



(12) **DEMANDE DE BREVET CANADIEN**
CANADIAN PATENT APPLICATION

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2017/01/02
(87) Date publication PCT/PCT Publication Date: 2017/06/29
(85) Entrée phase nationale/National Entry: 2018/06/21
(86) N° demande PCT/PCT Application No.: EP 2017/050039
(87) N° publication PCT/PCT Publication No.: 2017/109233
(30) Priorités/Priorities: 2015/12/24 (EP15382664.9);
2016/08/04 (EP16382386.7); 2016/12/05 (ES201631552)

(51) Cl.Int./Int.Cl. *C22C 38/00* (2006.01),
C22C 38/04 (2006.01), *C22C 38/06* (2006.01),
C22C 38/08 (2006.01), *C22C 38/10* (2006.01),
C22C 38/12 (2006.01), *C22C 38/14* (2006.01),
C22C 38/20 (2006.01), *C22C 38/22* (2006.01),
C22C 38/24 (2006.01), *C22C 38/28* (2006.01),
C22C 38/38 (2006.01), *C22C 38/42* (2006.01),
C22C 38/44 (2006.01), *C22C 38/46* (2006.01)

(71) Demandeur/Applicant:
ROVALMA, S.A., ES

(72) Inventeur/Inventor:
VALLS, ISAAC, ES

(74) Agent: NORTON ROSE FULBRIGHT CANADA
LLP/S.E.N.C.R.L., S.R.L.

(54) Titre : ACIER HAUTE PERFORMANCE DE GRANDE DURABILITE POUR APPLICATIONS STRUCTURALES,
MACHINES ET OUTILLAGE
(54) Title: LONG DURABILITY HIGH PERFORMANCE STEEL FOR STRUCTURAL, MACHINE AND TOOLING
APPLICATIONS

(57) Abrégé/Abstract:

Steels, in particular hot work steels having high toughness even for high thickness, including steels having long durability combined with mechanical, tribological and thermal properties for highly demanding applications, and steels which can achieve a very good environmental resistance and resistance to certain aggressive media combined with other relevant properties, are described. These steels may also be obtained at low cost. A method for the manufacture of steels having high thickness and manufacturing methods to shape the materials of the invention through several steps, including an additive manufacturing step to manufacture at least a part of an intermediate mold, a mold or a model, a Cold Isostatic Pressing (CIP) step, the elimination of the mold and densification among other steps, are also described.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(10) International Publication Number

WO 2017/109233 A1

(43) International Publication Date
29 June 2017 (29.06.2017)

(51) International Patent Classification:

C22C 38/00 (2006.01) *C22C 38/22* (2006.01)
C22C 38/04 (2006.01) *C22C 38/24* (2006.01)
C22C 38/06 (2006.01) *C22C 38/28* (2006.01)
C22C 38/08 (2006.01) *C22C 38/38* (2006.01)
C22C 38/10 (2006.01) *C22C 38/42* (2006.01)
C22C 38/12 (2006.01) *C22C 38/44* (2006.01)
C22C 38/14 (2006.01) *C22C 38/46* (2006.01)
C22C 38/20 (2006.01)

(21) International Application Number:

PCT/EP2017/050039

(22) International Filing Date:

2 January 2017 (02.01.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15382664.9 24 December 2015 (24.12.2015) EP
 16382386.7 4 August 2016 (04.08.2016) EP
 201631552 5 December 2016 (05.12.2016) ES

(71) Applicant: ROVALMA, S.A [ES/ES]; Carrer de la Collita, 1 - 3, 08191 Rubí, Barcelona (ES).

(72) Inventor: VALLS, Isaac; Carrer de la Collita, 1 - 3, 08191 Rubí, Barcelona (ES).

(74) Agent: ELZABURU S.L.P.; C/Miguel Ángel,21, 28010 Madrid (ES).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

WO 2017/109233 A1

(54) Title: LONG DURABILITY HIGH PERFORMANCE STEEL FOR STRUCTURAL, MACHINE AND TOOLING APPLICATIONS

(57) Abstract: Steels, in particular hot work steels having high toughness even for high thickness, including steels having long durability combined with mechanical, tribological and thermal properties for highly demanding applications, and steels which can achieve a very good environmental resistance and resistance to certain aggressive media combined with other relevant properties, are described. These steels may also be obtained at low cost. A method for the manufacture of steels having high thickness and manufacturing methods to shape the materials of the invention through several steps, including an additive manufacturing step to manufacture at least a part of an intermediate mold, a mold or a model, a Cold Isostatic Pressing (CIP) step, the elimination of the mold and densification among other steps, are also described.

