



(11)

EP 2 503 016 A1

(12)

## EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:  
26.09.2012 Bulletin 2012/39

(51) Int Cl.:  
**C22C 38/22 (2006.01)**      **C22C 38/18 (2006.01)**

(21) Application number: **10830974.1**(86) International application number:  
**PCT/BR2010/000375**(22) Date of filing: **10.11.2010**(87) International publication number:  
**WO 2011/060516 (26.05.2011 Gazette 2011/21)**

(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**

(30) Priority: **17.11.2009 BR PI0904607**

(71) Applicants:

- **Villares Metals S/A**  
SP - CEP 13177-900 (BR)
- **Barbosa, Celso Antonio**  
Parque Nova Campinas - Campinas - SP CEP 13085-910 (BR)
- **Mesquita, Rafael Agnelli**  
São Manoel - Americana - SP CEP 13472-060 (BR)

(72) Inventors:

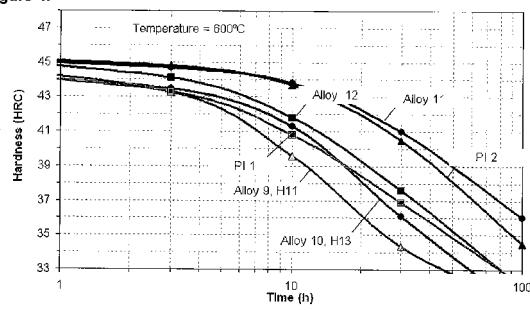
- **BARBOSA, Celso Antonio**  
Parque Nova Campinas - Campinas - SP  
CEP 13085-910 (BR)
- **MESQUITA, Rafael Agnelli**  
São Manoel - Americana - SP  
CEP 13472-060 (BR)

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

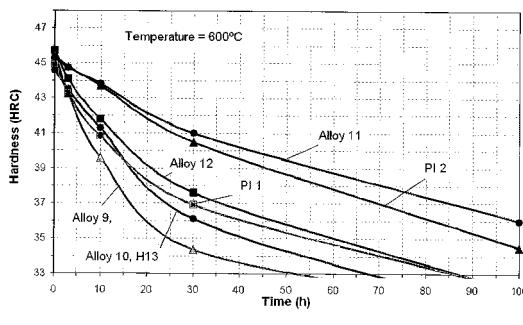
### (54) STEEL WITH HIGH TEMPER RESISTANCE

(57) STEEL WITH HIGH TEMPERING RESISTANCE, characterized by a composition of alloying elements consisting essentially of, in percent by mass, C between 0.20 and 0.50, Si lower than 1.0, P lower than 0.030, Cr between 3.0 and 4.0, Mo between 1.5 and 4.0, V between 0.1 and 2.0, Co lower than 1.5, being the remaining composed of Fe and inevitable deleterious substances. The steel is produced by processes involving ingot casting and hot/cold forming, or used with the cast structure; or by processes involving atomization or dispersion of the molten metal, such as powder metallurgy, powder injection or spray forming.

Figure 4:



a) Logarithmic scale



b) Linear scale

**Description**

**[0001]** This report deals with a steel designed for hot metal forming tools, typically in cases where the metal to be formed withstands temperatures above 600°C, even though processes at lower temperatures or even at room temperature can be used with the said steel. The steel in question has a composition that allows ranking it as hot work tool steel, whose main characteristic is increased resistance to loss of hardness at high temperature - called tempering resistance, while retaining high toughness and adequate thermal conductivity and hardenability. Such an effect is possible by carefully designing the alloy, and setting the optimum ranges of the elements P, Si, Mo and Cr.

**[0002]** The term hot work tools is applied to a large number of hot-forming operations, employed in industries and focused on the production of parts for mechanical applications, especially automotive parts. The most popular hot-forming processes are forging, extrusion or casting of non-ferrous alloys. Other applications performed at high temperature, typically above 500/600°C, can also be classified as hot work. In these applications, molds, dies, punches, inserts and other forming devices are classified by the generic term: hot work tools. These tools are usually made of steels, which require special properties to withstand high temperatures and the mechanical characteristics of the processes in which they are employed.

**[0003]** Among their key properties of hot work steels, the following stand out: hot resistance, more specifically tempering resistance, toughness, hardenability and physical properties such as thermal conductivity, specific heat, both correlated to thermal diffusivity, and thermal expansion coefficient.

**[0004]** For forging applications, hot forging of steels stands out, especially steels for mechanical construction applied to auto parts. In such operations, the forged billet withstands temperatures above 1100°C. During the forming process, it heats up the surface of the tool, given that the higher the contact period, the higher the temperature. Consequently, the heat generated requires high hot resistance from the steel used. The steel hardening mechanism for hot die forming is chiefly induced by the precipitation of fine carbides. Noteworthy are the Mo or W carbides, M<sub>2</sub>C-type, or V carbides, MC-type. For high-Cr steels, Cr-rich M<sub>7</sub>C<sub>3</sub> carbides also stand out, but also with Mo and V in solid solution. Despite their high stability, these carbides tend to coalesce after long periods of time at high temperatures, typically above 550°C - conditions easily reached within the tool operating range. As a consequence, the hardness of the area decreases, causing wear and hot plastic deformation, resulting in tool failure.

