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(71) Applicant: **Villares Metals S/A**
SP - CEP 13176-900 (BR)

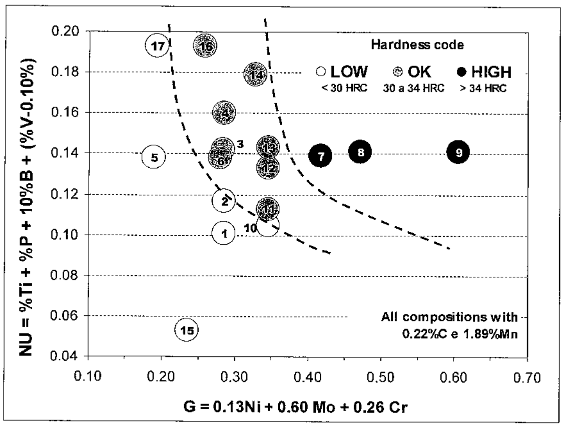
(72) Inventor: **BARBOSA, Celso Antônio**
Campinas - SP, 13100-081 (BR)

(74) Representative: **Earnshaw, Geoffrey Mark**
Murgitroyd & Company
Scotland House
165-169 Scotland Street
Glasgow G5 8PL (GB)

(54) BAINITIC STEEL FOR MOULDS

(57) 1 "BAINITIC STEEL FOR MOULDS", with a composition of alloy elements that consist, in mass percentage, of Carbon between 0.05 and 1.0; Manganese between 0.5 and 3.0; Phosphorous, Boron, Titanium and Vanadium given by the ratio NU = [Ti + P + 10 B + (V-0.10)], being the values of NU between 0.02 and 0.30, with titanium always above 0.005, boron always below 0.010 and Vanadium may be partially or totally replaced with Niobium, in the proportion of two parts in mass of niobium for one part of Vanadium; Nickel, Molybdenum and Chromium given by the ratio G = [0.13 Ni + 0,60 Mo + 0.26 Cr], with values of G above 0.10 and below 1.0; Sulphur up to 0.10; Silicon between 0.05 and 3.0; Nitrogen below 0.10; Calcium with contents up to 0.02; Aluminum below 0.5, Cobalt lower than 2.0, the remaining being substantially Iron and impurities that cannot be avoided in the elaboration process; for its production the final hardness may be obtained by calm air cooling, directly after hot conformation or by previous heating in furnace, even in blocks with section up to 1000 mm; the values of hardness, in Vickers scale, are defined by the equation: HV = (450 $\pm$ 140) %C + (210 $\pm$ 45), for values between 280 and 450 HV (30 to 45 HRC); for applications of high toughness, the steel of present invention may also be produced with quick cooling, from temperatures above 900°C, in water or oil mediums.

Figure 1



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Description

[0001] The present invention refers to bainitic steel for diverse applications in tools, moulds, mould holders, tool holders, having as its main characteristic the homogeneous hardness obtained through a bainitic transformation, without the need of high contents of expensive elements, such as nickel and molybdenum or quenching process. Consequently, such steels provide a considerable cost gain in alloy and the heat treatment of great blocks to which they are applied. The careful design of the alloy, based on its microstructure aspects, provides the steel subject of present invention with hardness and properties close to those of traditional hard alloys used in tools, moulds and bases, but with a significant decrease in their cost.

[0002] The tools and moulds generally are used in other material conformation processes, whether thermoplastic polymeric materials (commonly known as plastic materials) or metallic materials. Depending on the properties of the material used to manufacture them, the tools are used in processes at ambient temperature or at high temperatures that generally reach 700°C. The steels of this invention are applied particularly to moulds or tools that work at ambient temperature, or at temperatures below 500°C, as well as in mould or tool holders for general use. A typical example of such applications would be the moulds for plastic conformation, which generally do not exceed 300°C. Also, they are applied to mould and tool holders, which normally work at ambient temperature, but support the stress of tools used in several conditions.

[0003] Therefore, plastic moulds and mould holders may be considered as typical applications for this invention steels. In such applications, many characteristics of materials from which tools are made are important, some related to mould use and others related to their manufacturing. As to the characteristics of mould or mould holder use, the property of strength is important, being commonly related to the hardness of material, as well as to the homogeneity along the material section. On the other hand, properties such as answer to polishing, texturizing and machining capacity of the material are important for the economic manufacturing of mould or mould holder.

[0004] To reach such requirements, traditional steels suffer a heat treatment by means of quenching and tempering. The quenching treatment is complex for blocks with large dimensions, and need to be quickly cooled in oil tanks or in aqueous media changed with polymers. For blocks applied to large moulds, tanks with more than 80,000 liters are used, resulting in important operating difficulties. Besides the cooling process, the chemical composition of these materials must be improved, with the use of elements that promote hardenability, such as nickel, manganese and molybdenum. As Table 1 shows, these elements are found with significant contents in state of the art steels, also being related to final required hardness.

[0005] In this sense, new developments are being made. The objective of patents EP0805220 and US5855846, for example, is the production of bainitic steels with lower contents of alloy elements for application in moulds. However, in this invention, the hardness is obtained with highest contents of chromium (within the same range of DIN 1.2738), decreasing any possible gain in thermal conductivity and also generating higher cost. The invention US5695576, on the other hand, shows a use concept with high contents of Al and Si, which may damage the machining capacity of alloy, due to the presence of non-metallic inclusions. Also, high contents of Si may damage the hardenability, as will be shown in example 2. The patents PI9602054-7 and PI0308832-4 follow the same concept, but try to obtain only the highest hardness ranges (between 430 and 530 HB) and thickness lower than 200 mm, while the larger volume of applications are the moulds of 300 HB, without fulfilling this need. Neither of these patents show examples of application in great blocks (with thickness above 200 mm) without the need of quenching treatment (i.e., with air cooling). Also, they do not describe the possibilities to avoid possible brittling due to slow cooling, whether by adjustment of alloy or thermal treatment means.

Table 1: State of the art alloys. Only main alloy elements are shown, in percentage in mass and iron balance.

Designation DIN WNr Standard	C	Cr	Mn	Ni	Mo	Typical hardness (HRC)	Notes
1.2738*	0.40	2.0	1.4	1.1	0.20	32	General application
1.2311	0.40	2.0	1.5	-	-	32	Sections up to 500 mm (low hardenabiltity)
1.2312	0.40	2.0	1.5	-	-	32	S= 0.07; for applications with high volume of machining

(continued)

Designation DIN WNr Standard	C	Cr	Mn	Ni	Mo	Typical hardness (HRC)	Notes
1.2711*	0.52	0.75	0.7	1.8	0.3	40	V=0.10
1.2344*	0.36	5.0	-	-	1.2	40 a 50	V=1.0
*Most significant of the class.							

[0006] Therefore, the difficulties and costs involved in obtaining the hardness of tool steel blocks are clear, whether through the chemical composition or a special process of thermal treatment. Consequently, it is evident the need of a steel capable of being hardened to produce large blocks (with sections above 500 mm), without using quick cooling, and also without using significant contents of alloy elements. And preferably, such steel should be able to fulfill the entire hardness range applied to moulds, i.e., between 300 and 420 HB.

[0007] The matter of this invention is to fulfill all these needs.

[0008] The bainitic steel proposed in this invention may be hardened, without the needs of quenching, and also has a lean chemical compositions in terms of high cost elements, such as nickel, molybdenum and chromium.

[0009] In order to fulfill the conditions above, the alloys of present invention have alloy element compositions that, in percentage of mass, consist of:

* Carbon: between 0.05 and 1.0, preferably 0.1 and 0.7, typically 0.15 and 0.6.
* Manganese: between 0.5 and 5.0, preferably 1.0 and 3.0, typically between 1.5 and 2.5. Manganese may be replaced, partially or totally, with nickel or copper, at a ratio of 1 part in mass of manganese to 1 part in mass of copper or nickel.
* Phosphorus, boron, titanium and vanadium: they have a similar effect and, therefore, they must be dosed according to following ratio NU = [Ti + P + 10B + (V-0.10)]; where NU must have values between 0.02 and 0.30, typically between 0.06 and 0.20. Vanadium may be partially or totally replaced by niobium or tantalum, in a mass ratio where 1 part of vanadium is equivalent to 2 parts of niobium or tantalum.
* Titanium: independently of the ratio NU, the minimum titanium contents must be 0.005, typically above 0.015 and preferably above 0.020; however, it never must be higher than 0.10, preferably being below 0.05 and typically below 0.040.
* Boron: besides the ratio above, maximum contents of boron must be controlled, being below 0.010; preferably below 0.007, typically below 0.004.
* Nickel, molybdenum and chromium have similar effect and must be dosed according to following ratio: G = [0.13Ni + 0.60 Mo + 0.26 Cr]; the values of G must be above 0.1 and below 1.0, preferably between 0.2 and 0.5, typically between 0.25 and 0.4. Molybdenum may be partially or totally replaced with tungsten, in a ratio in mass where 1 part of molybdenum is equivalent to 2 parts of tungsten. In this ratio, Ni may be totally or partially replaced with copper, in a ratio where 1 part of nickel is equivalent to 1 part of copper.
* Nickel: besides those above, minimum contents of 0.1 nickel, preferably 0.3, typically 0.4.
* Chromium: besides being contained in ratio G, maximum contents of chromium may be applied of 1.5, preferably below 1.0, typically between 0.1 and 0.8.
* Sulphur: below 0.10, preferably below 0.05, typically between 0.001 and 0.010.
* Calcium: must be present in contents up to 0.010, preferably up to 0.005, typically between 0.0005 (5 ppm) and 0.003 (30 ppm).
* Aluminum: must be below 0.5, typically below 0.1, preferably below 0.02.
* Nitrogen: must be below 0.1, typically below 0.05, preferably between 0.003 and 0.015.
* Silicon: between 0.05 and 3.0, preferably between 0.1 and 2.0, typically between 0.3 and 1.5.

[0010] Iron balance and metallic or non-metallic impurities that are common to steel work processes.

[0011] Following are the reasons for specifying the composition of new material, describing the effect of each alloy element. The percentages indicated refer to mass percentage.

[0012] C: Carbon is the major responsible for the answer to thermal treatment, for the hardness of martensite or bainite, the latter being the most important micro constituent of present invention steels. Carbon contents, therefore, controls the final hardness obtained for steels of present invention, which may vary depending on application requirements. Consequently, carbon contents must be as higher as the necessary hardness (according to an equation defined below in example 5), according to the following equation: Hardness HV = (450 $\pm$ 140) %C + (210 $\pm$ 45).

[0013] However, contents must be below 1.0%, preferably below 0.7%, typically lower than 0.60%, so that, after quenching, the presence of retained austenite is not very high, and also in order to avoid the promotion of high quantities of secondary precipitated carbides in grain contours. According to above ration, carbon contents must be sufficient to promote needed hardness and mechanic resistance of material, and should be above 0.05%, preferably above 0.1 %, typically above 0.15%.

[0014] Mn: since the cost is not high and due to its effectiveness to increase the hardenability, the manganese must be used in high contents in the steel of present invention. Therefore, its contents must be higher than 0.5%, preferably higher than 1.0% and typically above 1.5%. However, when excessive, manganese increases retained austenite and the strain hardening of material, causes loss of machining capacity, and also increases the hydrogen solubility, and promotes the formation of flakes. Therefore, manganese contents must be limited to a maximum of 5.0%, preferably a maximum of 3.0%, being typically below 2.5%.