Claims

1. A hot work tool steel having the following composition, all percentages in weight percent:

%Ceq = 0.31 – 0.69	%C = 0.31 – 0.69	%N = 0 - 0.2	%B = 0 – 0.1
%Cr = 2.6 – 6.8	%Ni = 0 – 3	%Si = 0 – 1.8	%Mn = 0 – 5.8
%Al = 0 – 0.4	%Mo = 0 – 4.4	%W = 0 – 7.8	%Ti = 0 – 2
%Ta = 0 – 0.3	%Zr = 0 – 0.4	%Hf = 0 – 0.3	%V = 0 – 2.9
%Nb = 0 – 0.6	%Cu = 0 – 1.2	%Co = 0 – 2.9	%Moeq = 0.01-4.4
%La = 0 – 0.2	%Ce = 0 – 5 0.2	%Cs = 0 – 0.2	

the rest consisting of iron and trace elements

wherein,

$$\%Ceq = \%C + 0.86*\%N + 1.2*\%B; \text{ and}$$

$$\%Moeq = \%Mo + \frac{1}{2} \cdot \%W;$$

With the proviso:

If %B < 20ppm or % Ni < 0.25% then %Mn > 0.8%

2. A hot work tool steel according to claim 1, wherein:

%Mn > 2.1%; and/or

%P is less than 0.018%; and/or

%S is less than 0.0008%; and/or

%P + %S is less than 0.018%.

3. A hot work tool steel according to claim 1 or 2, wherein %Mn > 2.2%

4. A hot work tool steel having the following composition, all percentages in weight percent:

%Ceq = 0.18 – 1.9	%C = 0.18 – 1.9	%N = 0 - 0.1	%B = 0 – 0.1
%Cr < 2.6%	%Ni = 0 – 3	%Si < 0.48%	%Mn = 1.2 – 5.8
%Al = 0 – 0.4	%Mo = 1.2 – 6.4	%W = 0 – 7.8	%Ti = 0 – 2
%Ta = 0 – 0.3	%Zr = 0 – 0.4	%Hf = 0 – 0.3	%V = 0 – 1.4
%Nb = 0 – 0.6	%Cu = 0 – 1.2	%Co = 0 – 2.9	%Moeq = 1.2 – 6.4
%La = 0 – 0.2	%Ce = 0 – 0.2	%Cs = 0 – 0.2	

the rest consisting of iron and trace elements,

wherein,

$$\%Ceq = \%C + 0.86*\%N + 1.2*\%B, \text{ and}$$

$$\%Moeq = \%Mo + \frac{1}{2} \cdot \%W,$$

5. A hot work tool steel according to any of claims 1 to 4, wherein:

%P is less than 0.18%; and/or

%S is less than 0.008%; and/or

%P + %S is less than 0.18%.

6.A hot work tool steel having the following composition, all percentages in weight percent:

%C _{eq} = 0.4 - 4	%C = 0.4 - 4	%N = 0 - 0.6	%B = 0 - 4
%Cr = 0-11	%Ni = 0 - 9.5	%Si = 0 - 4	%Mn = 10 - 40
%Al = 0 - 17	%Mo = 0 - 10	%W = 0 - 6.2	%Ti = 0 - 6.4
%Ta = 0 - 3	%Zr = 0 - 3	%Hf = 0 - 3	%V = 0 - 12
%Nb = 0 - 3	%Cu = 0 - 6	%Co = 0 - 7	%Lu = 0 - 2
%La = 0 - 2	%Ce = 0 - 2	%Nd = 0 - 2	%Gd = 0 - 2
%Sm = 0 - 2	%Y = 0 - 2	%Pr = 0 - 2	%Sc = 0 - 2
%Pm = 0 - 2	%Eu = 0 - 2	%Tb = 0 - 2	%Dy = 0 - 2
%Ho = 0 - 2	%Er = 0 - 2	%Tm = 0 - 2	%Yb = 0 - 2
%P=0-2	%S=0-2		

the rest consisting of iron and trace elements

wherein,

$$\%C_{eq} = \%C + 0.86 * \%N + 1.2 * \%B,$$

wherein %Al+%Si+%Cr+%V>2% and

if %C>0.9% then %Al<10%

7.A hot work tool steel according to any claim 1 to 6, wherein %Ni is between 0.1 and 8%.