**[0005]** Improving the resistance of the material against loss of hardness or tempering resistance, is thus critical to improving the performance of the tools that operate under high temperature conditions. Examples of such applications are tools used in hot forging of steel parts or other metal alloys, extrusion of non-ferrous alloys and dies for casting non-ferrous alloys (being the latter two applications more important to Al alloys). The same goes for other applications, such as extrusion or casting of non-ferrous alloys. E.g., in forging steel applications, the temperature of the pre-forms to be forged is about 1200°C. Even considering the short contact time with the tools (seconds), their surface heat up significantly, causing loss of hardness due to tempering of these surfaces. Considering the extrusion of aluminum alloys or other non-ferrous alloys, the billet temperature is lower, ranging from 400 to 600°C. However, in these applications, the contact time is significantly longer (tens of minutes to hours of operation). Moreover, local friction generated by the tool / aluminum contact intensifies heating, increasing the loss of hardness of the tool steel and, consequently, leading to steel wear. In pressurized casting dies, the molten metal is injected at high pressure and temperature (around 700°C), also heating the surface of the die. In this case, failure is due mainly to thermal fatigue cracking caused by the successive heating and cooling of the working surface of the die. But, the high heat exchange between molten aluminum and the die surface favors the heating of the surface areas, generating, as in other applications, loss of hardness and, consequently, triggering the fatigue cracking process.

**[0006]** This mechanism of post-heating loss of hardness is, therefore, critically important to hot work tool steels; thus, increasing the strength of the material against this phenomenon is something desirable. Concerning the steel employed, improved hot resistance is usually obtained through the use of higher grades of those elements that form secondary carbides such as Mo, W and V, or by solid solution hardening. Although effective in increasing hot resistance, the excessive increase of the grade of these elements implies reduced toughness, poor thermal diffusivity and conductivity or significant increase of production costs. This latter economic factor is really important nowadays, given the high cost of raw materials used as a source of alloy elements Mo, W and V.

**[0007]** To provide a better understanding of this invention, we describe below some of the state-of-the-art steels currently used (chemical composition is summarized in Table 1). The H11 and H13 steels stand out, as these are the tool steels mostly used for hot works. These materials contain 5% Cr providing adequate hardenability and to assist with hot resistance, 0.9% V and 1.2% Mo to improve hot resistance, and generally low grades of P and S to promote adequate toughness. However, for improving tempering resistance, higher Mo grades would be needed. The DIN 1.2365 and DIN 1.2367 are steels used for such purpose. They have a high Mo grade to improve hot resistance. However, if the content of this element is increased within the structure of the DIN 1.2367 steel, toughness and thermal conductivity and diffusivity tend to drop. In the 1.2365 steel, this thermal conductivity reduction is counterbalanced by increasing the Mo content and decreasing the Cr content. However, the lower the Cr content, the lower the hardenability, limiting the applications

in large tools. It is important emphasize that attention should be paid to the thermal conductivity and toughness properties. During the work, the increase in thermal conductivity is important such that the tool steel is able to homogenize quickly the difference of temperature between the material formed and the tool core, thus reducing stresses and thermal cracking. And, in case cracking occurs, the toughness of the material is also critical because it delays propagation and, consequently, thermal fatigue damage. Thus, it is clear that only increasing the Mo content, as exemplified by steel DIN 1.2367 and DIN 1.2365, is not sufficient for overall improvement of the properties of hot work steels.

Table 1: Typical chemical composition of state-of-the-art steels. The sum Mo + V + Co is shown because these elements have the highest cost, and are closely related to the final cost of the tool steel. Content in percentage by weight and Fe balance. The sum Mo + W + V + Co is shown because these elements impact the alloy cost the most.

Designation	C	Si	Cr	Mo	W	V	Co	Mo+W+V+Co
H11	0.36	1.0	5.0	1.2	-	0.5	-	1.7
H13	0.38	1.0	5.0	1.2	-	1.0	-	2.2
DIN 1.2365	0.36	0.3	2.8	2.8	-	0.5	-	3.3
DIN 1.2367	0.38	0.3	5.0	3.0	-	0.5	-	3.5
PI 9909160-7	0.36	0.2	5.0	2.3	-	0.5	-	2.8

**[0008]** A new steel type has been developed more recently and is described in PI 9909160-7. This material has, similarly to DIN 1.2367, higher Mo content, but lower Si and P content to improve toughness. In this case, cost increase is avoided by not using a high Mo content, but the hot resistance gain is not significant in comparison to steel H13.

**[0009]** Given this scenario, it is evident the need for a tool steel with hot resistance higher than that of state-of-the-art steel H13, but without using excessive alloying elements which might affect thermal conductivity and material cost. Also, the material used should feature high hardenability, which allows it to be applied to large tools.

**[0010]** Therefore, the steel of the present invention will fulfill all these needs.

**[0011]** The initial purpose of the invention was to investigate the influence of the Cr and Mo content on hot work tool steels that allowed identifying some synergy between the two elements and hot resistance. More specifically, when an increase of the Mo content is followed by a reduction of the Cr content, a more significant effect on the hot strength can be observed. In addition, a reduced Cr content improves thermal conductivity, thereby reversing the negative effect of a higher Mo content. On the other hand, the Cr content must be carefully balanced, because very low values, as previously mentioned, impair hardenability and limit the application to tools with average section dimension above 100 mm. Therefore, the material of the present invention shows a chemical composition with ideal arrangement of the Cr and Mo contents, capable of overcoming the tempering resistance properties of state-of-the-art steels, with no significant cost increase and proper thermal conductivity, toughness and hardenability.

