] The following heat treatment was varied out to Y2 keel block samples as obtained in example 3.:



(i) heating up to 900°C for two hours and cooling in calm air followed by:

(ii) heating up to 650°C for two hours and cooling down in calm air.

**[0063]** Two tensile metal samples coming from keel-blocks have been extracted, having a diameter of 6 mm and threaded heads of M8. These test bars were tested according to UNE-EN ISO 6892-1:2017 standard. Mechanical properties were calculated as the average of these two results.

**[0064]** The results shown in Table 5 shows that Alloy 6 has similar mechanical properties as G26CrMo4. Whereas alloy 9 has higher Rm and Rp0.2 values than G42CrMo4, and also a good elongation value. The alloys of the invention are lighter in comparison with an alternative G26CrMo4 and G42CrMo4 (EN10293). Alloys 6 and 9 of the present invention have been heat treated following the normalizing plus tempering treatment according to the present invention, in comparison to conventional CrMo alloyed heat treatment of quenching plus tempering.

Table 5: Mechanical properties comparison for alloy 6 with CrMo alloyed steel with similar Rp0.2p and Rm

Alloy	Heat treatment	Rp0.2 [MPa]	Rm [MPa]	E [%]	Density [g/l]
G26CrMo4	QT	>450	600-750	>16	7.84
6	NT	455	645	18.9	7.40
QT: Quenching plus tempering. NT: Normalizing plus tempering					

Table 6: Mechanical properties comparison for alloy 9 with CrMo alloyed steel with similar Rp0.2p and Rm

Alloy	Heat treatment	Rp0.2 [MPa]	Rm [MPa]	E [%]	Density [g/l]
G42CrMo4	QT	>600	800-950	12	7.84
9	NT	664.5	907	7.55	7.39
QT: Quenching plus tempering. NT: Normalizing plus tempering					

**[0065]** The alloy steel of the invention, having a medium manganese and aluminium content, presents a structure consisting of a main matrix of martensite, with variables quantities of ferrite/austenite. The martensite phase corresponds to the dark grey colour, and the ferrite/austenite phase corresponds to the clearer parts, the white phase, in the Metallographic images obtained by Light Optical Microscopy (LOM), shown in Figures 4 to 6.

**[0066]** The modification in the chemical composition has a direct effect on the final microstructure of the alloy steel, and thus on mechanical properties. The increase in aluminium quantity increases the quantity of ferrite (white phase) for a fixed value of carbon, manganese and silicon (see Figure 5). The increase in carbon content increases the quantity of martensite for a fixed value of manganese, aluminium and silicon (see Figure 6).

**[0067]** The density of the alloyed steel of the present invention is lower than the reference value for medium alloyed steel (7.84 g/cm<sup>3</sup>); the highest is the aluminium content, the lowest is the density; whereas no similar effect is observed for C, at contents 0.18 and 0.62 wt.% (see Figures 7 to 9). The density decrement is particularly significant for Al content higher than 2 wt. %. The most favourable cases are 6 and 9 with reduction in percentage compared with the theoretical values of G42CrMo4 and G26CrMo4 (7.84 g/l), being reduced to values of 7.39kg/l (Alloy 6) and 7.40 kg/l (Alloy 9) this represents a reduction of about 5.6-5.7 % in weight. Example 4 shows that Alloy 6 has similar mechanical properties than G26CrMo4, meanwhile alloy 9 has similar Rm and Rp0.2 values than G42CrMo4 and also a good elongation value.

**[0068]** The alloy of the invention does not show a density variation when C content increases from 0.18 wt. % to 0.62 wt. %, as shown in figures 10 and 12.

**[0069]** Elastic yield (Rp0.2) and tensile strength (Rm) slightly increase or are maintained when carbon content increases from 0.2 to 0.4, but increases significantly for C content of 0.6 wt. % (Figures 13 and 15). It is also observed how Rp0.2 and Rm values in the 0.6 wt. % carbon trials don't vary significantly when modifying Al content from 1 to 3 wt. % (Figure 16).

## Claims

1. An alloy steel, comprising:

from 1.8 to 6.0 wt. % Aluminium (Al);  
 from 2.5 to 4.0 wt. % Manganese (Mn);  
 from 0.1 to 0.8 wt. % Carbon (C);  
 from 0.1 to 1.0 wt. % Silicon (Si);  
 0.1 wt. % or less of impurities;  
 iron (Fe) until reaching 100 wt. %.

2. The alloy steel of claim 1, wherein the impurities are at least one of phosphorus and sulphur.

3. The alloy steel of any one of claims 1 and 2, comprising aluminium in an amount of at least 2.0 wt. %; and in an amount of at most 5.0 wt %, preferably of at most 4.0 wt. %, more preferably of at most 3.1 wt. %.

4. The alloy steel of any one of claims 1 to 3, comprising manganese in an amount of at least 2.0 wt. %, preferably at least 2.3 wt. %, more preferably at least 2.5 wt. %; and in an amount of at most 3.8 wt. %, preferably of at most 3.6 wt. %, more preferably of at most 3.4 wt. %.

5. The alloy steel of any one of claims 1 to 4, comprising carbon in an amount of at least 0.12 wt. %, preferably of at least 0.15 wt. %, more preferably of at least 0.18 wt. %; and in an amount of at most 0.74 wt. %, preferably of at most 0.68 wt. %, more preferably of at most 0.62 wt. %.