8.A hot work tool steel having the following composition, all percentages in weight percent:

%C _{eq} = 0.25 - 2.5	%C = 0.25 - 2.5	%N = 0 - 2	%B = 0 - 2
%Cr= 2.5 - 12	%Ni= 3 - 12	%Si= 0 - 2	%Mn= 0 - 3
%Al= 0.5 - 5	%Mo= 0 - 10	%W= 0 - 15	%Ti= 0 - 3.8
%Ta = 0 - 2	%Zr = 0 - 4	%Hf = 0 - 3	%V= 0 - 1
%Nb = 0 - 2.9	%Cu = 0 - 4	%Co = 0 - 7	%S= 0 - 2
%Se = 0 - 1	%Te = 0 - 1	%Bi = 0 - 1	%As= 0 - 1
%Sb = 0 - 1	%Ca = 0 - 1	%P = 0 - 2	%Pb= 0 - 2
%Cs=0-2	%Sn=0-2		

the rest consisting of iron and trace elements,

wherein

$$\%C_{eq} = \%C + 0.86 * \%N + 1.2 * \%B,$$

With the proviso that:

when %C_{eq}=0.25 - 0.44%, then %V<0.85% and %Ti+%Hf+%Zr+%Ta <0.1%

when %C_{eq}=0.45 - 2.5%, then %V<0.6%;

9.A hot work tool steel having the following composition, all percentages in weight percent:

%C _{eq} = 0.4 - 4	%C = 0.4 - 4	%N = 0 - 1	%B = 0 - 4
%Cr = 0 - 11	%Ni = 0 - 12	%Si = 0 - 2.5	%Mn = 0 - 6
%Al = 0 - 2.5	%Mo = 0 - 10	%W = 0 - 6	%Ti = 0 - 2
%Ta = 0 - 3	%Zr = 0 - 4	%Hf = 0 - 3	%V = 0 - 12
%Nb = 0 - 3	%Cu = 0 - 2	%Co = 0 - 12	%P = 1.5-10

the rest consisting of iron and trace elements,

wherein

$$\%C_{eq} = \%C + 0.86 * \%N + 1.2 * \%B,$$

10.A hot work tool steel having the following composition, all percentages in weight percent:

%C _{eq} = 0.4 - 2.9	%C = 0.4 - 2.9	%N = 0 - 0.6	%B = 0 - 4
%Cr = 2.1-11	%Ni = 0- 9.5	%Si = 0 - 4	%Mn = 0 - 12
%Al = 0 - 9	%Mo = 0 - 6	%W = 0 - 6.2	%Ti = 0- 4.9
%Ta = 0 - 3	%Zr = 0 - 6	%Hf = 0 - 3	%V = 0 - 12
%Nb = 0 -3	%Cu = 0 - 6	%Co = 0 - 7	%Lu = 0 - 2
%La = 0 - 2	%Ce = 0 - 2	%Nd = 0 - 2	%Gd = 0 - 2
%Sm = 0 - 2	%Y = 0 - 2	%Pr = 0 - 2	%Sc = 0 - 2
%Pm = 0 - 2	%Eu = 0 - 2	%Tb = 0 - 2	%Dy = 0 - 2
%Ho = 0 - 2	%Er = 0 - 2	%Tm = 0 - 2	%Yb = 0 - 2