**[0012]** In order to satisfy the above conditions, the steel of the present invention has a composition of alloying elements, which, in percentage by mass consists of:

- 0.20 to 0.50 C, preferably 0.3 to 0.45 C, typically 0.36 C
- 3.0 to 4.0 Cr, preferably 3.5 to 3.9 Cr, typically 3.8 Cr
- 1.5 to 4.0 Mo, preferably 2.0 to 3.0 Mo, typically 2.5 Mo.

**[0013]** Given its chemical similarity to W, Mo can be replaced with W, a 2 W: 1 Mo ratio by mass.

- 0.1 to 2.0 V, preferably 0.3 to 1.0 V, typically 0.5 V; V can be partially or fully replaced with Nb, following a 1.0% Nb: 0.5% V ratio.
- up to 1.0 Si, preferably up to 0.5 Si, typically 0.3 Si
- Max 0.030 P, preferably max 0.015 P, typically max 0.010 P.

**[0014]** Balance by iron and metallic or non-metallic deleterious substances inevitable to the steelmaking process, in which said non-metallic deleterious substances include but are not limited to the following elements, in percentage by mass:

- Max 0.10 S, preferably max 0.020 S, typically max 0.008 S.

•Max 1.5 Al, Mn or Co, preferably up to 1.0 Al, Mn or Co, typically below 0.5 Mn, Al and Co.

**[0015]** Next, we describe the ratios of the specification of the composition of the new material. The percentages listed refer to percent by mass.

**[0016]** C: Carbon is primarily responsible for martensite hardening under low temperature conditions. Together with the alloying elements, carbon acts in the secondary hardening, important for the hardening at high temperature. For such effects, carbon contents of at least 0.20% are recommended, preferably above 0.30%. On the other hand, very high C contents, cause excessive precipitation of grain-shaped carbides at the time of quenching (especially when Mo and V contents are high), and result in increased hardness and volume of secondary carbides. Thus, toughness is generally impaired. , the C content should be limited to a maximum value of 0.50%, preferably below 0.40%. This limitation also plays a role in the reduction of the amount of retained austenite, preventing problems associated with dimensional instability and brittleness.

**[0017]** Cr: The chromium content should be higher than 3.0%, preferably greater than 3.5%, because this element favors hardenability, which is important for application in large tools. However, the Cr content should be limited. The present invention has incorporated the concept of reducing the Cr content to improve tempering resistance. This is an important effect, because the final tempering resistance is higher than that of state-of-the-art steels. The mechanisms that cause this effect are thought to be related to the formation of secondary Cr carbides,  $M_7C_3$ -type, which dissolve Mo and V are the first carbides to be formed. Therefore, the lower the Cr content, the lower the volume of  $M_7C_3$  carbides and, thus, the greater the amount of Mo and V available for secondary hardening. The end result is a significantly higher tempering resistance when the alloy Cr content is lower than that of state-of-the-art alloys. Even in relation to the PI 9909160-7 alloy, there is a significant tempering resistance gain. This is significant because the alloys have Mo equivalent grades (Mo is a pricey alloying element), showing that the present invention is able to reach high hot resistance values without excessively increasing the Mo content. For all such effects, the Cr content should be below the 5.0% content of conventional steels, being the preferred Cr content lower than 4.0%. Finally, the ideal Cr content required to maximize tempering resistance identified in the present invention should be set between 3.0% and 4.0%. In addition to the heat resistance property, a lower Cr content improves thermal conductivity, also preserving this property as the Mo content rises. Therefore, this shorter Cr range aims at a careful adjustment for maximum tempering resistance and adequate thermal conductivity.

**[0018]** Mo and W: high Mo contents are used in the alloy of the present invention to improve tempering resistance properties. This is possible by the formation of chemically-stable, Mo-rich tempering carbides, especially the  $M_2C$  carbide. Thus, the alloy of the present invention must contain at least 1.5%, preferably above 2.0%. On the other hand, excessively high Mo grades can harm toughness due to precipitation of pro-eutectic carbides at the time of quenching, and may significantly increase the cost of the alloy, making its application in many tools unfeasible. Hence, the Mo content should be limited to 4.0%, preferably below 3.0%. Tungsten and molybdenum produce similar effects in the tool steel of the present invention, forming  $M_2C$  or  $M_6C$  secondary carbides. Thus, they can be jointly specified through the tungsten equivalent relationship ( $W_{eq}$ ) given by the sum  $W + 2Mo$ , which normalizes the differences in atomic weight between the two elements.

**[0019]** V: Vanadium is primarily important for the formation of MC secondary carbides. Because they are very thin, these carbides block the movement of dislocation lines, increasing mechanical strength. V also improves grain growth, allowing high austenitizing temperatures (above 1000°C). For such effects, V must be above 0.1%, preferably above 0.3%. However, excessively high V grades may generate primary, difficult-to-solubilize carbides, thus reducing toughness. Hence, the V content should be lower than 2.0%, preferably below 1.0%.

**[0020]** Si: silicon produces a strong effect on secondary hardening and toughness. At high levels, Si increases the secondary hardness up to quenching temperatures of 600°C. However, the study of the present invention showed that a lower Si content was important to reduce the loss of hardness under high temperature conditions, thereby increasing tempering resistance. A lower Si content also results in significant increase of toughness, having this effect been applied to the present invention. Therefore, the Si content of the material of the present invention must be lower than 1.0%, typically below 0.5%.