6. The alloy steel of any one of claims 1 to 5, comprising silicon in an amount of at least 0.15 wt. %, preferably of at least 0.15 wt. %, more preferably of at least 0.21 wt.%; and in an amount of at most 0.79 wt. %, preferably of at most 0.58 wt. %, more preferably of at most 0.37 wt. %.

7. The alloy steel of any one of claims 1 to 6, comprising:

from 1.8 to 3.1 wt. % Aluminium (Al);  
 from 3.0 to 4.0 wt. % Manganese (Mn);  
 from 0.18 to 0.62 wt. % Carbon (C);  
 from 0.21 to 0.37 wt. % Silicon (Si);  
 0.1 wt. % or less of impurities;  
 iron (Fe) until reaching 100 wt. %.

8. A process for the manufacture of the alloy steel of claims 1 to 7, comprising the following steps:

- (i) Introducing into a furnace the pure elements, at a purity of 99-100 wt. %, or ferroalloys, of the alloy to be prepared,;
- (ii) Introducing the charge obtained in step (i) into a vacuum chamber, and generating vacuum in the range of 0.2 to 20 mbars;
- (iii) Initiating the heating of the charge;
- (iv) Introducing high purity argon at room temperature at a flow rate of between 0.5 l/min to 5 l/min until arriving at between 2.5 -50 mbars;
- (v) Increasing the temperature of the charge up to between 1550 and 1700°C;
- (vi) Maintain the charge in its molten condition for at least 4 minutes for homogenization;
- (vii) Pouring the charge into a mold, allow it to solidify and to cool down below 200°C, thus obtaining an alloy;
- (viii) Submitting the alloy to a normalizing heat treatment, wherein the alloy steel is heated up to a temperature of between 780 and 1250 °C during between 1 and 30 hours; and cooling down in calm air until reaching room temperature;
- (ix) Submitting the normalized alloy to a subsequent tempering heat treatment, wherein the alloy steel is heated up to between 500 and 780 °C, during 1 to 10 hours, and finally cooled down in calm air until reaching room temperature.

9. The process according to claim 8, wherein in normalizing heat step (viii) the temperature is between 820 and 1100 °C, preferably between 835 and 1100 °C, more preferably between 850 and 1000 °C, even more preferably between 865 and 950 °C, most preferably between 880 and 920 °C.

10. The process according to any one of claims 8 and 9, wherein in normalizing heat step (viii) the heating is maintained during between 1 and 20 hours, preferably between 1 and 10 hours, more preferably between 1 and 5 hours, most

preferably between 1.5 and 2.5 hours.

11. The process according to any one of claims 8 to 10, wherein in the tempering heat treatment step (ix) the temperature is between 500 and 780°C, preferably between 600 and 700°C.

12. The process according to any one of claims 8 to 11, wherein in tempering heat treatment step (ix) the heating is maintained during between 1 and 10 hours, preferably between 1 and 5 hours, more preferably between 1 and 5 hours, most preferably between 1,5 and 2.5 hours.

13. A heat-treated alloy steel, obtained by the method according to any one of claims 8 to 12.

14. A machinery part, **characterized in that** it comprises the alloy steel as claimed in any one of claims 1 to 7 or 13.

15. The machinery part according to claim 14, **characterized in that** it is selected from machine shafts, industrial machines and vehicles cogwheels, spanners, cardan forks, crankshafts, camshafts, steering box forks, body and white components and engine mounts.