[0015] P, B, Ti and V: these four elements have a fundamental role in the steel of present invention, acting jointly to decrease the nucleation of diffusion phases, such as ferrite or perlite phases. Depending on the volumetric fraction, these phases may significantly decrease the hardness, and turn infeasible using the material. The explanation of the decrease of nucleation is based on the concentration of these elements in austenite grain contours; these regions have high free energy and, therefore, they are the initial regions of ferrite and perlite formation. When occupied by phosphorous or boron, or even in the presence of titanium and vanadium carbonitrides, the grain contours are unavailable for the formation of diffusion phases, ferrite or micro constituent perlite phases. Consequently, when these phases are inhibited, the thermodynamic conditions generate a bainite formation, with higher hardness and, in the alloys of present invention, also homogeneous along the bar section.

[0016] In this sense, the strongest effect is caused by boron, which was empirically determined as being 10 times higher than that of titanium and phosphorus. In the case of vanadium, part of contents added (about 0.07%) is in sodium solution at 700°C, the temperature at which perlite or ferrite are formed. For this reason, the ratio treats vanadium through the formula (V - 0.10). The titanium also promotes the formation of carbonitrides, but since their solubility is low, the titanium is fully considered in the ratio. Therefore, we come to a ration for NU, which correlates the joint effect of these elements:

$$NU = \%Ti + \%P + 10\%B + (\%V\text{-}0.07\%)$$

[0017] When the total of this ratio is very low, this means that the effect of occupying the grain contours is low, and the diffusion phases must be formed more quickly. The results of several compositions indicate that the minimum amount of this relation must be 0.02%, typically 0.06%.

[0018] However, extremely high contents of phosphorous, boron, titanium or vanadium promote brittling for several reasons. Titanium and vanadium are strong formers of carbides that, when excessive, may facilitate the propagation of cracking. The excess of carbides is also undesirable for mould applications, since they harm the machining and polishing capacities of material. On the other hand, phosphorous, when segregated excessively in grain contours and other interfaces, promotes brittling by decreasing local cohesion (weakening chemical links between atoms in the interfaces). Excessive boron also may promote similar effects to that of phosphorous, however with the great disadvantage of providing the formation of carbides in grain contours, promoting brittling of these regions and material as a whole. For these reasons, maximum contents of these elements must be controlled, with the definition of a limit for NU ratio. The results shown in the examples indicate that the NU must be below 0.30%, typically below 0.20%.

[0019] Ti: although it has been already described above, titanium also has another effect on steel of present invention - to "protect" boron from the reaction with nitrogen (due to higher affinity of titanium with nitrogen than boron with nitrogen). Therefore, it allows boron to have a segregation effect on contours, avoiding its combination with nitrogen. To achieve such effect, titanium must be higher than 0.010%, typically above 0.015%.

[0020] B.: As a strongest brittling effect by boron was identified, this element must also be individually limited, with a maximum of 0.010%, preferably a maximum of 0.007% and typically below 0.004%.

[0021] Ni, Mo e Cr: these three elements promote an increase of hardenability, due to its effect on the growth of diffusion phases, whether distributed in pearlite micro constituents or by proeutectoid ferrite. After formation, these phases have balance contents and, to be formed, the diffusion of elements in excess must occur. The time for this diffusion may delay the formation process, being the effect of chromium, molybdenum and nickel related to this. Traditionally, this effect is quantified by hardenability factors, used in following equation:

$$G = [0.13Ni + 0.60\,Mo + 0.26\,Cr]$$

[0022] This equation shows the combined effect of three elements when inhibiting the growth of formed phase. Associated to previous factor, which inhibits nucleation, it is possible to inhibit the formation of diffusion phases, in the morphology of proeutectoid ferrite or pearlite, thus generating the formation of bainite - with higher hardness and mechanic resistance. Therefore, the value of G must assume a minimum value of 0.1%, preferably above 0.2%, typically above 0.25%. For thinner gauges (for example, lower than 400 mm), lower values of G may be sufficient, such as values between 0.1 % or 0.2%. This is interesting to decrease the final cost of alloy, since nickel, molybdenum and chromium had a significant valorization in the last few years. Besides the cost, contents of these elements must be controlled, to inhibit the formation of martensite. If this phase is obtained, the superficial hardness of blocks or bars will be very superior to nucleus hardness. In other words, excessively high contents of ratio G promote loss of homogeneity of target hardness, besides increasing the cost of alloy. The value of G must be lower than 1.0%, preferably lower than 0.5% and typically lower than 0.4%. The three elements may be replaced with copper that, although being a significant contaminant of scrap material, has a similar effect on hardenability. If copper is used, it must replace nickel, molybdenum or chromium in mass equivalent proportions.

[0023] Ni: besides those above, minimum contents of nickel may be applied to avoid the precipitation of carbides and increase the toughness. In these cases, minimum contents of nickel must be 0.1%, preferably 0.3%.

[0024] Cr: besides being contained in ratio G, maximum contents of chromium may be applied to avoid loss of thermal conductivity. Therefore, chromium contents must be limited to 1.5%, preferably below 1.0% and typically between 0.1 % and 0.8%.

[0025] S: in the steel of this invention, sulphur forms inclusions of manganese sulphide, which become elongated by hot forming process. Since they are malleable and liquid at temperatures developed in the machining process, these inclusions facilitate the break of the flute and lubricate the cutting tool, improving the machining capacity. Therefore, sulphur contents must be above 0.001%, preferably above 0.005%, typically above 0.010%. However, since not all applications require high machining capacity, the use of a sulphur band is optional. Although helping with machining process, the inclusions of manganese sulphide damage the superficial quality given by polishing and also the mechanical properties. Therefore, sulphur contents must be below 0.20%, preferably below 0.05%, typically below 0.010%.

[0026] Ca: calcium also has an effect on inclusions, changing the hard inclusions of aluminum, which harm the machining capacity, decreasing the size (spheroidizing) the inclusions in general. However, the calcium contents control is complex, due to its high reactivity. As such, the use of calcium may also be considered optional, for those cases where high machining and polishing capacities are needed. When used, calcium must be in contents above 5 ppm, preferably above 10 ppm, typically above 20 ppm. Excessive contents of calcium may promote the attack of refractories used in channels and cast devices, excessively increasing the inclusion fraction. Therefore, when added, the final contents of calcium must be below 100 ppm, preferably below 50 ppm, typically below 30 ppm.

[0027] Al: since it forms hard aluminum inclusions, the aluminum contents may not be too high, to avoid damages to machining. It must be below 0.5%, typically below 0.1 %, preferably below 0.05%.

[0028] N: nitrogen is needed to form titanium and vanadium carbonitrides, which inhibit grain growth, help decreasing the free energy of grain contour and avoid nucleation of diffusion phases. On the other hand, excessive nitrogen may react with boron and inhibit the effect of this element in decreasing the energy of grain contour. Also, excessively high contents of nitrogen promote higher formation of titanium carbonitrides, which is harmful to material machining capacity. So, nitrogen must be below 0.1%, typically below 0.05%, preferably between 0.003% and 0.015%.

[0029] Si: besides its use as de-oxidant, which is important in situations where aluminum contents are low, as is the case with the steel of this invention, silicon has an important effect in the formation of carbides. This element inhibits the formation of cementite and, as shown in the examples, of other carbides that precipitate in grain contours and undermine the material. For all these effects, contents of silicon must be between 0.05% and 3.0%, preferably between 0.1 % and 2.0%, typically between 0.3% and 1.5%.

[0030] The process of material production, more specifically its thermal treatment, is also important. As described, the material was designed to have very high hardenability and capacity of homogeneous hardening along the section. Therefore, the material may be air cooled, for most gauges. Such cooling must be employed from a heating temperature above critical AC_3 temperature (approximately 850°C), from a furnace or even directly after hot conformation of material. To obtain better toughness, quicker cooling may be used, for example, through water, oil or forced convection of air, or even water spray. Therefore, the cooling method during hardening may vary, depending on equipment and the toughness required to specific application. This is possible only due to the high hardenability, provided by the fine adjustment of chemical composition previously defined.

[0031] In the following description of experiments performed and compositions studied, reference is made to the attached figures, where:

Figure 1 refers to the graphical distribution of studied compositions as a function of NU and G factors, evaluating the hardness obtained after cooling at 0.05°C/s, beginning on 1,150°C. Hardness between 30 and 34 HRC is considered adequate ("OK"), since this is the main hardness range where state of the art steels are used;

Figure 2 refers to a continuous cooling transformation (CCT) curve, which is typical in the steel of this invention, showing the phases that were formed. Field B indicates bainite, while M and F mean, respectively, martensite and ferrite. Note that for air cooled thick gauges, hardness around 310 HV is obtained, generating the 32 HRC required by application;

Figure 3 refers to a continuous cooling transformation (CCT) curve, which is typical in the state of the art DIN 1.2738 steel, showing the phases that were formed. Fields B_S e B_i indicate, respectively, superior and inferior bainite, while M and P mean, respectively, martensite and pearlite.

Figure 4 refers to hardness measurements in two industrial blocks, in two different gauges, showing high hardness uniformity.

Figure 5 refers to the evaluation of different alloys 18 to 21, as to the toughness to impacts. Gauges and micrographics are shown, in order to relate the values obtained with carbides precipitation.

Figure 6 refers to micrographics obtained for compositions 25 to 28, with different silicon contents. Compositions are shown in Table 5.

Figure 7 refers to micrographics obtained for compositions 29 to 32, with different phosphorous contents. Compositions are shown in Table 5.

Figure 8 refers to micrographics obtained for compositions 33 to 36, with different boron contents. Compositions are shown in Table 5.

Figure 9 refers to microstructures and toughness of samples that were submitted to thermal treatment by solubilization, followed by slow cooling to 950, 850, 750 e 600°C temperatures. Attack: Nital 2%. Increase: 200X.

Figure 10 refers to the evaluation of ratio obtained for hardness as compared to carbon contents: a) comparison of accurate calculated values and by measured hardness; b) equations that forecast the values of hardness between superior and inferior limits, for a variation of ± 20 HB.

[0032] EXAMPLE 1: In order to define the compositions of steel of this invention, several alloys were produced and compared to the state of the art ones. Experimental bars were produced, and chemical compositions that were obtained are shown in Table 2, being hereafter called by their sequence numbers; for comparison, a study of a typical composition of DIN 1.2738 steel (very used in plastic moulds and other applications in tool bases) was conducted. Before discussing the results of hardness, it is interesting to note in Table 3 the significant decrease of alloy elements in this invention compositions, which is converted to lower cost.

[0033] Table 2 shows the values of NU and G, from ratios previously described, related to inhibition of nucleation and growth of diffusion phases. For each composition, studies of dilatometry were made, and the hardness obtained for cooling rate of 0.05 °C/s is also shown in Table 2, being this cooling equivalent to a block of 400 mm air cooled. The objective of such hardness is to be within the range of 30 to 34 HRC, for typical applications of moulds and plastic mould holders. Therefore, the hardness in this range is called as "OK", being the strength out of this range denominated high or low.

[0034] When these results are in the graphical form, as shown in Figure 1, ideal working fields of alloys in this invention are determined; in other words, fields with a combination of NU and G generate hardness within the target range. Therefore, this takes us to working limits of the alloys of this invention, in terms of the elements that form NU (Ti, P, B e V) and G (Cr, Ni and Mo).

Table 2 : Alloys of this invention, studied with different values for Ti, V, B, V, Ni, Cr and Mo, to determine the effect of NU and G ratios.