the rest consisting of iron and trace elements

wherein,

$$\%C_{eq} = \%C + 0.86 * \%N + 1.2 * \%B, \text{ and}$$

Wherein

$$\%Al + \%Si + \%Cr + \%Ti + \%Zr > 0.41\%$$

11. A hot work tool steel having the following composition, all percentages in weight percent:

%C _{eq} = 0.41 - 2.9	%C = 0.41 - 2.9	%N = 0 - 0.4	%B = 0 - 1.3
%Cr = 0 - 11.9	%Ni = 0 - 5.9	%Si = 0 - 3.9	%Mn = 1.6 - 11.9
%Al = 0 - 4.9	%Mo = 0 - 4.4	%W = 0 - 7.8	%Ti = 0 - 4.9
%Ta = 0 - 4.9	%Zr = 0.6 - 8.9	%Hf = 0 - 14	%V = 0 - 9.9
%Nb = 0 - 2.8	%Cu = 0 - 3.9	%Co = 0 - 2.9	%Zreq = 0.6 - 8.9
%La = 0 - 0.2	%Ce = 0 - 5 0.2	%Cs = 0 - 0.2	%Moeq = 0 - 4.4

the rest consisting of iron and trace elements wherein,

$$\%C_{eq} = \%C + 0.86 * \%N + 1.2 * \%B; \text{ and}$$

$$\%Zreq = \%Zr + 1/2 \%Hf; \text{ and}$$

$\%Moeq = \%Mo + 1/2 \%W$; and

$\%Mn + \%Zr + \%Ta + \%Hf + \%Ti > 4\%$

12. A hot work tool steel having the following composition, all percentages in weight percent:

$\%Ceq = 0.61 - 3.5$ $\%C = 0.41 - 2.9$ $\%N = 0 - 0.4$ $\%B = 0 - 3.0$

$\%Cr = 0 - 11.9$ $\%Ni = 0 - 5.9$ $\%Si = 0 - 3.9$ $\%Mn = 1.6 - 11.9$

$\%Al = 0 - 4.9$ $\%Mo = 0 - 4.4$ $\%W = 0 - 7.8$ $\%Ti = 0.55 - 9.0$

$\%Ta = 0 - 4.9$ $\%Zr = 0 - 4.9$ $\%Hf = 0 - 3$ $\%V = 0 - 9.9$

$\%Nb = 0 - 2.8$ $\%Cu = 0 - 3.9$ $\%Co = 0 - 2.9$ $\%La = 0 - 0.2$

$\%Ce = 0 - 5.0.2$ $\%Cs = 0 - 0.2$ $\%Moeq = 0 - 4.4$

the rest consisting of iron and trace elements wherein,

$\%Ceq = \%C + 0.86 * \%N + 1.2 * \%B$; and

$\%Moeq = \%Mo + 1/2 \%W$; and

$\%Mn + \%Zr + \%Ta + \%Hf + \%Ti > 2.1\%$

13. A method for the manufacture of a hot working tool steel according to any of claims 1 to 12 having a thickness of more than 303 mm comprising the following steps:

- a) providing a tool steel according to any one of previous claims 1 to 12;
- b) applying to the tool steel a tempering treatment consisting on at least a partial austenization at a temperature above 980°C; and
- c) Optionally apply one or several machining steps and/or heat treatments below the austenization temperature of the material. (also including cryogenic treatments)
- d) tempering the material at least once at a temperature above 520°C,
- e) Optionally apply one or several machining steps and/or heat treatments below the austenization temperature of the material. (also including cryogenic treatments)

14. A manufacturing method comprising the following steps:

- Usage of an additive manufacturing method to manufacture a model a mold or an intermediate mold or partial mold.
- Filling at least part of the mold with particulate material comprising at least one metallic phase.
- Usage of a Cold Isostatic Pressing (CIP) step
- Elimination of the mold.

and a densification step which can be sintering, Hot Isostatic Pressing (HIP) or any other involving high enough temperatures

15. A manufacturing method comprising the following steps:

- Usage of an additive manufacturing method to manufacture an intermediate mold or a part of an intermediate mold.
- (might also include) assembling this part of the intermediate mold to other parts.
- Filling at least part of the mold with particulate material comprising at least one metallic phase.
- Manufacturing a cover mold with a very flexible material using the filled intermediate AM fabricated mold of the previous steps.
- Usage of a Cold Isostatic Pressing (CIP) step
- Elimination of the mold.
- and a densification step which can be sintering, Hot Isostatic Pressing (HIP) or any other involving high enough temperatures.