**[0021]** P: reduction of the P content also results in significant increase of toughness, because this element can be segregated on the grain surface and, thereby, diminishes cohesion in these surfaces. Therefore, P content should be lower than 0.030%, typically below 0.015%.

**[0022]** Residual Elements: Other elements such as Mn and Al should be considered as deleterious substances associated with the steelmaking deoxidation processes or inherent to the manufacturing processes. Hence, the Mn and Al content should be limited to 1.5%, preferably below 1.0%. The Co content should also be limited to the same values, due to its beneficial effect on hot resistance and strong impact on the alloy cost. In terms of formation of inclusions, the sulfur content should be controlled, because such inclusions may lead to cracking during operation; therefore the S content should remain below 0.050%, preferably below 0.020%.

**[0023]** The alloy, as described above, can be produced as rolled or forged products through conventional or special

processes such as powder metallurgy, spray forming or continuous casting, such as wire rods, bars, wires, sheets and strips.

[0024] The figures attached herein have been referenced to in the description of the experiments carried out, and their contents are listed below:

- 5 - Figure 1 shows the effects of P and Si on alloys 1-8, in terms of post-tempering toughness and hardness.
- Figure 2 compares alloys 1 to 8, but showing P effect on toughness, depending on the quenching temperature.
- Figure 3 shows the distribution of carbides in the high and low Si content alloys, demonstrating a better distribution in low Si content alloys, which explains their superior toughness.
- 10 - Figure 4 compares the reduction of hardness versus time at 600°C, showing tempering resistance. The greater the displacement to the right, the higher the alloy's tempering resistance.
- Figure 5 shows a comparison of thermal conductivity values for some of the alloys investigated.
- Figure 6 shows a comparison of toughness of alloys 9 to 12 and alloys IP 1 and IP 2; the data produced by the un-notched impact test (7 x 10 mm test specimens) and Charpy V
- 15 - Figure 7 shows the hot forging punch to which the industrially-produced IP 2 steel was applied and compared with the state-of-the-art H13 steel. Note: a) wear failures and cracking; b) hardness profile, showing drop in working areas (distance from surface = zero).

EXAMPLE 1: Effect of Silicon and Phosphorus:

[0025] Eight experimental ingots were initially produced to evaluate the effect of Si and P on the state-of-the-art H11 steel. The compositions are shown in Table 2. The hardness and impact results are shown in Figure 1. Note the strong Si influence on hardness for quenching temperatures below 500°C, even though the same effect is not observed for quenching temperatures above 600°C; the hardness of both the alloys with high and low Si content is about the same.

25 The P effect is compared in Figure 2 for different tempering temperatures. In this case, it was possible to observe that a decreasing P content improves significantly the toughness of Si-rich alloys, but this effect is less significant on alloys with low Si content.

[0026] Therefore, the results show that the best combination, in terms of toughness, would be alloys with low P and Si content. Alloys of high Si content are only viable for situations when hardness values higher than 52 HRC are employed and, for such, tempering temperatures below 600°C are also adopted. In these cases, the decrease of the P content is even more critical.

[0027] The reasons for these significant Si and P effects have not been fully defined, but early scientific results conducted by the inventors of this patent show a relationship with the formation of secondary carbides. In alloys with high Si content, the secondary carbides tend to concentrate in areas of high diffusion (lath or grain surfaces), because of the difficulties imposed by Si onto the cementite formation process. On the other hand, in alloys with low Si content, cementite is rapidly formed, leading to a better distribution of secondary carbides formed at higher temperatures. Figure 3 shows the images of transmission electron microscopy that illustrate these observations.

40 Table 2: Chemical composition of the various Si and P contents analyzed for the state-of-the-art H11 alloy.

Alloy:	1	2	3	4	5	6	7	8
C	0.36	0.34	0.36	0.36	0.36	0.35	0.36	0.35
Si	<b>0.05</b>	<b>0.32</b>	<b>0.98</b>	<b>1.92</b>	<b>0.05</b>	<b>0.33</b>	<b>1.01</b>	<b>1.90</b>
Mn	0.35	0.35	0.35	0.35	0.34	0.35	0.35	0.35
P	<b>0.023</b>	<b>0.028</b>	<b>0.024</b>	<b>0.012</b>	<b>0.012</b>	<b>0.012</b>	<b>0.011</b>	<b>0.008</b>
S	0.004	0.004	0.004	0.003	0.004	0.004	0.005	0.003
Co	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.06
Cr	5.09	5.13	5.06	5.08	5.08	5.03	5.10	5.05
Mo	1.28	1.31	1.33	1.24	1.32	1.32	1.33	1.23
Ni	0.20	0.19	0.19	0.20	0.19	0.20	0.19	0.20
V	0.44	0.44	0.42	0.41	0.44	0.44	0.45	0.43
W	0.10	0.11	0.11	0.10	0.11	0.10	0.11	0.10
Nb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

(continued)

Alloy:	1	2	3	4	5	6	7	8
Al	0.029	0.020	0.023	0.036	0.024	0.022	0.036	0.043
W <sub>eq</sub> (=W+2Mo)	1.48	1.53	1.55	1.44	1.54	1.52	1.55	1.43

EXAMPLE 2: Effect of Cr and Mo:

[0028] To assist in the definition of the effect of Cr and Mo, seven additional experimental ingots have been produced, comprehending four state-of-the-art steels: H11, H13 and the steel described in PI 9909160-7 and two alloys proposed for the present invention (see Table 3). These two compositions lead to a reduction of the Si and P contents described in example 1 but also to distinct balances of Cr and Mo.