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	V	Ti	Al	B	N	HRC	HV	G	NU	HARDNESS
					(ppm)					(ppm)	(ppm)	(ppm)	(ppm)	0.05°C/s	0.05°C/s			
1	0.21	0.42	1.91	0.010	27	0.53	0.17	0.34	0.10	320	290	29	120	20.5	205	0.28	0.10	LOW
2	0.21	0.44	1.92	0.023	32	0.53	0.17	0.34	0.10	330	300	31	110	29.8	298	0.28	0.12	LOW
3	0.21	0.42	1.89	0.051	35	0.52	0.17	0.35	0.10	310	280	30	100	30.0	300	0.28	0.14	OK
4	0.2	0.44	1.89	0.067	39	0.53	0.17	0.34	0.10	320	270	31	90	31.3	313	0.28	0.16	OK
5	0.22	0.45	1.91	0.047	28	0.12	0.24	0.10	0.10	310	310	30	63	29.3	293	0.19	0.14	LOW
6	0.21	0.45	1.89	0.047	29	0.47	0.24	0.10	0.10	310	290	30	62	31.0	310	0.28	0.14	OK
7	0.21	0.47	1.9	0.047	28	1.00	0.24	0.10	0.10	320	290	30	61	36.8	368	0.42	0.14	HIGH
8	0.22	0.46	1.87	0.047	35	0.98	0.25	0.51	0.10	340	330	30	61	38.0	380	0.47	0.14	HIGH
9	0.21	0.46	1.89	0.047	60	1.50	0.25	0.51	0.10	340	330	30	59	38.8	388	0.61	0.14	HIGH
10	0.22	0.42	1.88	0.049	22	0.58	0.25	0.34	0.10	20	400	24	60	22.5	225	0.35	0.11	LOW
11	0.22	0.42	1.88	0.049	22	0.58	0.25	0.34	0.10	100	400	24	60	32.0	320	0.35	0.11	OK
12	0.22	0.42	1.88	0.049	22	0.58	0.25	0.34	0.10	300	400	24	60	33.1	331	0.35	0.13	OK
13	0.22	0.42	1.88	0.049	22	0.58	0.25	0.34	0.10	400	400	24	60	34.0	340	0.35	0.14	OK
14	0.20	0.28	1.88	0.047	190	0.61	0.21	0.33	0.14	310	150	31	95	30.5	305	0.33	0.18	OK
15	0.20	0.29	1.90	0.049	250	0.61	0.05	0.35	0.01	310	200	33	89	28.1	281	0.23	0.05	LOW
16	0.20	0.28	1.88	0.052	230	0.70	0.05	0.35	0.15	320	220	29	110	30.6	306	0.26	0.19	OK
17	0.22	0.40	1.86	0.052	80	0.57	0.05	0.11	0.15	300	180	31	98	28.6	286	0.19	0.19	LOW

Table 3 : Composition similar to that of DIN 1.2738 steel. studied in the example.

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	**V**	Ti	Al	B	N
					(ppm)					(ppm)	(ppm)	(ppm)	(ppm)
ET1	0.36	0.40	1.57	0.013	0.0015	1.81	0.24	0.7	0.02	-	290	-	60

[0035] The explanation for this result is directly related to the nucleation and growth mechanisms. First, the elements that promote the decrease of energy in grain contour are fundamental and, therefore, they avoid formation of diffusion compounds, which cause lower hardness (whether proeutectoid ferrite or ferrite and cementite in pearlite morphology). Such role is provided by the elements that form the NU factor of the formula. Titanium and vanadium tend to form precipitated compounds in grain contours (carbides or carbonitrides), decreasing the free energy of these regions. At ferrite or pearlite formation temperature (around 700°C), the solubility of titanium is low, being ignored; however, the solubility of vanadium is high and, therefore, its content is decreased by a factor of 0.07%, equivalent approximately to vanadium in solid solution at 700°C. On the other hand, phosphorous and boron tend to segregate and concentrate in these regions, causing as well the decrease of its energy, consequently avoiding nucleation of diffusion phases. The effect of boron was empirically determined as about 10 times higher the phosphorous effect and, therefore, its factor is multiplied by 10. Besides the intrinsic effect of titanium in the formation of carbonitrides, these compounds remove the free nitrogen from matrix, which tends to react with boron and eliminate the important effect of boron when segregated in the grain contour.

[0036] Besides avoiding nucleation, the presence of the elements that inhibit the growth of diffusion phases is important. The elements that form this factor in the alloy of this invention are manganese, nickel and chromium. The graphic of Figure 1 shows these elements, accounted by the factor G, being the multiplier indexes obtained from classic results of hardenability of elements. Manganese is not accounted in G, because it is constant in all alloys. At very high contents, these elements promote excessive hardenability, generating the formation of martensite and over increasing the hardness. And, in very low quantities, the hardness becomes very low. This occurs because, even being the nucleation inhibited by high NU values, the high growth trend generates the formation of a significant quantity of ferrite or pearlite, decreasing the hardness.

[0037] From 17 alloys shown in graphic of Table 1, some represent very well the effect of the alloy elements studied, as is explained below. Alloys 1 and 2 show the effect of phosphorous contents that, when very low, generates low values of NU, and do not reach required hardness. However when this is higher than 0.020% (alloy 2), hardness is very close to the required one. Alloys 5 and 17 have low chromium, nickel or molybdenum contents, thus damaging the ratio G and, consequently, not achieving the required hardness. On the other hand, alloys 7, 8 and 9 show that contents excessively high of Cr and Ni elements result in high values of G, causing excessively high hardness (due to the formation of part of martensite). Alloy 15 shows the importance of vanadium that, at low contents, generates significant decrease of NU value and, consequently, significant decrease of hardness. Therefore, vanadium may be considered absolutely needed for the alloy.

[0038] One last and important comment refers to alloy 10. This alloy is the only that is out of proposed list, but the reason is simple. Alloy 10 has low contents of titanium, which would cause the decrease of NU value. However, the decrease of hardness was much more significant than foreseen. This occurs because the lack of titanium generates loss of boron effect, since the lack of titanium leaves more free nitrogen to react with boron and, therefore, to promote loss of its effect (described by some authors as effective boron). This synergetic effect cannot be explained by NU and G equations and, therefore, the alloys of this invention have a special requirement as to titanium.

[0039] To give an example, Figure 2 shows the CCT curve of a typical composition of this invention, which may be compared (in Figure 3) to the CCT curve of DIN 1.2738 steel of the state of the art.

[0040] Once the best composition is defined by pilot studies described in example 1, several industrial lots were produced, with different geometries, as shown in Table 4. Figure 4 shows the hardness profile and a photograph of two large blocks produced according to the above composition. The hardness around 285 to 310 H/B (30 to 34 HRC) was obtained with both, without any trend of fall in nucleus regions.

[0041] EXAMPLE 2: In spite of the homogeneous hardness within the adequate range, the industrial heats, particularly in blocks with sections higher than 400 mm, showed a significantly lower toughness than DIN 1,2738 steel (the reference for this application), with values for the impact test without inserts of about 200 joules (test specimen with 7x10 mm). The comparison between values of toughness to microstructure of material showed that the main cause of such low values is the precipitation of carbides in grain contours, as shows Figure 5. Therefore, alternatives were developed for the alloys of this invention to avoid the precipitation of these carbides and the consequent brittling of large blocks.

[0042] As to chemical composition, it was observed that the quantity of carbides grows as boron contents increases and decreases when silicon contents increases, with no significant effect for phosphorous contents; Table 5 shows chemical the compositions used in this evaluation. The conclusions may be based on the compositions of Table 6, with results shown in Figures 6 to 8. It was also observed that nickel has an important effect, as shows the comparison in Figure 5 of alloys 18 and 19, for the same gauge; alloy 18 showed lower quantities of carbides, due to lower contents of nickel.

Table 4: Alloys of present invention, produced in industrial quantities, in blocks with different dimensions, showing the values for hardness obtained, as well as G and NU ratios.

Alloy	C	Si	Mn	P	S (ppm)	Cr	Mo	Ni	V	Ti (ppm)	Al (ppm)	B (ppm)	N (ppm)	Ca (ppm)	Block Dimension (mm x mm)	HB meas ured	HRC conve rted	G	NU
18	0.22	0.4	1.9	0.05	20	0.58	0.25	0.34	0.15	320	100	30	80	6	400x750 and 700x900	302	32	0.35	0.21
19	0.22	0.44	1.89	0.051	90	0.56	0.07	0.32	0.13	310	100	38	130	15	400x750	302	32	0.23	0.20
20	0.23	0.41	1.82	0.049	16	0.55	0.21	0.12	0.13	360	70	46	74	30	400x1200	302	32	0.28	0.21
21	0.29	0.42	1.88	0.027	21	0.55	0.22	0.04	0.15	360	70	25	84	24	400x750 and 850x1200	321	34	0.28	0.19
22	0.23	0.42	1.87	0.028	25	0.55	0.22	0.40	0.14	320	110	25	98	14	400x750 and 850x1200	302	32	0.33	0.18
23	0.23	0.39	1.81	0.027	28	0.60	0.23	0.42	0.14	350	100	23	110	11	400x750	321	34	0.35	0.18
24	0.22	0.37	1.87	0.029	24	0.57	0.22	0.39	0.14	290	90	18	93	11	400x1000	321	34	0.33	0.17

[0043] In the case of boron, although important for the hardenability (example 1), excessive contents help with the formation of these carbides: note that for the quantity of carbides (Table 6) there is twice the increase when boron increases from 20 to 40 ppm.

[0044] Probably, this is due to a high condition of metastability, when high contents of boron are concentrated in grain contours, helping with carbide precipitation.

[0045] The phenomenon is stronger for large bars, with intense microsegregation effects, generating an increase in the local concentration of boron.

[0046] Figure 8 shows this effect, being quite clear the increase in the carbide quantity in samples with higher contents of boron (the precipitation was promoted by a treatment that simulates the cooling of blocks with nucleus higher than 800 mm section, with very slow cooling at 36°C/h).

[0047] A similar effect, however less intense, occurs with the decrease of silicon contents, as shown in Figure 7; the use of silicon contents above 0.40% tends to reduce the formation of these carbides. However, as shown in Table 6, the increase in Si contents reduces the hardenability of this invention material (the fundamental property), particularly for contents above 1.0% (high volume of ferrite in alloy with 2%Si, according to Table 6).

[0048] Therefore, for the production of large bars with high toughness and adequate hardenability, the use of high contents of silicon (between 0.2 and 1.0%), and minimum boron contents is more suitable, being this minimum defined by the factor NU described in Example 1.

Table 5: Alloys of present invention produced to study the effect of P, B and SI contents in the precipitation of carbides that generate brittle in blocks with large dimensions.