Figure 1

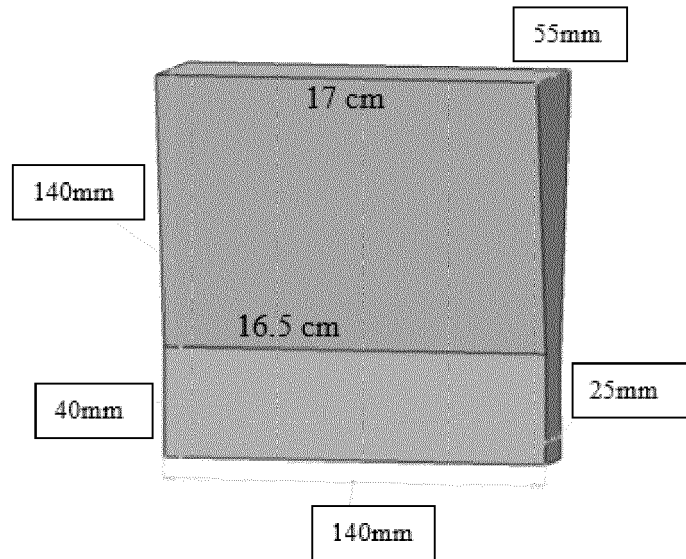


Figure 2

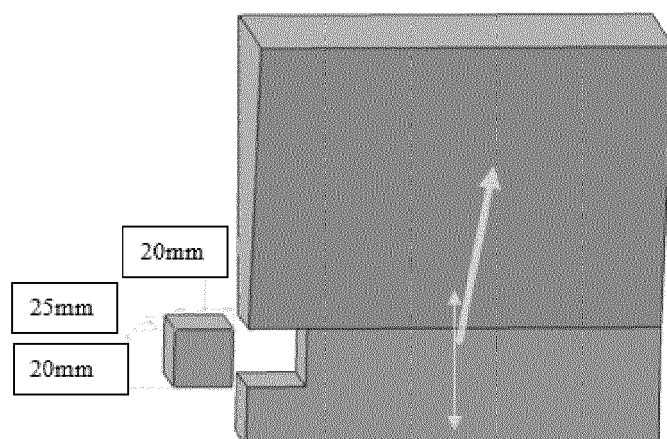


Figure 3

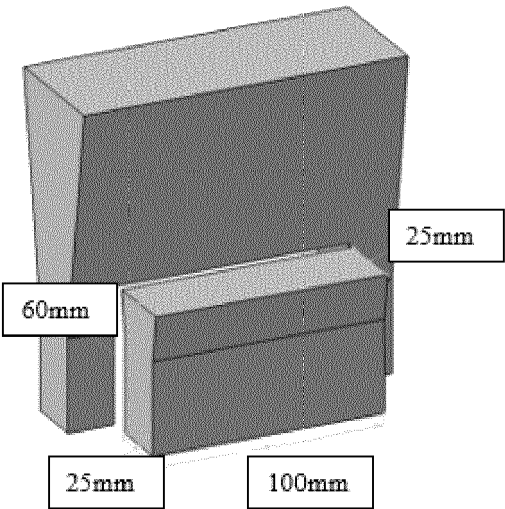


Figure 4

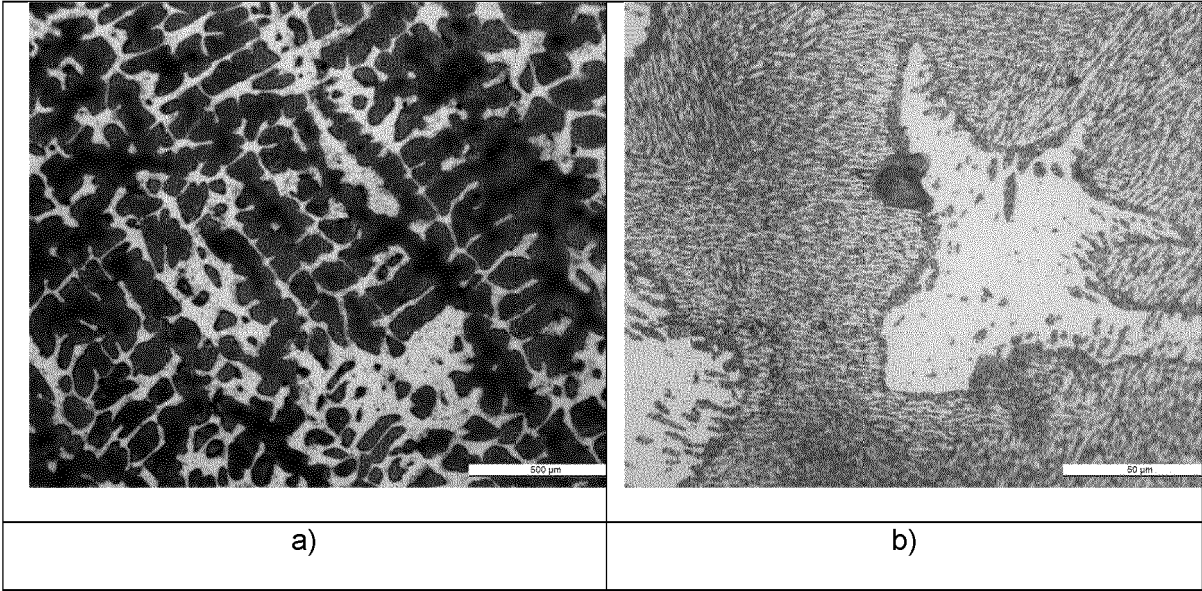


Figure 5

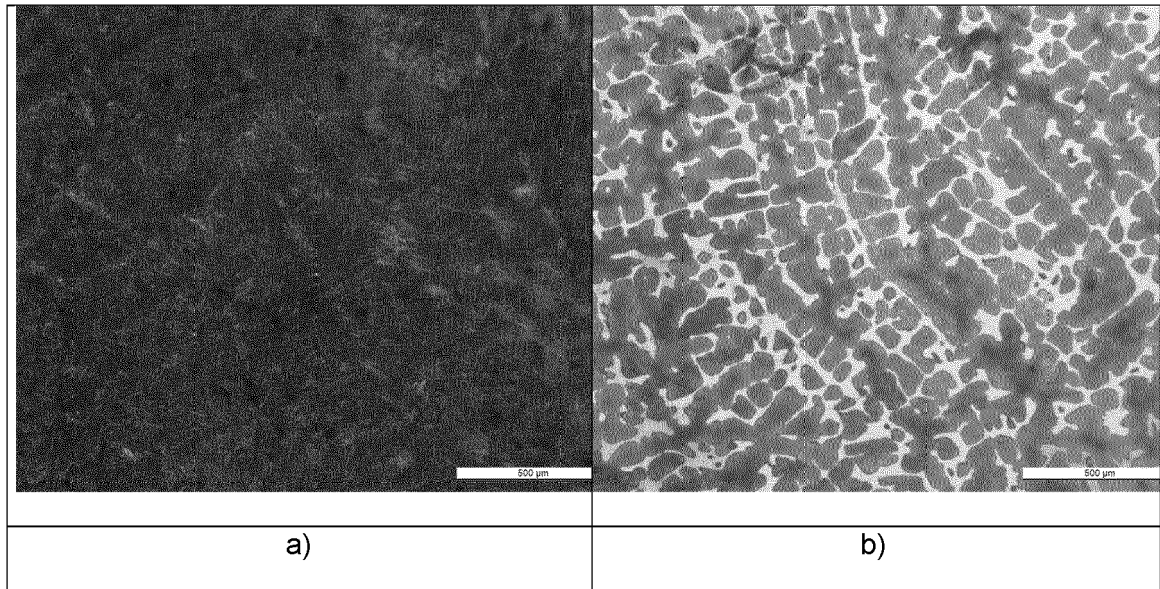


Figure 6

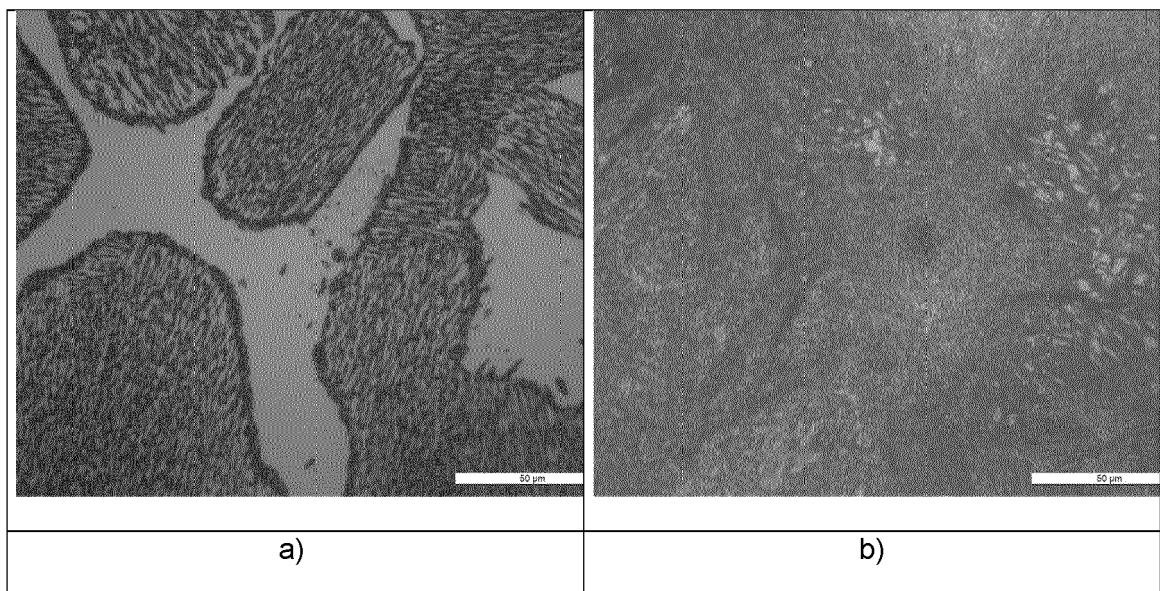


Figure 7

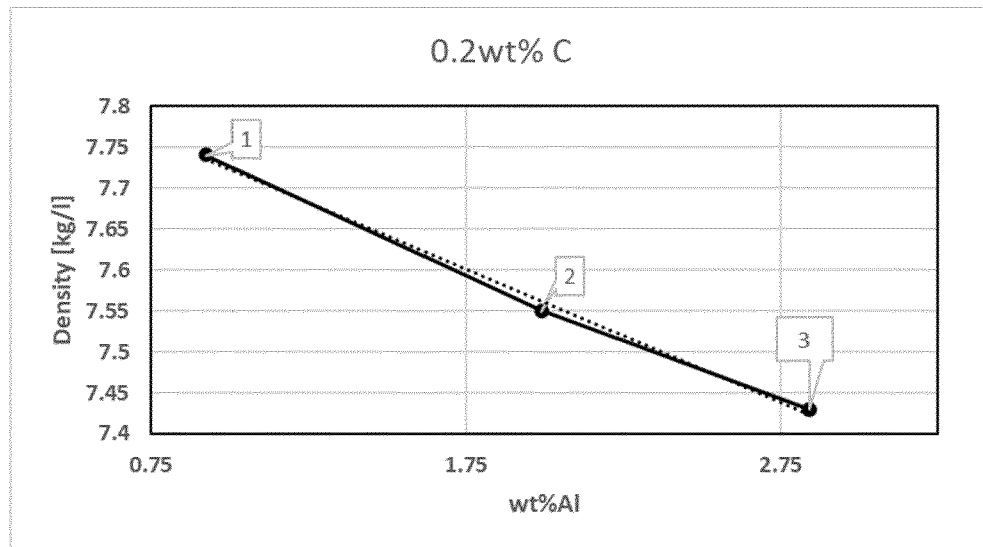


Figure 8

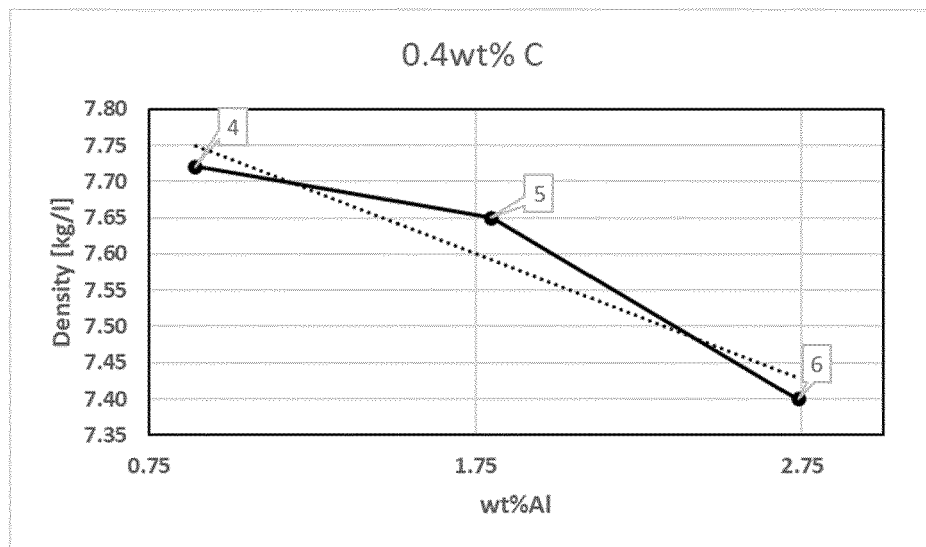


Figure 9

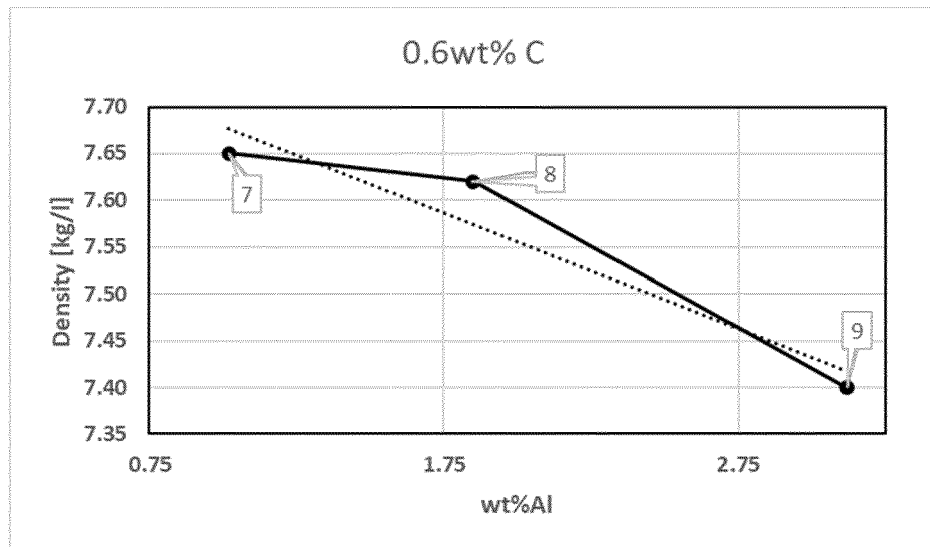