[0029] As mentioned, the purpose of the IP 1 and IP 2 alloys is to obtain greater resistance to loss of hardness, i.e., tempering resistance. Therefore, hardness reduction after different exposure periods at 600°C was evaluated and the results are shown in Table 4. The time increments followed a logarithmic scale, as depicted in the chart of Figure 4b. These results show that, when comparing alloys IP 1 and H11, hot resistance rises simply by modifying the Si and P contents (but the effect is likely to be related only to Si, since P does not play a role in the carbide formation process)

[0030] However, this gain in hot resistance by reducing the Si content is not sufficient to produce results significantly higher than those of H13. Therefore, a higher Mo content together with a lower Cr content in the IP 2 alloy was used. For that case, a significant variation of the hot resistance could be verified, which provided increased hardness after the same exposure period. And, as shown in Figure 4a, the same drop in hardness obtained for the H13 steel occurs after far longer periods in the case of alloy IP 2. For example, hardness reduces from 45 HRc to 35 HRc at a temperature of 600°C after an exposure period of 25 hours, whereas the same phenomenon takes place in alloy IP 2 after only 60 hours.

[0031] This significant tempering resistance improvement is related not only to the increase of the Mo content but also to the reduction of the Cr content. This effect is clear after comparing the differences between alloy PI2 and alloy 12 (patent PI 9909160-7). It also explains the high tempering resistance results obtained for alloy 11.

Table 3: Chemical composition of state-of-the-art steels and those proposed for the present invention.

Alloy:	9	10	11	12	IP 1	IP 2
Note:	H11	H13	DIN 1.2365	Patent 9909160-7	Current invention	
C	0.36	0.4	0.31	0.35	0.35	0.35
Si	1.02	0.96	0.3	0.13	0.3	0.31
Mn	0.48	0.34	0.3	0.49	0.27	0.3
P	0.025	0.023	0.023	0.009	0.007	0.01
S	0.005	0.006	0.005	0.005	0.005	0.006
Co	0.02	0.02	0.01	0.02	0.01	0.02
Cr	5.03	5.23	2.85	4.99	4.96	3.78
Mo	1.4	1.31	2.8	2.28	1.39	2.49
Ni	0.19	0.20	0.20	0.19	0.20	0.19
V	0.34	0.85	0.5	0.57	0.42	0.52
W	0.03	0.02	0.02	0.02	0.02	0.02
Nb	<0.010	0.02	0.02	0.01	<0.010	0.005
Al	<0.005	0.014	0.019	0.009	<0.005	0.005
W <sub>eq</sub> (=W+2Mo)	2.8	2.6	5.6	4.6	2.8	5.0
W + Mo + Co + V	1.79	2.2	3.33	2.89	1.84	3.05

Table 4: Loss of hardness after exposure at 600°C for various exposure periods Initial hardness around 45 HRC

	Alloy 9	Alloy 10	Alloy 11	Alloy 12	IP 1	IP 2
<b>Cr and Mo%:</b>	5Cr 1.4Mo	5.2Cr 1.3Mo	2.8Cr 2.8Mo	5.0Cr 2.3Mo	5.0Cr 1.4Mo	3.8Cr 2.5Mo
<b>Initial</b>	45.5	44.6	45.3	45.7	44.9	45.4
<b>3h</b>	43.3	43.5	44.7	44.1	43.3	44.8
<b>10h</b>	39.6	41.3	43.8	41.8	40.8	43.7
<b>30h</b>	34.4	36.1	41.0	37.6	36.9	40.5
<b>100h</b>	31.1	30.7	36.0	32.0	32.1	34.5

**[0032]** Despite the interesting effect on tempering resistance, Cr contents should not drop to excessively low levels to prevent damaging the hardenability and thus, limiting its application in large tools. This can be considered the major setback of the state-of-the-art DIN 1.2365 steel (alloy 11), i.e., excellent tempering resistance but low hardenability. Table 5 illustrates these Cr x hardenability issues based on dilatometer test results. The IP 2 composition can be considered ideal under this aspect, with Cr content lower than that of steel H13 (alloy 10), to provide increased tempering resistance, but not as low as that of steel DIN 1.2365 (alloy 11). The higher Mo content of alloy IP 2 also helps achieving proper hardenability levels, which compensates the effect resulting from the Cr content reduction and ensures its application in large tools.

**[0033]** A further advantage of using a lower Cr content than that of alloy 12 and other state-of-the art alloys is the ability to maintain adequate thermal conductivity. As shown in Figure 5, this property tends to fall as the Mo content increases (compare alloys 12 and 10), and to rise as the Cr content goes down (alloys 11 and IP 2). Therefore, in addition to being considered ideal with regard to hot resistance, the combination of the Cr and Mo contents of alloy IP 2 allows maintaining thermal conductivity at levels even higher than those of the traditional H13 steel (alloy 10).

Table 5: Results of the TRC curve developed for the investigated steels, used in hardenability evaluation. The lower the critical rate and the higher the hardness after quenching at 0.1 °C, the higher will be the hardenability.