Alloy	**C**	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Ni**	**V**	**W**	**Ti**	**Al**	**B**	**N**
					(ppm)						(ppm)	ppm	(ppm)	(ppm)
25	0.23	**0.05**	1.84	0.026	0.003	0.56	0.26	0.41	0.15	0.03	310	420	**59**	77
26	0.23	**0.38**	1.83	0.026	0.003	0.56	0.26	0.41	0.15	0.03	310	420	**57**	71
27	0.23	**0.95**	1.83	0.026	0.003	0.56	0.26	0.41	0.15	0.03	310	450	**60**	70
28	0.24	1.94	1.84	0.026	0.002	0.57	0.26	0.41	0.15	0.03	310	470	**58**	68
29	0.22	0.42	1.89	**0.010**	0.003	0.58	0.27	0.41	0.15	0.02	340	200	56	75
30	0.22	0.42	1.89	**0.025**	0.003	0.58	0.27	0.41	0.15	0.02	340	200	55	75
31	0.22	0.42	1.89	**0.050**	0.003	0.58	0.27	0.41	0.15	0.02	340	200	55	75
32	0.22	0.42	1.89	**0.075**	0.003	0.58	0.27	0.41	0.15	0.02	340	200	55	75
33	0.20	0.41	1.87	0.027	0.003	0.50	0.25	0.41	0.15	<0.01	310	160	**20**	78
34	0.20	0.41	1.85	0.026	0.003	0.49	0.25	0.41	0.15	<0.01	310	160	**40**	75
35	0.20	0.41	1.86	0.028	0.003	0.49	0.25	0.41	0.15	<0.01	310	160	**70**	68
36	0.20	0.42	1.86	0.027	0.003	0.49	0.25	0.41	0.15	<0.01	310	160	**120**	66

[0049] The metallurgical reasons for such effects have distinct explanations, which may be discussed in this document. In high contents, boron tends to concentrate in grain contours, forming complex carbides, particularly with Fe and Cr. Through electronic microscopy analysis performed in the steels of present invention, these two elements were found, as well as traits of Mo. Therefore, a decrease in boron contents eliminates carbides in the origin of problem. However, this decrease cannot be excessive, because to avoid formation of ferrite the presence of boron is required in grain contours, as described in example 1. On the other hand, silicon has low solubility in iron carbide (cementite), avoiding its formation in steels. Since these carbides in the steel of this invention also have high contents of iron, the silicon mechanism may be understood as the same that occurs with cementite.

Table 6: Quantitative measurements of volumetric fraction of carbides in grain contours, by the composite image analysis method of manually identified carbides. Analysis of 10 fields by sample with 100x magnification, totaling a scan of 14 mm^2 for each sample. Previously to measurement, samples were submitted to solubilization at 1.150°C and low cooling at 36 °C/h. Representative images are shown in Figures 6 to 8.

Composition	Volumetric Fraction of Carbides (%) *	Volumetric Fraction of Ferrite
Alloy 25/0.05% Si	0.40	0%
Alloy 26/0.41% Si	0.30	0%
Alloy 27/1.0% Si	0.25	0%
Alloy 28/2.0% Si	0.17	30%
Alloy 28/0.010% P	0.33	28%
Alloy 29/0.025% P	0.36	0%
Alloy 30/0.050% P	0.42	0%
Alloy 31/0.075% P	0.31	0%
Alloy 32/20 ppm B	0.016	0%
Alloy 33/40 ppm B	0.031	0%
Alloy 34/20 ppm B	0.085	0%
Alloy 35/20 ppm B	0.24	0%
* Heats with variations of B, alloys 32 to 35, have lower carbon contents (see Table 5); therefore, they may not be compared with those of other variations, but they may be compared among them, highlighting boron effect.		

[0050] EXAMPLE 3: Besides the change in chemical composition, a way to avoid such precipitation is to promote the quick cooling - from high temperature, where carbides are not present yet. These tests were performed as shown in Figure 9; note that below 800°C the drop in toughness is more significant, particularly between 750°C and 600°C, being this drop followed by carbide precipitation.

[0051] In order to reduce such intense precipitation, after forging or after a treatment of austenitizing/solubilization, the block may be quickly cooled. Such process was designed based on the results of numerical simulation, and may be applied by cooling in oil or water. In the case of water, to avoid cracks, some steps on air may be introduced, reducing the temperature difference existing between the surface and nucleus. Table 7 shows the results of such experiments, observing a significant increase of strength when the cooling speed is superior. Obviously, this process must be applied to large blocks, where cooling rates are inherently low, or in situations requiring high strength. In opposite cases, air cooling may be applied.

Table 7: Data from simulation and results obtained in impact test bodies, for different conditions of cooling of present invention steel blocks. The values for the impact energy refer to test bodies without inserts, section 7x10mm, transversal direction.

Block section	Cooling *	$t_{(900-600)}$	Impact energy
420 mm x 1040 mm	Calm Air	130 min	55 J
	Water = 30 min, after T_S = 700°C	60 min	156 J
* The process proposed in water may be performed in oil; for the 400mmx1000mm gauge, with permanence for 60 min in oil. T_S = surface temperature.			

[0052] EXAMPLE 4: In previous examples, chemical composition and thermal treatment of steel proposed for this invention were defined. Due to the use of titanium in the chemical composition, hard particles of carbonitrides are formed - resulting in higher wear of tools, and damaging material machining capacity. For mould applications, the aspects of machining are essential.

[0053] To avoid this, alloys of present invention were studied in terms of highest contents of sulphur and calcium. These two elements influence the formation of inclusions. Sulphur forms manganese sulphides, which have low hardness and help breaking the chip and tool lubrication. On the other hand, calcium changes hard aluminum inclusions, generating complex inclusions with better machining capacity. The addition of calcium also spheroidizes the inclusions, generating better polishing conditions, which is also an important operation for plastic moulds.

[0054] Table 8 shows the results of machining for the steel of this invention, with this change in sulphur and calcium contents in alloy 19, and without this change in alloy 18. By comparison, the same test was performed with DIN 1.2738 steel (reference for application in moulds). There is a noticeable increase in the tooled volume, with change performed in calcium and sulphur contents (of alloys 18 and 19).

[0055] An alternative to improve machining capacity would be to reduce the volumetric fraction of carbonitrides, thus reducing the cause of accelerated wear of tools. The combination of the effect of decreasing carbonitride volume plus the use of high contents of sulphur and calcium was used in alloy 37. Although similar in composition to alloy 19, there was a significant increase in machining capacity, associated to a drastic decrease of titanium cabonitride volume. In this case, the decrease of carbides was performed by the increase of solidification speed, through the use of a smaller bar. However, the same may occur by reducing contents of nitrogen or titanium. Since titanium is important for NU factor, discussed in example 1, the use of low contents of nitrogen, as controller of carbonitride volume, proves to be most important.

Table 8 : Comparison of machining capacity of alloys 18, 19 and state of the art alloy, measured by the volume tooled up to the end of tools lifecycles (V_B = 0.20 mm). Test conditions: tool = hard metal P25 coated with TiN, with 25 mm diameter, cut speed = 270 m/min, advance = 0,25 mm/tooth, cut depth = 0,75 mm and working penetration = 10 mm. Below are the results of chemical compositions. Carbonitride volumetric fraction was measured by computer image analysis, in 20 fields at 500 x in each sample, totaling a scan of 0.56 mm^2.

Alloy	**Tooled Volume**	**Fraction Volume of Carbonitride larger than 8 microns**
ET1 (DIN 1.2738)	380 cm^3	(absent)
18	210 cm^3	0.23%
19	270 cm^3	
37	580 cm^3	0.025%

Alloy	C	Si	Mn	P	S	Cr	Mo	Ni	V	Ti	Al	B	N	Ca
					(ppm)					(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
ET1	0.39	0.4	1.66	0.011	16	1.87	0.17	0.74	<0.01	<50	90	<10	44	17
18	0.22	0.40	1.90	0.050	20	0.58	0.25	0.34	0.15	320	100	30	80	6
19	0.22	0.44	1.89	0.051	90	0.56	0.07	0.32	0.13	310	100	38	130	15
37	0.21	0.41	1.88	0.026	70	0.59	0.26	0.34	0.10	260	74	27	74	22

[0056] EXAMPLE 5: The entire design of previous alloy was based to provide 30 to 34 HRC hardness, since this is the main use range for mould steels. For conventional steels, higher hardness may be obtained using different conditions of annealing treatment. In the steel of present invention, with direct hardening through forging, this may not be performed. Therefore, this invention also tried to provide an alternative to increase hardness, through a change in chemical composition.

[0057] From the base composition described in Example 1, compositions with different carbon contents were produced, simulating by dilatometry the cooling of a nucleus in a block with section of about 400 mm (rate of 0.05°C/s). The results in Table 9 and Figure 10 show that higher hardness may be obtained when highest contents of carbon are used. Based on these data, a ratio was experimentally obtained for carbon contents and hardness after slow cooling. This is the ratio:

$$\text{Hardness HV} = 450\ \%\text{C} + 210.$$

(hardness obtained after cooling at 0.05°C/s, equivalent to air cooling of a block with 400 mm thickness).

Table 6: HV hardness values, obtained after cooling at 0.05°C/s in compositions with different carbon contents.

Alloy	**C**	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Ni**	**V**	**W**	**Ti**	**Al**	**B**	**N**	**HV**
					(ppm)						(ppm)	(ppm)	(ppm)	(ppm)	rate 0,05°C/s
38	0.23	0.28	1.88	0.047	0.002	0.61	0.21	0.33	0.14	<0.01	310	150	31	95	**305**
39	0.30	0.28	1.88	0.049	0.002	0.61	0.21	0.33	0.14	<0.01	320	150	32	98	**356**
40	0.39	0.28	1.87	0.049	0.002	0.61	0.21	0.33	0.14	<0.01	320	150	31	88	**376**
41	0.45	0.28	1.87	0.051	0.002	0.61	0.21	0.33	0.14	<0.01	320	150	32	86	**412**

[0058] Therefore, this example shows that it is possible to assign different hardness to the alloy of this invention, adjusting carbon contents. For example, for hardness 315 HV (approximately 32 HRC), the range obtained in Example 1 is confirmed, being necessary 0.23% of carbon. On the other hand, for hardness of 400 HV (about 40HRC), 0.42% of carbon contents would be necessary.

[0059] As shown in Table 1, the state of the art steels for that same hardness range have carbon contents significantly higher: DIN 1.2738, hardness of 32 HRC and 0.36% of carbon, and DIN 1.2711, hardness of 40 HRC and 0.52% of carbon. This fact has an interesting consequence for the welding processes, which are very used in moulds. Since they work with lowest carbon contents, the hardness of heated region will be much lower in the steel of present invention, as compared to state of the art steels. For carbon contents of 0.23%, the steel of present invention generates an approximate hardness of 45 HRC in the region affected by welding, while this hardness is about 60 HRC for DIN 1.2738 steel and 64 HRC for DIN 1.2711. This fact helps in many machining operations after welding, as well as in the aspect after polishing or texturisation.

[0060] Small variations in indexes of previous equations may produce adequate results, within the necessary hardness range for the applications. For a $\pm$ 20 HB variation, commonly accepted in the industry, the ratio may vary according to Figure 10b, being described by following relations: Superior hardness = 590 % C + 165 and Inferior Hardness = 310 %C + 255. Therefore, a final equation for hardness as a function of carbon contents may be described as follows:

$$\text{Hardness HV} = (450 \pm 140)\ \%C + (210 \pm 45).$$

[0061] Therefore, depending on the industrial application and the necessary hardness, carbon contents in the steel of present invention must be calculated by above equation.

Claims

1. "BAINITIC STEEL FOR MOULDS", **<u>characterized</u> by** a chemical composition of elements that consist, in mass percentage, of Carbon between 0.05 and 1.0; Silicon up to 1.0, Manganese between 0.5 and 5.0; Phosphorous, Boron, Titanium and Vanadium given by the ratio NU = [Ti + P + 10 B + (V-0,10)], being the values of NU between 0.02 and 0.30, with titanium always above 0.005, boron always below 0.010 and Vanadium may be partially or totally replaced with Niobium, in the proportion of two parts in mass of niobium for one part of Vanadium; Nickel, Molybdenum and Chromium given by ratio G = [0.13 Ni + 0.60 Mo + 0.26 Cr], with values of G above 0.10 and below 1.0; Sulphur up to 0.20; Silicon between 0.05 and 3.0; Nitrogen below 0.10; Calcium with contents up to 0.010; Aluminum below 0.5, Cobalt lower than 2.0, the remaining being substantially Iron and impurities that cannot be avoided in the elaboration process.