Figure 10

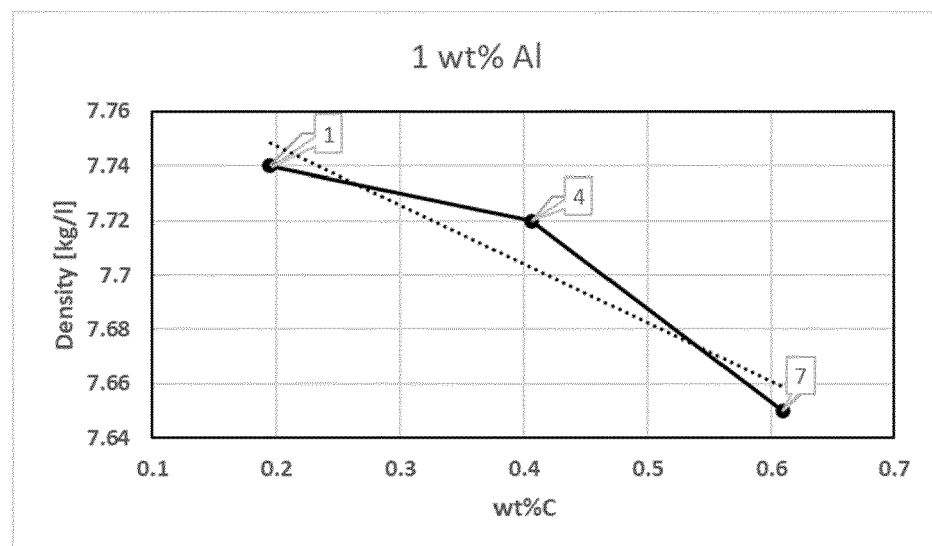




Figure 11

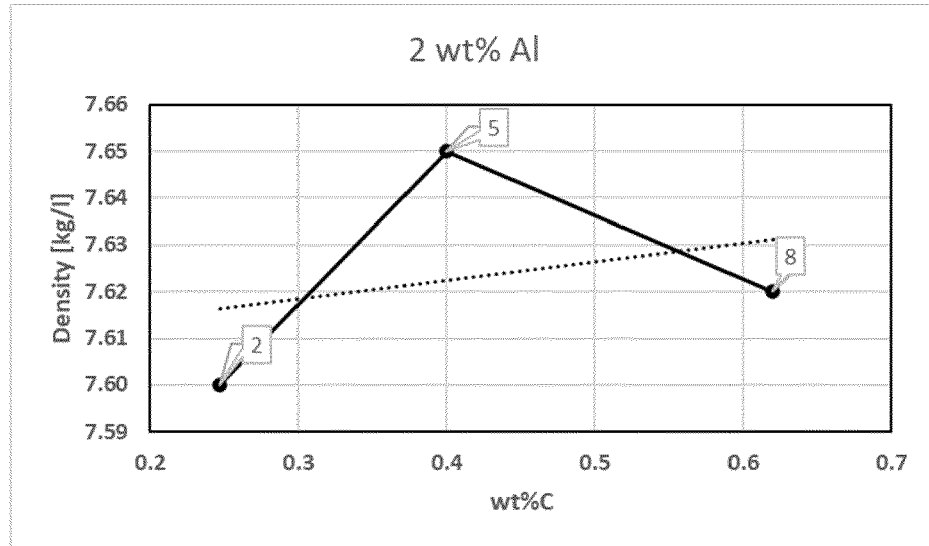


Figure 12

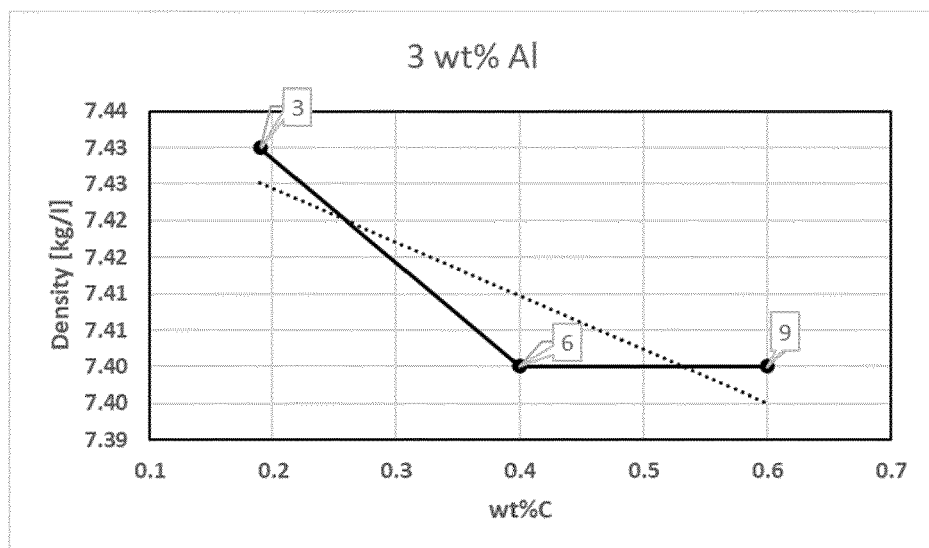


Figure 13

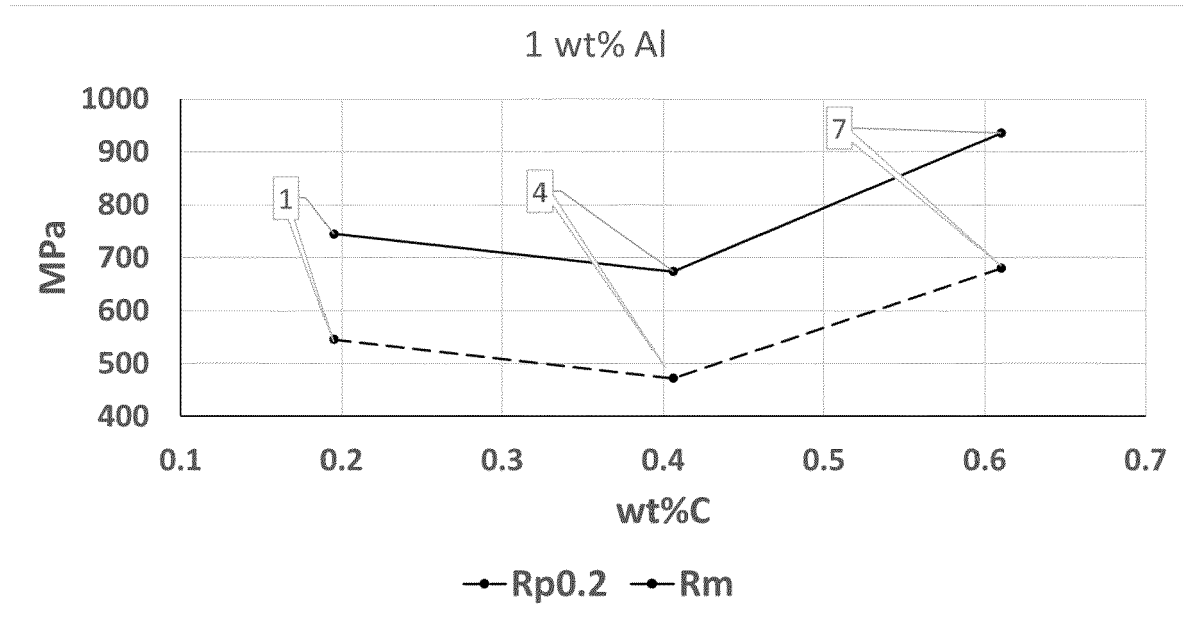


Figure 14

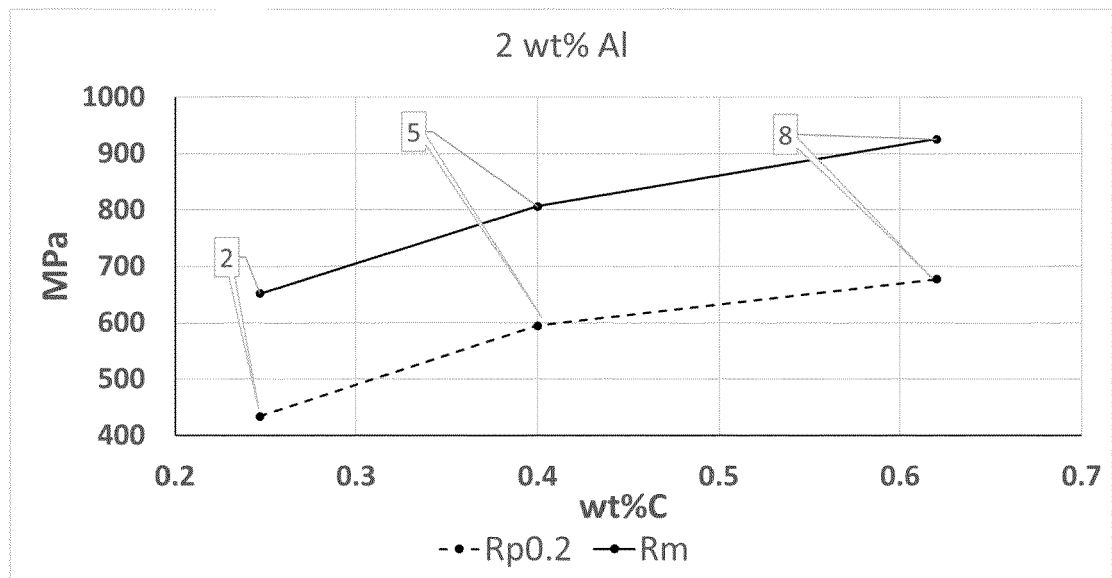


Figure 15

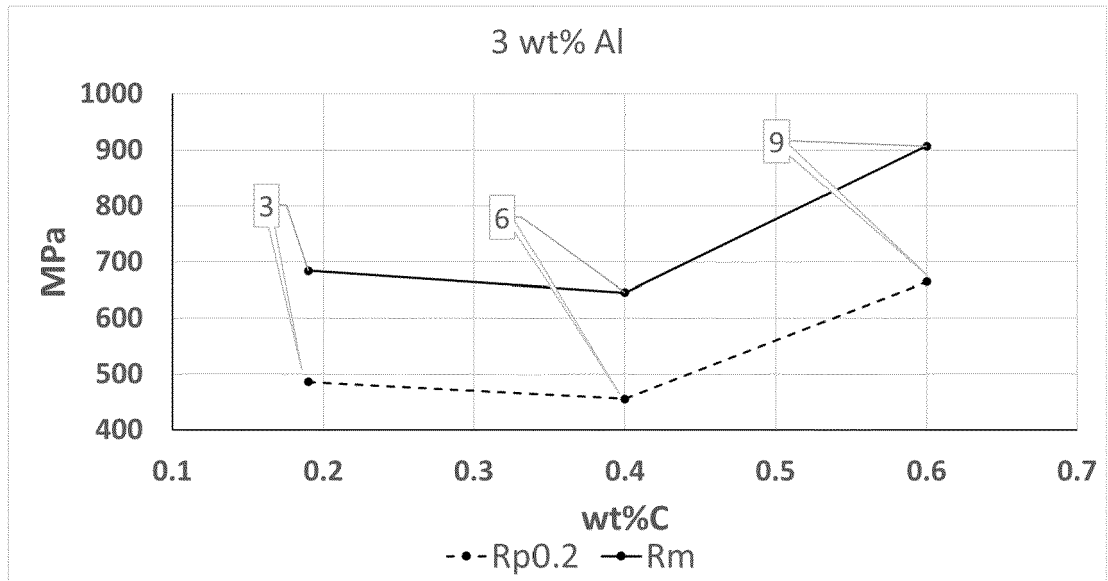


Figure 16

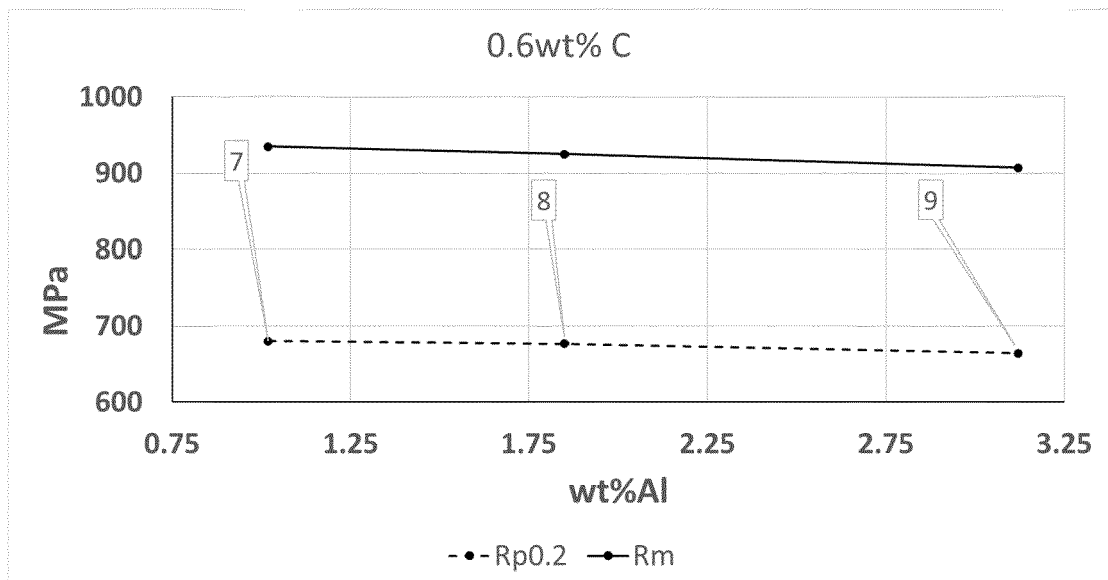
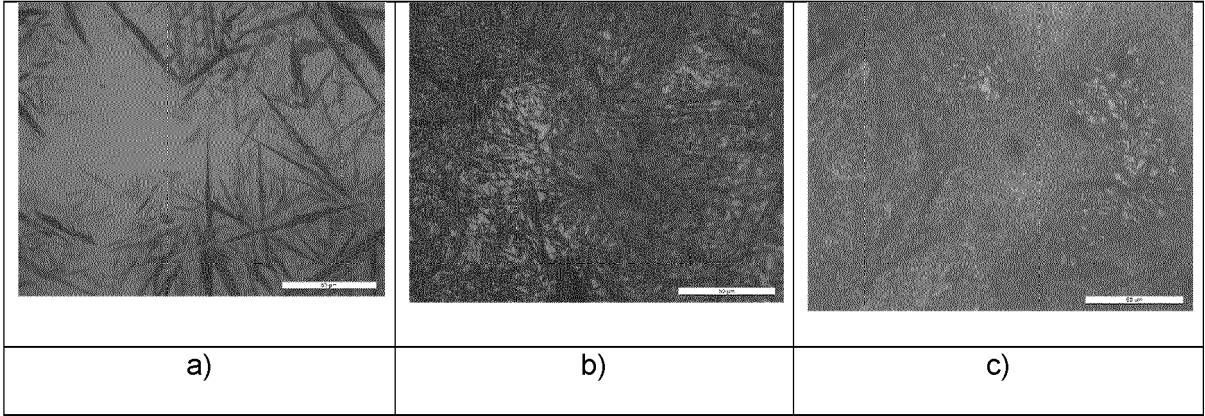


Figure 17





## EUROPEAN SEARCH REPORT

Application Number  