	Alloy 10 H13	Alloy 11 DIN 1.2365	Alloy 12 PI 9909160-7	IP1	IP 2
Critical rate to start the bainite-forming process (°C/s)	0.2	8.0	0.3	0.5	0.5
Hardness after quenching at 0.1 °C/s (HV)	538	389	534	512	486

**[0034]** Superior tenacity is another gain of alloys IP 1 and IP 2 in relation to the state-of-the-art H11, H13 and DIN 1.2365 alloys (alloys 9 to 11). These results can be compared in Figure 6. Note the gain of alloy IP 2 in relation to alloy 11, which, similarly, has high tempering resistance. That is, in addition to superior hardenability, the balance of the IP 2 chemical composition makes this alloy significantly tougher than alloy 11. The effect, in this case, is primarily associated with lower Si and P contents, as discussed in example 1.

### EXAMPLE 3: Field Test

**[0035]** A field study is detailed next, with alloy IP 2 being compared to steel H13 in forging tools. The results were analyzed based on the failure modes and on the properties of materials.

**[0036]** The process in question deals with high-speed warm forging (see Figure 7a). Despite the fact that the forged billets are exposed to a temperature lower than the usual hot forging temperature, high processing speed makes the contact between the heated billet and the matrix to extend, thus heating its surface. The process is also developed under high cooling conditions, thereby promoting thermal shock on the surface region.

Process data

## [0037]

5      Product: shaft end.  
 Tool: Warm forging precision punch  
 Forged Material: Modified SAE 1045 and 1050 steels  
 Billet temperature: approximately 900°C.  
 Cooling: Intense, water-cooled.  
 10     Blow application speed: high.  
 Tool steel previously used: AISI H13 (hardness: 53 HRC).  
 Steel tested: IP 2, at same hardness.

15     [0038] Figure 7a shows the punch analyzed after the end of its life. Since this type of forging produces parts of high dimensional accuracy, deviations of tenths of mm compromise the quality of the part produced. The end of its life is caused by wear on the protruding and rounded surfaces and occurrence of thermal cracking (see Fig. 7a). After the end of its life, the matrix was destroyed and analyzed. Figure 7b shows the data concerning hardness vs. distance from the contact surface; note hardness decrease close to subsurface areas. Wear is actually related to this loss of hardness during the work, regardless of core hardness. The occurrence of thermal cracking is also associated with loss of hardness, 20     as surfaces of lower hardness become more sensitive to the occurrence of thermal cracking. Therefore, increased tempering resistance is essential to further increasing the tool's life time.

25     [0039] The steel of the present invention, IP 2, was then tested and approved for the application, increasing the tools life time by 56%. In numerical values, 5000 parts made of H13 steel could be forged up to the end of the tool's life and this figure increased to 7500 parts made of steel IP 2; the comparative analysis of the tempering curves and hardness vs. time developed for steels H13 (alloy 10) and IP 2, Figures 4 and 6, provides a better understanding of the phenomenon. For both cases the steel hardness decreases when subjected to high temperatures, the greater the drop, the longer the time and the higher the temperature employed. However, there is greater stability of alloy IP 2 at high temperature. Thus, during the forging process, the failure will occur after a higher number of strokes, resulting in the yield gain that was observed.

30

## Claims

1. STEEL WITH HIGH TEMPERING RESISTANCE, characterized by a composition of alloying elements consisting essentially of, in percent by mass, C between 0.20 and 0.50, Si lower than 1.0, P lower than 0.030, Cr between 3.0 and 4.0, Mo between 1.5 and 4.0, V between 0.1 and 2.0, Co lower than 1.5, being the remaining composed of Fe and inevitable deleterious substances.
2. STEEL WITH HIGH TEMPERING RESISTANCE, characterized by a composition of alloying elements consisting essentially of, in percent by mass, C between 0.30 and 0.50, Si lower than 0.8, P lower than 0.020, Cr between 3.0 and 4.0, Mo between 2.0 and 3.0, V between 0.1 and 1.0, Co lower than 1.0, being the remaining composed of Fe and inevitable deleterious substances.
3. STEEL WITH HIGH TEMPERING RESISTANCE, characterized by a composition of alloying elements consisting essentially of, in percent by mass, C between 0.30 and 0.45, Si lower than 0.5, P lower than 0.015, Cr between 3.2 and 3.9, Mo between 2.0 and 3.0, V between 0.3 and 1.0, Co lower than 1.0, being the remaining composed of Fe and inevitable deleterious substances.
4. STEEL WITH HIGH TEMPERING RESISTANCE, characterized by a composition of alloying elements consisting essentially of, in percent by mass, C between 0.30 and 0.40, Si lower than 0.4, P lower than 0.010, Cr between 3.5 and 3.9, Mo between 2.2 and 2.8, V between 0.3 and 0.8, Co lower than 0.5, being the remaining composed of Fe and inevitable deleterious substances.
5. STEEL WITH HIGH TEMPERING RESISTANCE, as per any of claims 1 to 4, characterized by a Mo : W replacement ratio corresponding to 1 Mo : 2 W.
6. STEEL WITH HIGH TEMPERING RESISTANCE, as per any of claims 1 to 5, characterized by a Vanadium : Niobium / Titanium replacement ratio corresponding to 1 V : 2 Nb / 1 Ti.

**EP 2 503 016 A1**

7. STEEL WITH HIGH TEMPERING RESISTANCE as per any of claims 1 to 6, applied to molds, matrixes and multiple-use tools, for formation of solid or liquid materials, at room temperature or at temperatures up to 1300°C.
- 5 8. STEEL WITH HIGH TEMPERING RESISTANCE as per any of claims 1 to 6, used in metal-forming tools subject to temperatures between 300 and 1300°C, and also in other applications such as forging, extrusion or casting ferrous or nonferrous alloys.
- 10 9. STEEL WITH HIGH TEMPERING RESISTANCE produced by processes involving ingot casting and hot/cold forming, or even used with the cast structure.
10. STEEL WITH HIGH TEMPERING RESISTANCE produced by processes involving atomization or dispersion of the molten metal, such as powder metallurgy, powder injection or spray-forming process.