2. "BAINITIC STEEL FOR MOULDS", according to claim 1, **<u>characterized</u> by** a chemical composition of elements that consist, in mass percentage, of Carbon between 0.10 and 0.6; Silicon up to 1.0, Manganese between 0.8 and 3.0; Phosphorous, Boron, Titanium and Vanadium given by the ratio NU = [Ti + P + 10 B + (V-0.10)], being the values of NU between 0.08 and 0.30, with titanium always above 0.005, boron always below 0.010, titanium between 0.005 and 0.10, and Vanadium may be partially or totally replaced with Niobium, in the proportion of two parts in mass of niobium for one part of Vanadium; Nickel, Molybdenum and Chromium given by ratio G = [0,13 Ni + 0,60 Mo + 0.26 Cr], with values of G above 0.20 and below 0,50; besides this ratio, Chromium contents must be between 0.1 and 1.5, and Nickel contents above 0.3; Sulphur up to 0.05; Silicon between 0.05 and 3.0; Nitrogen below 0.05; Calcium contents up to 0.005; Aluminum below 0.1, Cobalt lower than 1.0, the remaining being substantially Iron and impurities that cannot be avoided in the elaboration process; the material may be produced in blocks of up to 850 mm of thickness, being obtained the hardness between 250 and 450 HV through air cooling from a temperature above 700°C, and the value of this hardness is given by the equation HV = (450 $\pm$ 140) %C + (210 $\pm$ 45).

3. "BAINITIC STEEL FOR MOULDS", according to claim 2, **<u>characterized</u> by** a chemical composition of elements that consist, in mass percentage, of Carbon between 0.10 and 0.6; Silicon between 0.05 and 0.6; Manganese between 1.3 and 3.0; Phosphorous, Boron, Titanium and Vanadium given by the ratio NU = [Ti + P + 10 B + (V-0.10)], being the values of NU between 0.10 and 0.20, with titanium always above 0.010, boron always below 0.0050, and Vanadium may be partially or totally replaced with Niobium, in the proportion of two parts in mass of niobium for one part of Vanadium; Nickel, Molybdenum and Chromium given by ratio G = [0.13 Ni + 0.60 Mo + 0.26 Cr], with values of G above 0.25 and below 0.40; besides this ratio, Chromium contents must be between 0.1 and 1.0, and Nickel contents between 0.2 and 1.0; Sulphur between 0.001 and 0.010; Silicon between 0.20 and 1.5; Nitrogen

between 0.0040 and 0.0150; Calcium with contents between 0.0005 and 0.0030; Aluminum below 0.05, Cobalt lower than 1.0, the remaining being substantially Iron and impurities that cannot be avoided in the elaboration process; the material may be produced in blocks of up to 850 mm of thickness, being obtained the hardness between 280 and 450 HV through air cooling, directly after hot conformation, with the value of this hardness given by the equation HV = (450 $\pm$ 140) %C + (210 $\pm$ 45).

4. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, **characterized by** a chemical composition of elements consisting essentially, in mass percentage, of Carbon between 0.18 and 0.52, Chromium between 0.30 and 0.60, Molybdenum between 0.10 and 0.50, Nickel between 0.30 and 0.50, Vanadium between 0.04 and 0.10; Boron between 0.0010 and 0.0030; Sulphur between 0.0010 and 0.0100; Calcium between 0.005 and 0.030; Nitrogen between 0.0030 and 0.0100; where final use hardness is obtained directly after forging or lamination, with relatively high gauges, thicknesses between 100 and 1000 mm, without the need to use oil or water hardening processes; thermal treatment must be calm air cooling with forced convection, being the Vickers hardness value determined by alloy carbon contents, according to following ratio: HV = (450 $\pm$ 140) %C + (210 $\pm$ 45), for hardness values between 280 and 420 HV, equivalent to 29 and 42 HRC.

5. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, **characterized by** a G ratio lower than 0.10, for applications in gauges lower than 400 mm of thickness, being G calculated by following ratio: G= [0.13 Ni + 0.60 Mo + 0.26 Cr], where symbols represent contents in mass percentage of relevant elements.

6. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, **characterized by** manganese contents, partially or totally replaced with Nickel or Copper, in equal quantities, in mass percentage.

7. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, **characterized by** containing, in mass percentage, the elements Niobium, Zirconium or Tantalum replacing, partially or totally the elements Titanium or Vanadium, in a relation of 2 parts of Niobium corresponding to 1 part of Vanadium or Titanium, and 1 part of Tantalum or Zirconium corresponding to 2 parts of Vanadium or Titanium.

8. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, characterized for showing, in mass percentage, Boron between 0.0015 and 0.0030; Silicon between 0.40 and 1.2.

9. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, characterized for showing, in mass percentage, Sulphur between 0.002 and 0.090 and Calcium between 0.0005 and 0.0030.

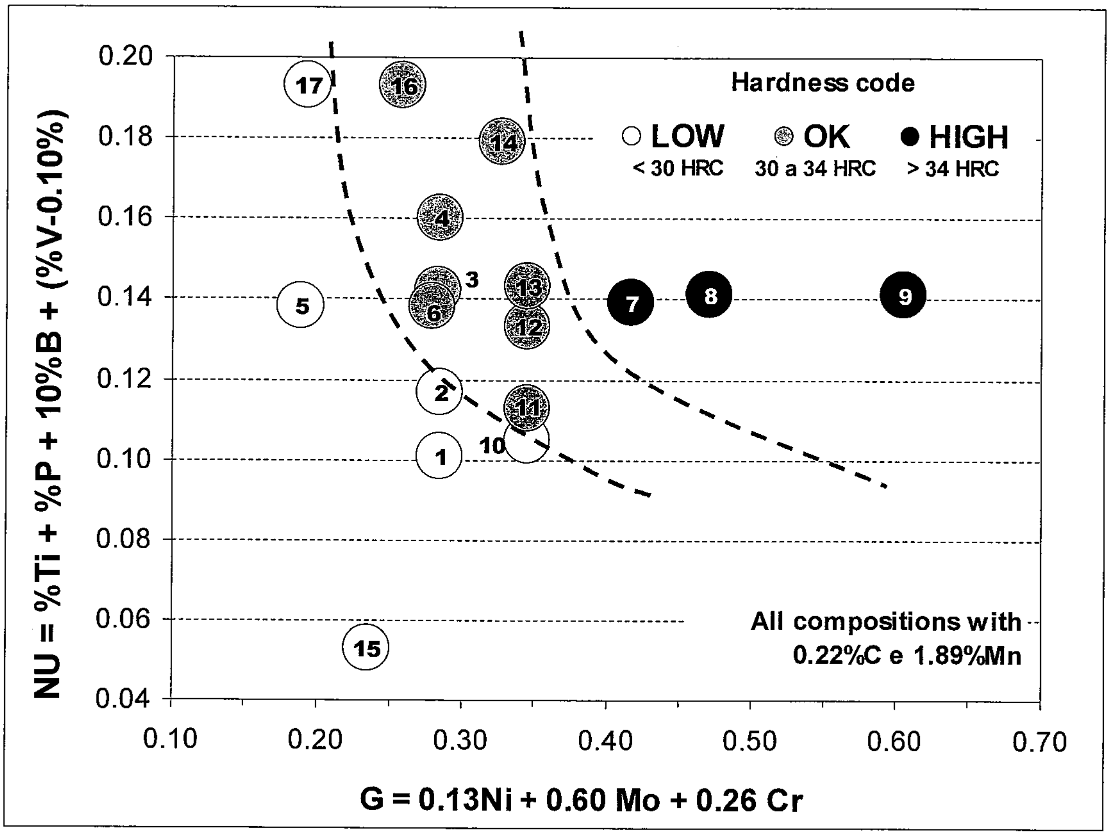
10. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, **characterized by** a final hardness obtained by air cooling, directly after hot conformation or through previous heating in furnace, being the final hardness obtained (in the Vickers scale) given by the equation: HV = (450 $\pm$ 70) %C + (210 $\pm$ 22), or even an equation equivalent via a hardness conversion by the measures of other scales.

11. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, characterized for having, in parts per million in mass, sulphur between 0.002 and 0.30, and calcium between 0.0005 and 0.010, and by having in its microstructure a volumetric fraction of carbonitrides lower than 0.25%, applied to situations where high machining capacity is needed.

12. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 3, **characterized by** having an increase in toughness via quick cooling, after hot conformation or heating at temperatures above 900°C.

13. "BAINITIC STEEL FOR MOULDS", according to any claim from 1 to 12, **characterized by** having an increase in toughness via quick cooling, after hot conformation or heating at temperatures above 900°C, being this cooling process given by following thermal treatment: air cooling up to the temperature of 700°C, then going to a water tank for 30 minutes (maintaining the temperature of water below 80°C), followed by air cooling up to the ambient air temperature; in case of parts susceptible to cracks, the time of water cooling may be replaced with 60 minutes in oil cooling, maintaining constant all other conditions of thermal treatment.

Figure 1


Hardness code
LOW
< 30 HRC
OK
30 a 34 HRC
HIGH
> 34 HRC
All compositions with
0.22%C e 1.89%Mn
NU = %Ti + %P + 10%B + (%V-0.10%)
G = 0.13Ni + 0.60 Mo + 0.26 Cr
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.10
0.20
0.30
0.40
0.50
0.60
0.70
1
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11
12
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14
15
16
17

Figure 2

Element	Contents (%)
C	0,21
Si	0,29
Mn	1,88
P	0,049
S	0,002
Co	0,05
Cr	0,61
Mo	0,21
Ni	0,33
V	0,14
W	<0,01
Cu	0,2
Ti	0,033
Nb	<0,01
Al	0,015
Sn	<0,005
N	0,0089
B	0,0055