EP 20 38 3154

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	CN 108 707 819 A (UNIV NORTH CHINA) 26 October 2018 (2018-10-26)	1-7, 13-15	INV. C22C37/10
A	* paragraphs [0002], [0014] - [0017]; examples 1, 2 *	8-12	C22C38/02 C22C38/04 C22C38/06
X	CN 106 868 399 A (UNIV NORTHEASTERN) 20 June 2017 (2017-06-20)	1-3,5-7, 13-15	C21D1/28 C21D9/28
A	* paragraphs [0002], [0031] - [0039]; example 2 *	4,8-12	C21D9/30 C21D9/32 C21D9/46
X	CN 108 546 881 A (UNIV NORTHEASTERN) 18 September 2018 (2018-09-18)	1-3,5,6, 13-15	
A	* paragraphs [0002], [0019] - [0024]; example 1 *	4,7-12	
X	WANG HESONG ET AL: "A medium-Mn steel processed by novel twin-roll strip casting route", MATERIALS SCIENCE AND TECHNOLOGY, vol. 35, no. 10, 24 May 2019 (2019-05-24), pages 1227-1238, XP055807407, GB ISSN: 0267-0836, DOI: 10.1080/02670836.2019.1618620 Retrieved from the Internet: URL:https://www.tandfonline.com/doi/pdf/10 .1080/02670836.2019.1618620?needAccess=tru e>	1-3,5,6, 13-15	TECHNICAL FIELDS SEARCHED (IPC) C22C C21D C21C
A	* paragraph [Introduction]; table 1 *	4,7-12	
A	JP 2004 292876 A (KOBE STEEL LTD) 21 October 2004 (2004-10-21) * the whole document *	1-15	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 27 May 2021	Examiner Martinavicius, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

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

EP 20 38 3154

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

27-05-2021

10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 108707819 A	26-10-2018	NONE	
CN 106868399 A	20-06-2017	NONE	
CN 108546881 A	18-09-2018	NONE	
JP 2004292876 A	21-10-2004	NONE	

15

20

25

30

35

40

45

50

55

EPO FORM P0459

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

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Non-patent literature cited in the description**

- **XU et al.** *ISIJ International*, 2015, vol. 55 (3), 662-669  
**[0007]**