15

20

25

30

35

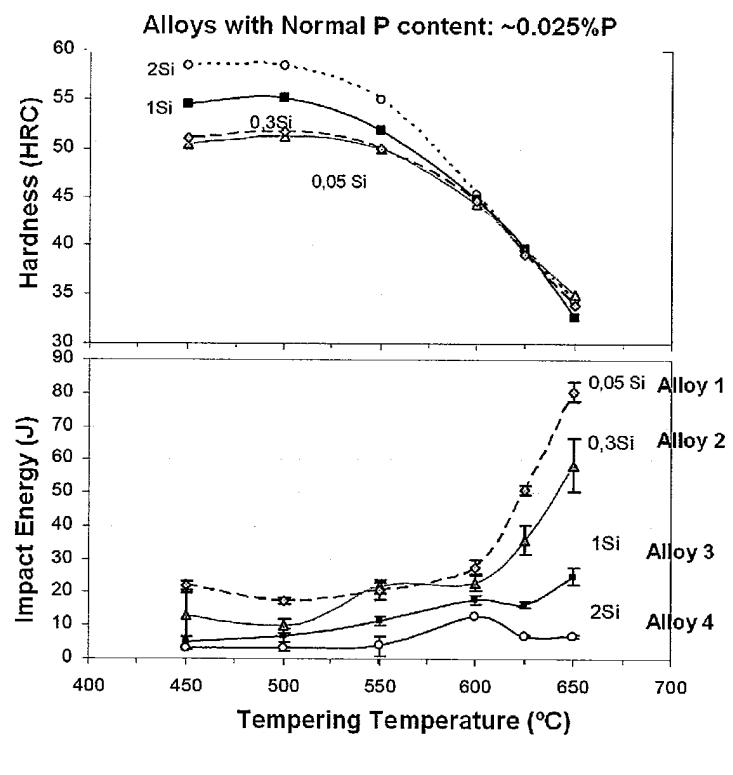
40

45

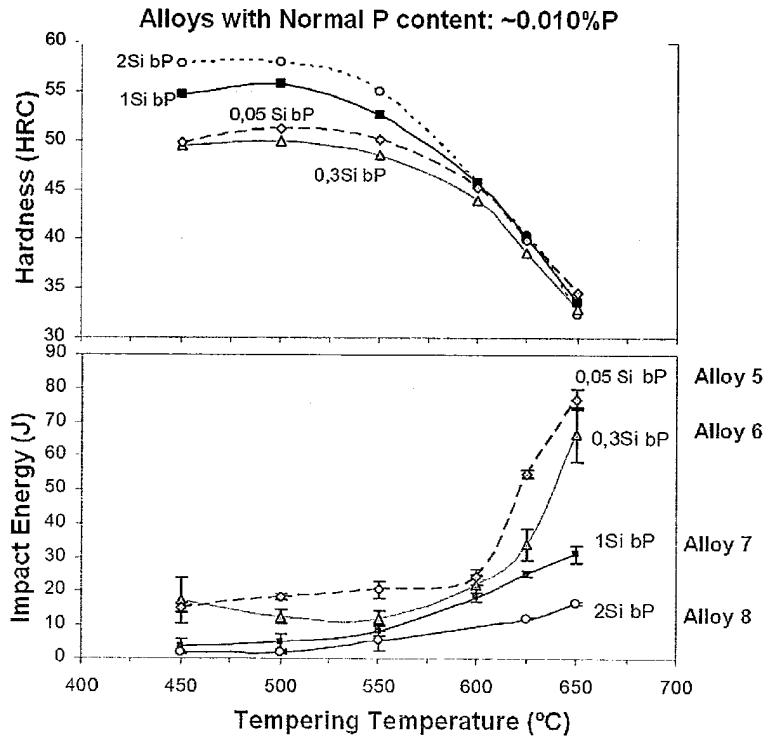
50

55