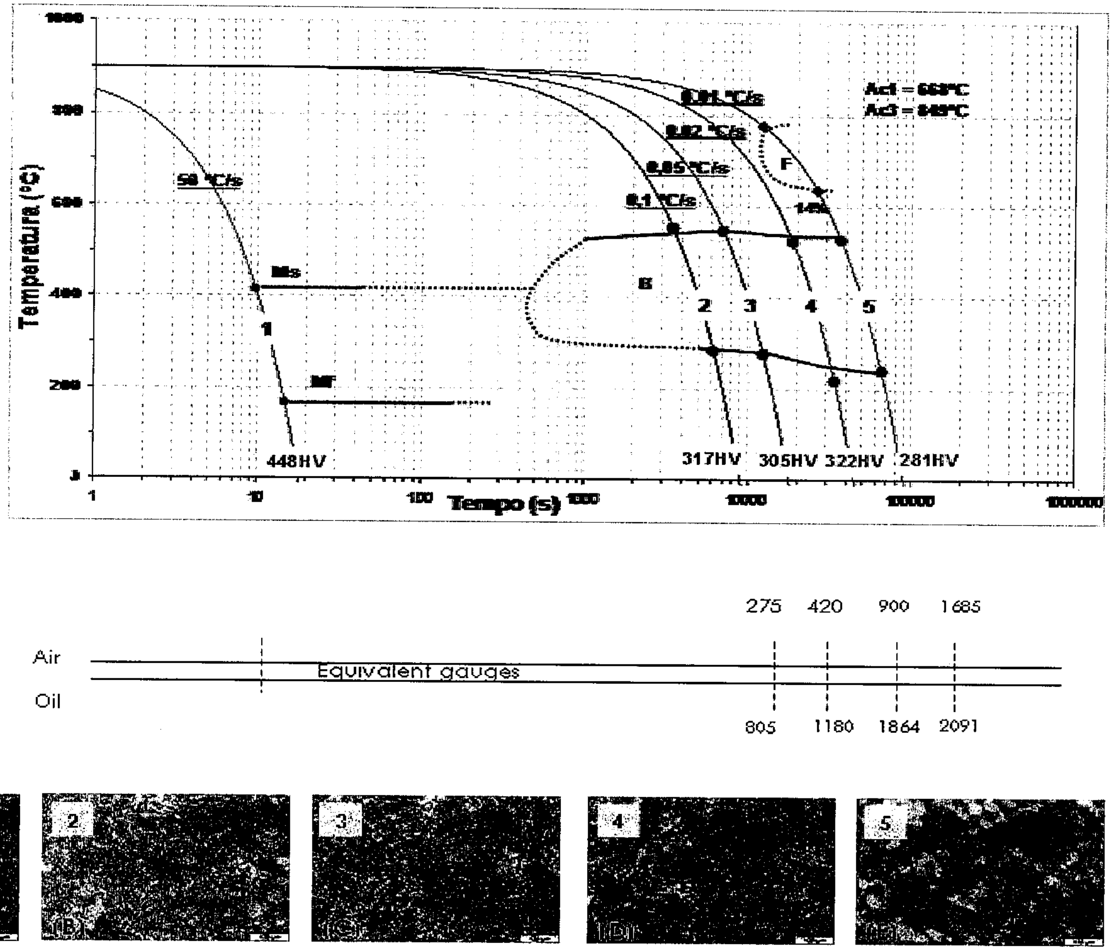


Figure 3

Element	Contents (%)
C	0,36
Si	0,40
Mn	1,57
P	0,015
S	0,0015
Co	<0,01
Cr	1,81
Mo	0,24
Ni	0,70
V	0,02
W	0,02
Cu	0,05
Al	0,007
Ca	0,0016
N	0,006

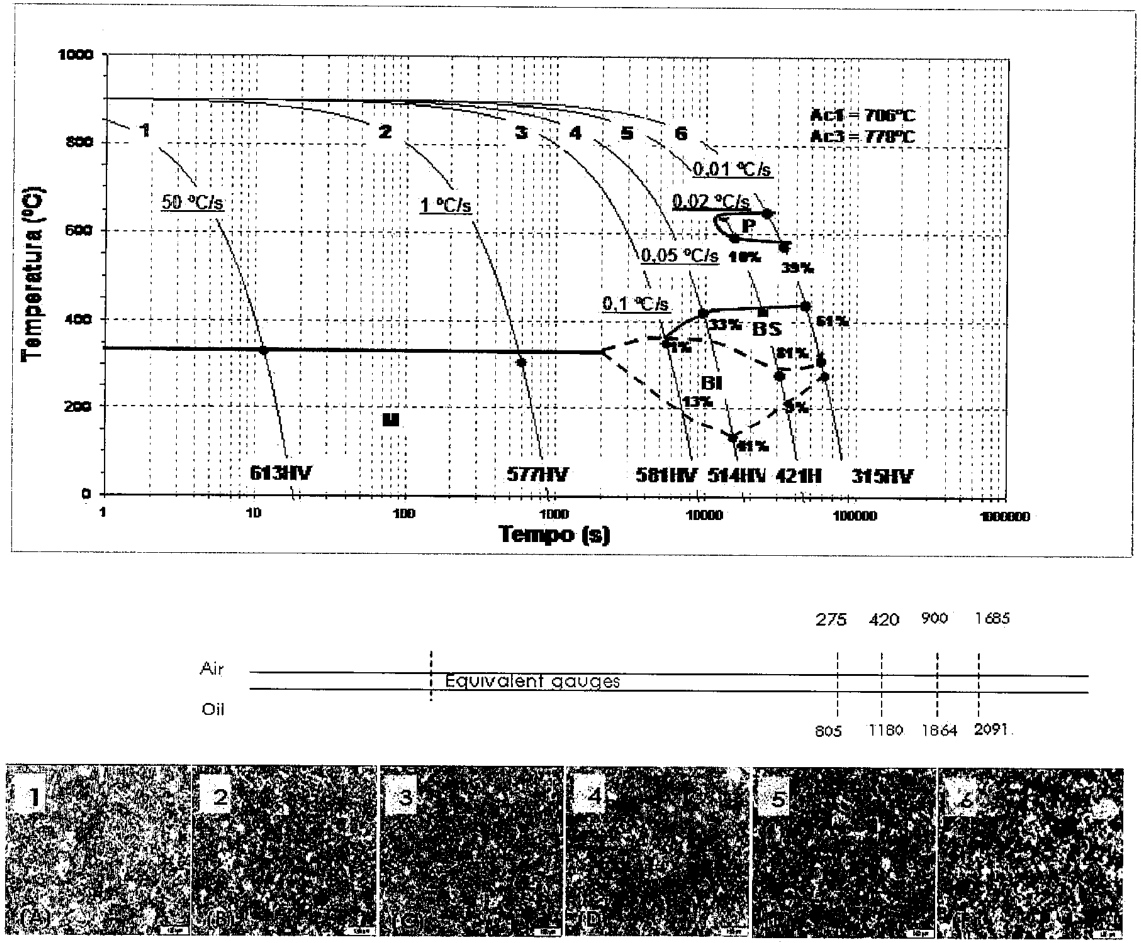
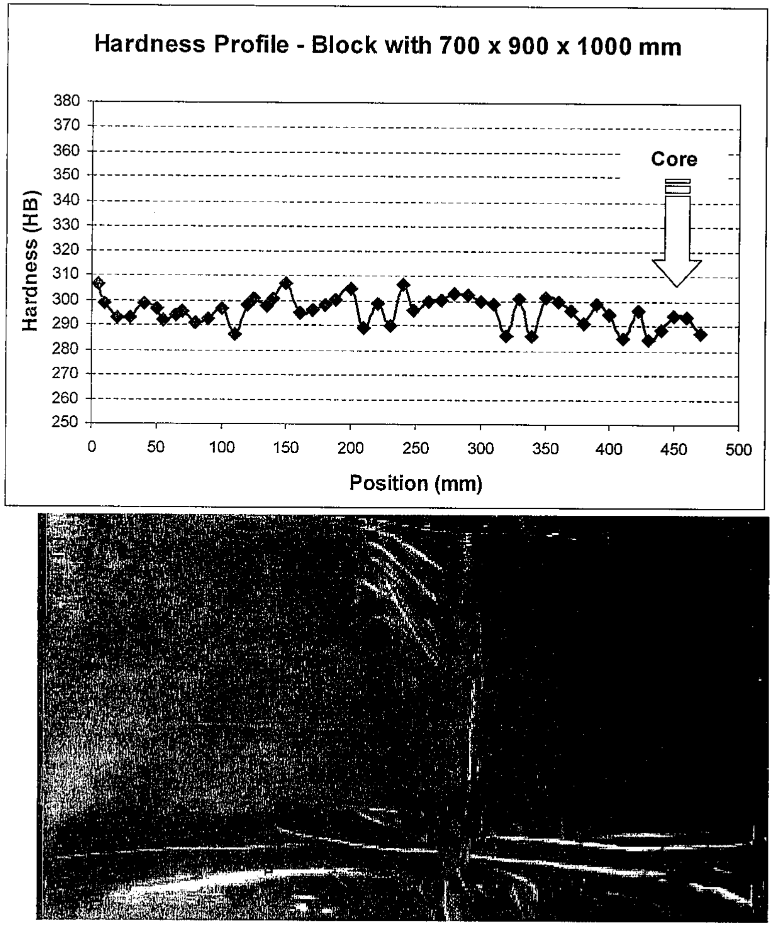
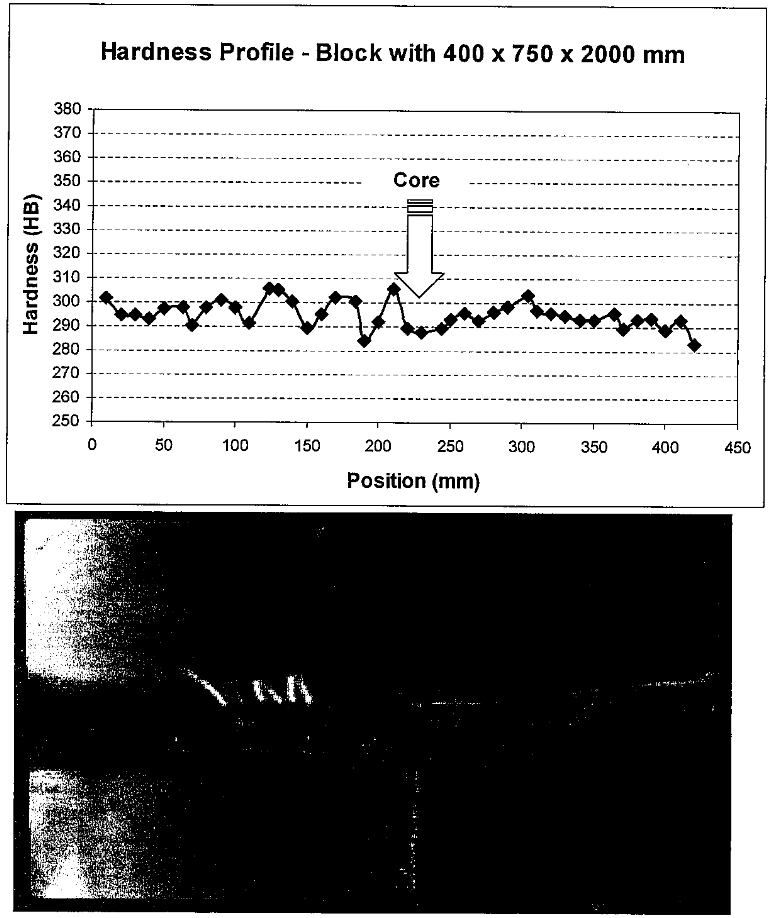


Figure 4


Hardness Profile - Block with 700 x 900 x 1000 mm
Hardness (HB)
380
370
360
350
340
330
320
310
300
290
280
270
260
250
0
50
100
150
200
250
300
350
400
450
500
Position (mm)
Core

a)


Hardness Profile - Block with 400 x 750 x 2000 mm
Hardness (HB)
380
370
360
350
340
330
320
310
300
290
280
270
260
250
0
50
100
150
200
250
300
350
400
450
Position (mm)
Core

b)

Figure 5

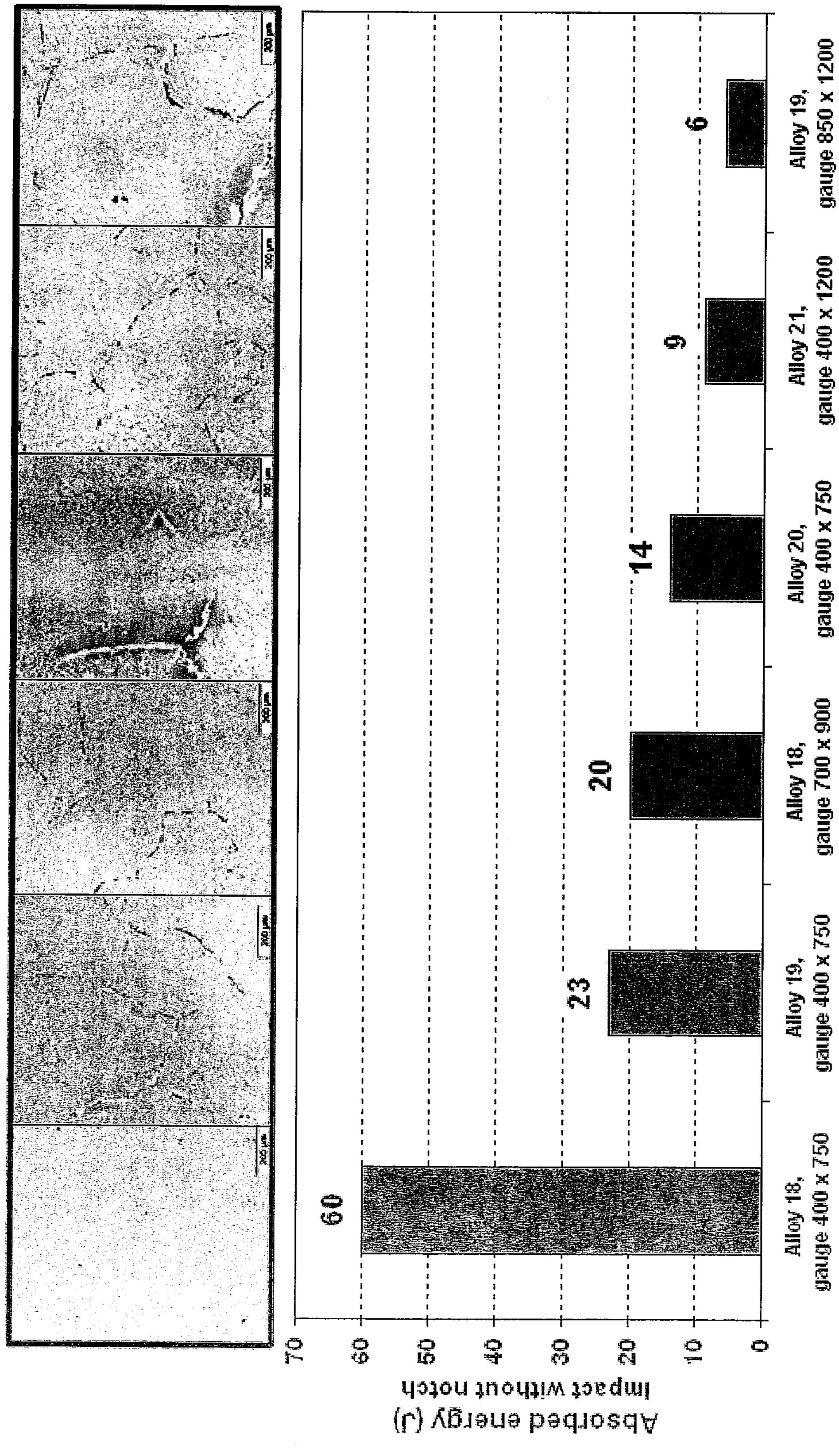
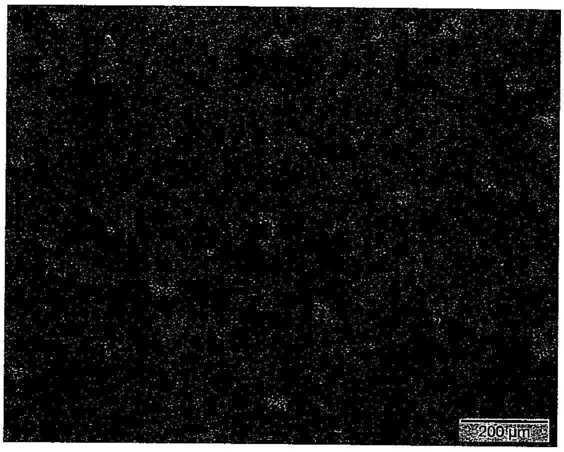
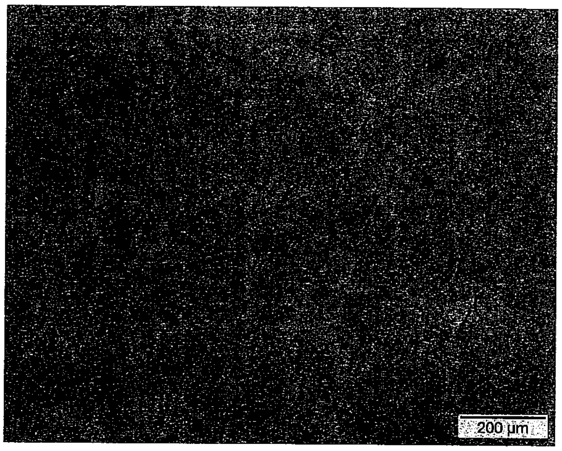

Absorbed energy (J)
Impact without notch
0
10
20
30
40
50
60
70
60
23
20
14
9
6
Alloy 18, gauge 400 x 750
Alloy 19, gauge 400 x 750
Alloy 18, gauge 700 x 900
Alloy 20, gauge 400 x 750
Alloy 21, gauge 400 x 1200
Alloy 19, gauge 850 x 1200

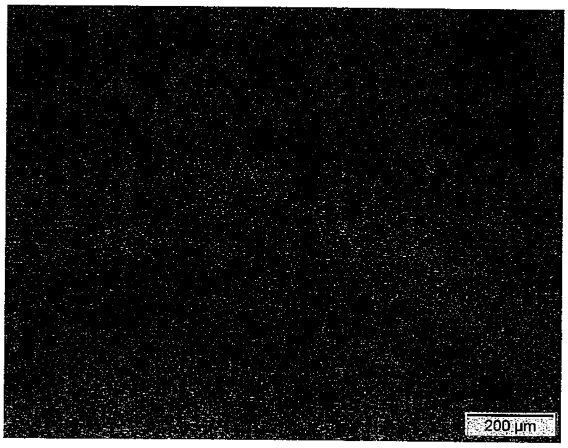
Figure 6



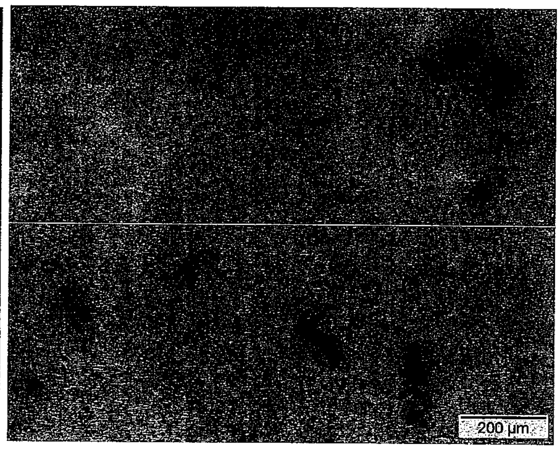
(a) 0.05% Si



(b) 0.40% Si

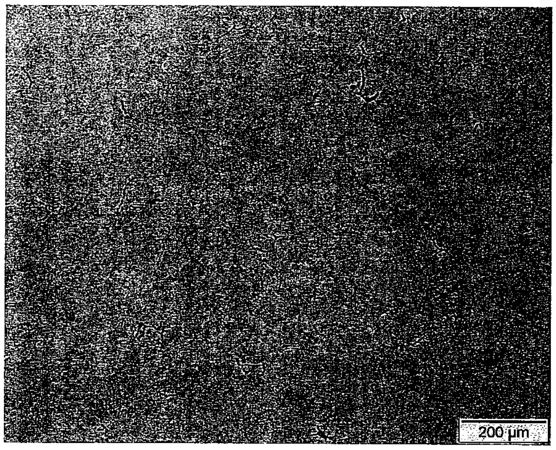


(c) 1.0% Si



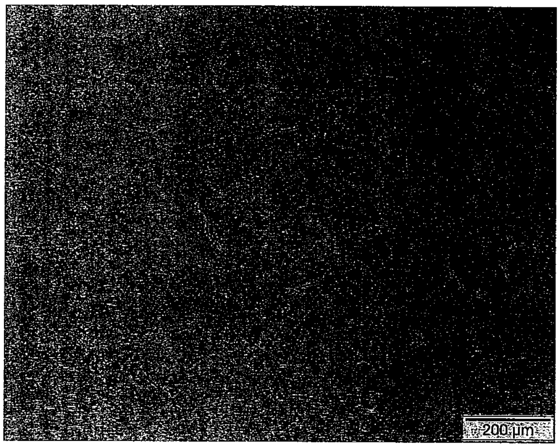
(d) 2.0% Si

Figure 7



(a) 0.010% P

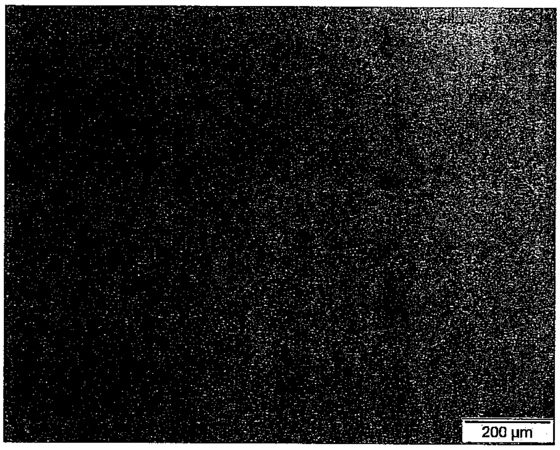
(b) 0.025% P



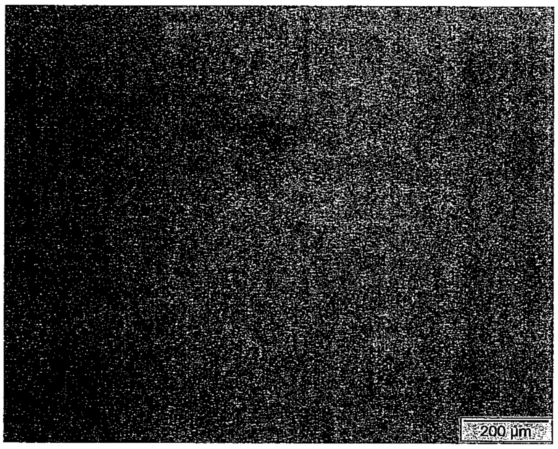
(c) 0.050% P

(d) 0.075% P

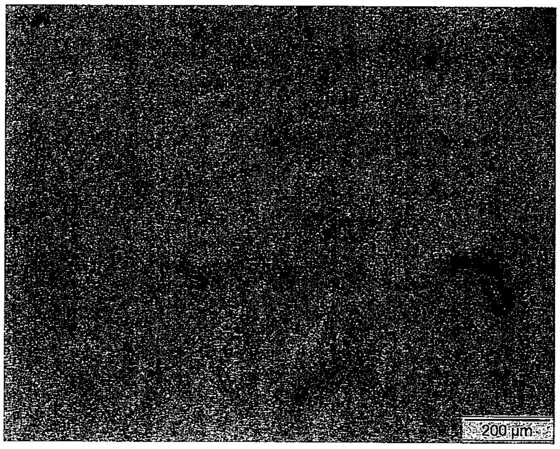
Figure 8



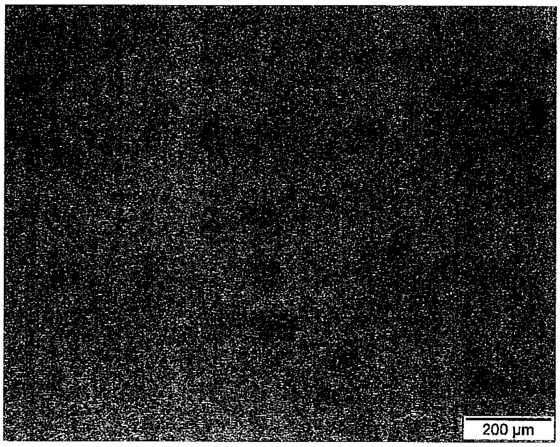
(a) 20 ppm B



(b) 40 ppm B



(c) 70 ppm B



(d) 120 ppm B

Figure 9

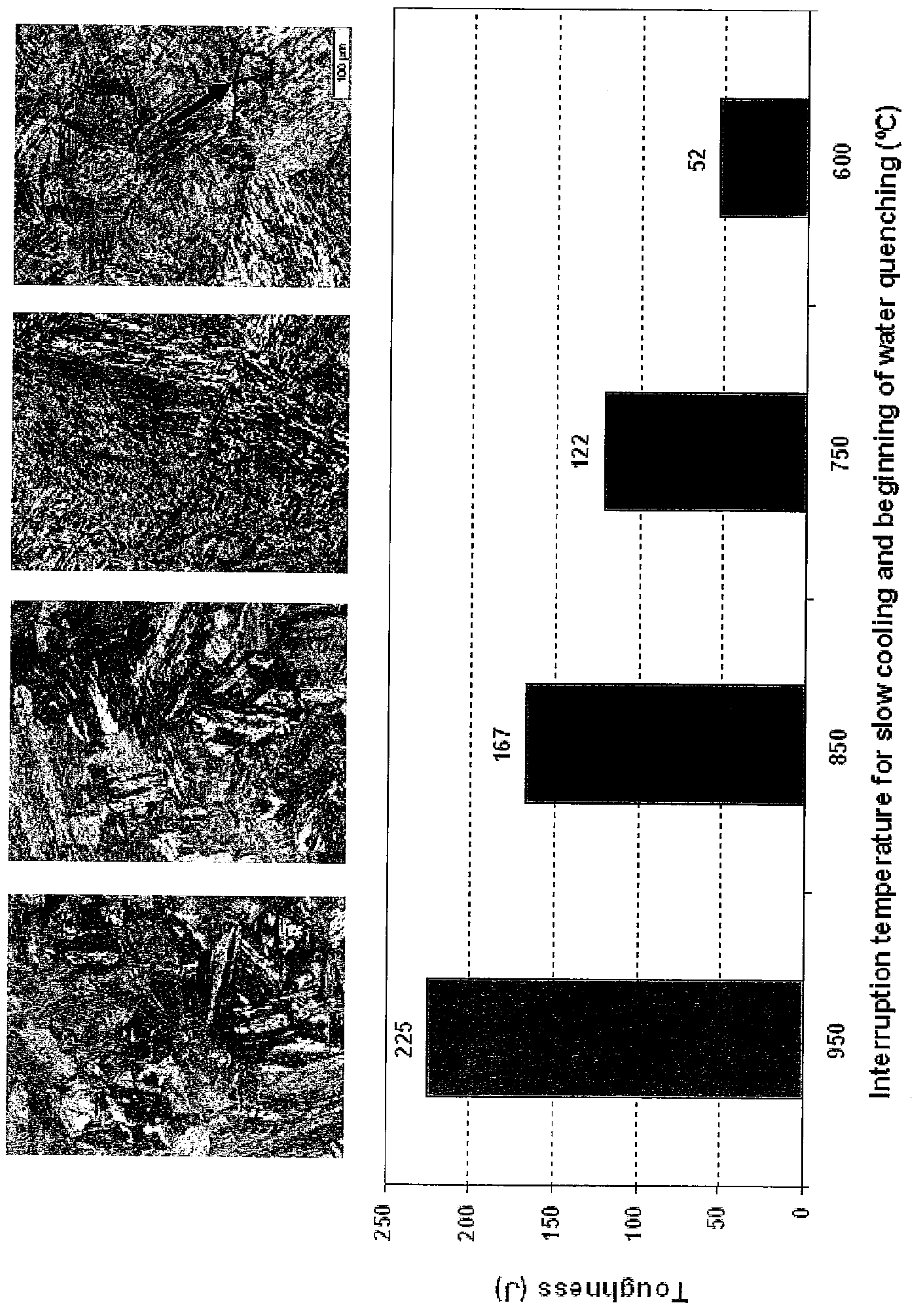
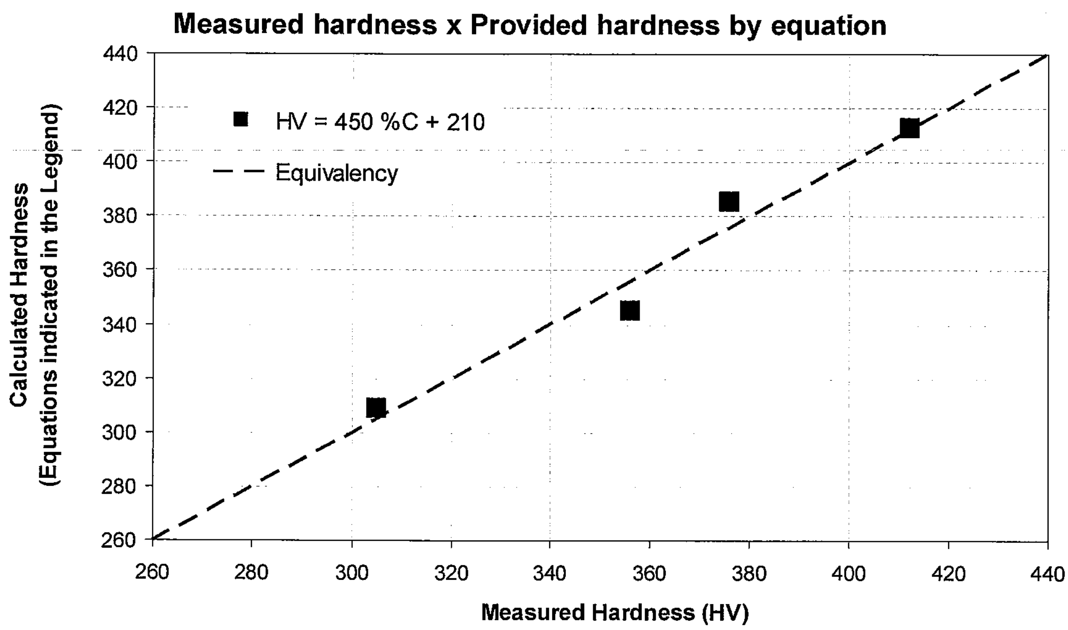
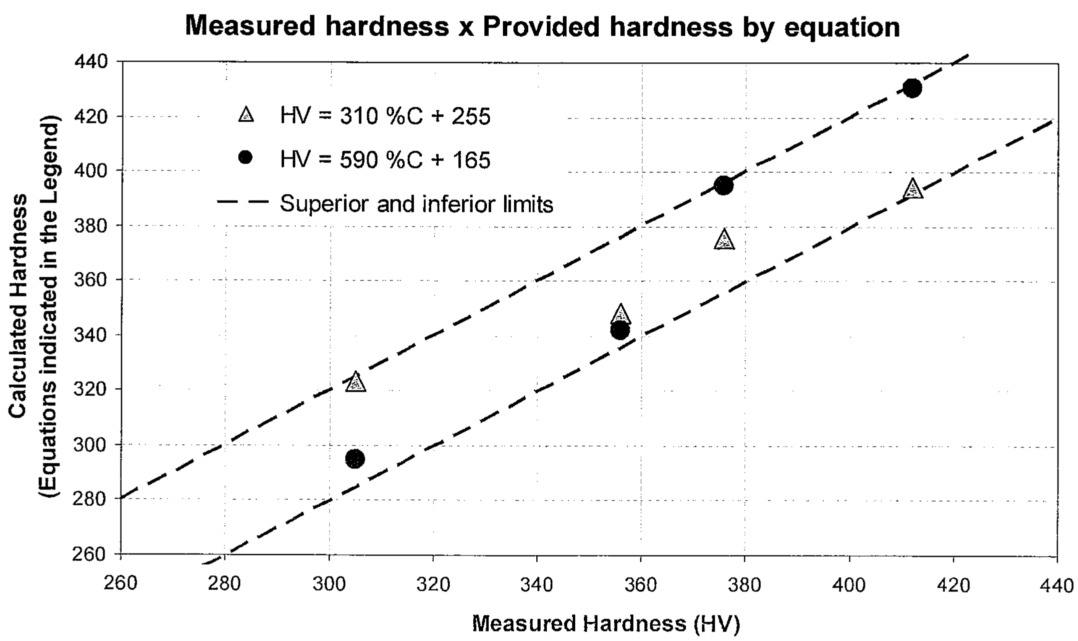

100 µm
225
167
122
52
950
850
750
600
250
200
150
100
50
0
Toughness (J)
Interruption temperature for slow cooling and beginning of water quenching (ºC)

Figura 10


Measured hardness x Provided hardness by equation
HV = 450 %C + 210
Equivalency
Calculated Hardness
(Equations indicated in the Legend)
Measured Hardness (HV)
260
280
300
320
340
360
380
400
420
440

a)


Measured hardness x Provided hardness by equation
HV = 310 %C + 255
HV = 590 %C + 165
Superior and inferior limits
Calculated Hardness
(Equations indicated in the Legend)
Measured Hardness (HV)
260
280
300
320
340
360
380
400
420
440

b)

INTERNATIONAL SEARCH REPORT

International application No. PCT/BR2010/000121

A. CLASSIFICATION OF SUBJECT MATTER

IPC (2010.01) C22C 38/54; 38/58; 38/12; 38/00; C21D 9/00

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)

IPC 2010.01: C22C 38/00 - 38/54; C22C 38/58; C21D 9/00

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)

http://fachdatenbanken.dpma.de; epodoc

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5919415 A (ASCOMETAL SA [FR]) 06 July 1999 (1999-07-06)	1-13
A	EP 1178126 A1 (NIPPON STEEL CORP [JP]) 06 February 2002 (2002-02-06)	1-13
A	US 20060162825 A1 31 December 1969 (--)	1-13
A	US 20040226635 A1 31 December 1969 (--)	1-13
A	EP 2006407 A1 (NIPPON STEEL CORP [JP]) 24 December 2008 (2008-12-24)	1-9, 11

☒ Further documents are listed in the continuation of Box C.　☒ See patent family annex.

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

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

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

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Date of the actual completion of the international search	Date of mailing of the international search report
09 SEP 2010 (09.09.2010)	**15 SEP 2010 (15.09.2010)**

Name and mailing address of the ISA/	Authorized officer
INSTITUTO NACIONAL DA PROPRIEDADE INDUSTRIAL Rua Mayrink Veiga nº 9, 18º andar cep: 20090-050, Centro - Rio de Janeiro/RJ	**Rockfeller Maciel Peçanha**
Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR2010/000121

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to claim No.
A	WO 2009014238 A1 (NIPPON STEEL CORP [JP]) 29 January 2009 (2009-01-29)	1-9, 11
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Form PCT/ISA/210 (continuation of second sheet) (July 2009)

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EP 2006407 A1	2008-12-24	CN 101341269 A	2009-01-07

Form PCT/ISA/210 (patent family annex) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

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PCT/BR2010/000121

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REFERENCES CITED IN THE DESCRIPTION

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