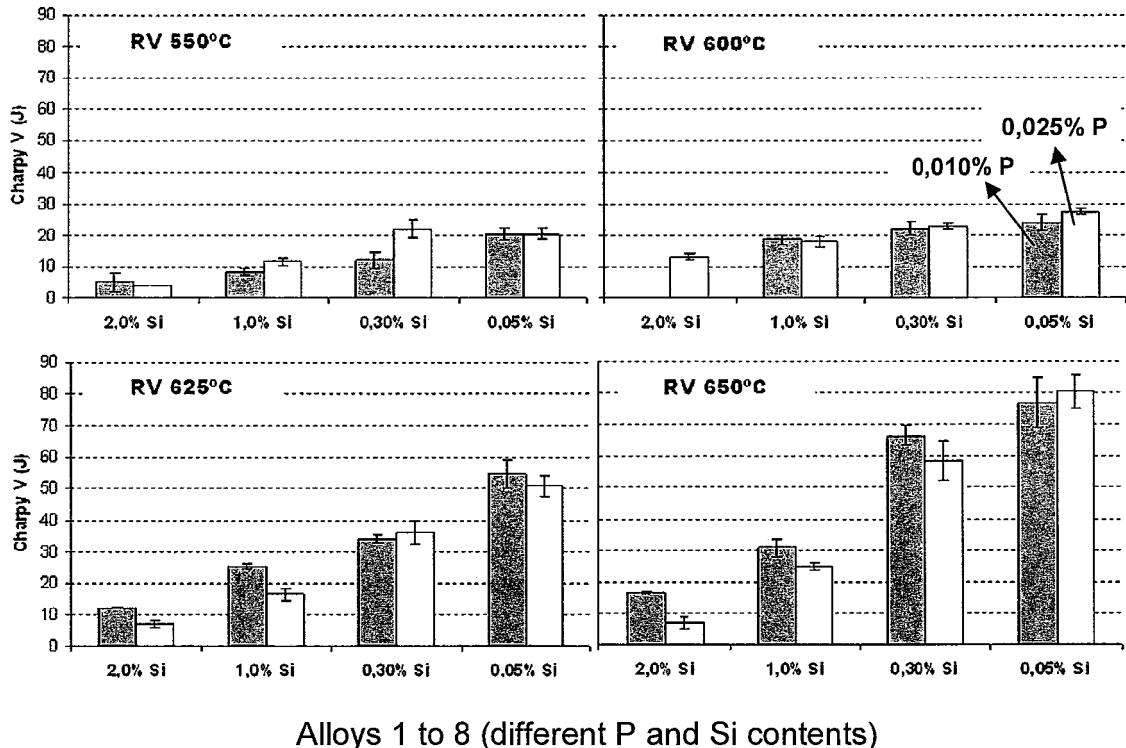
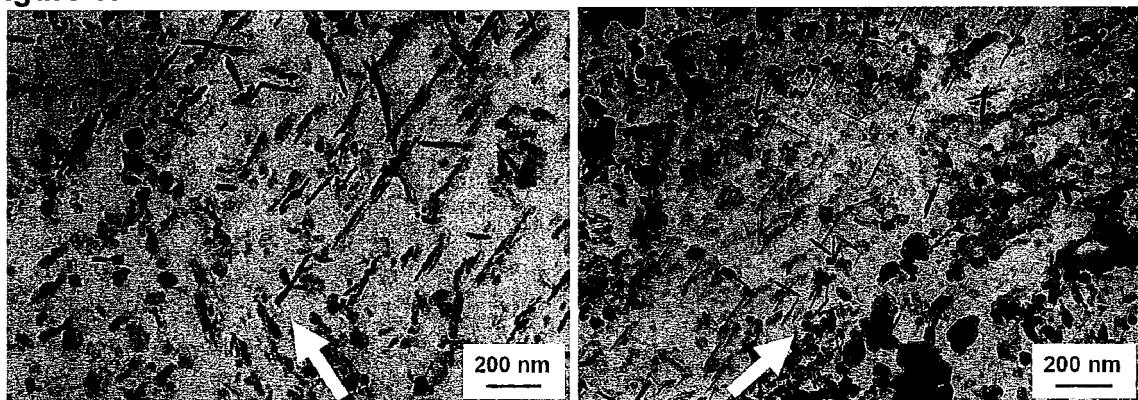
Figure 1:

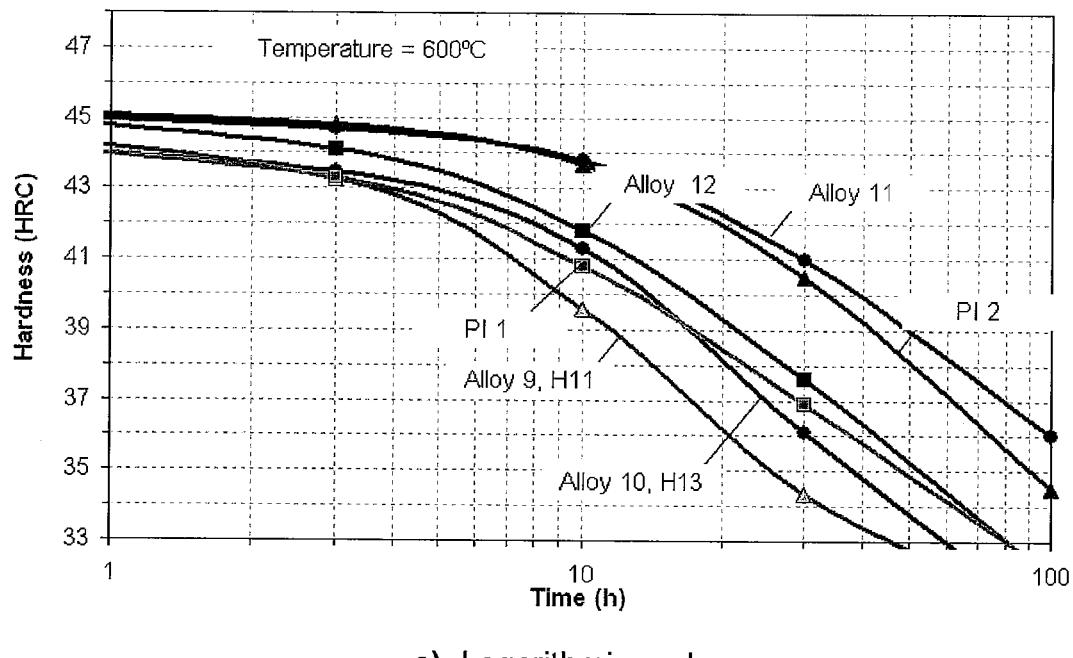
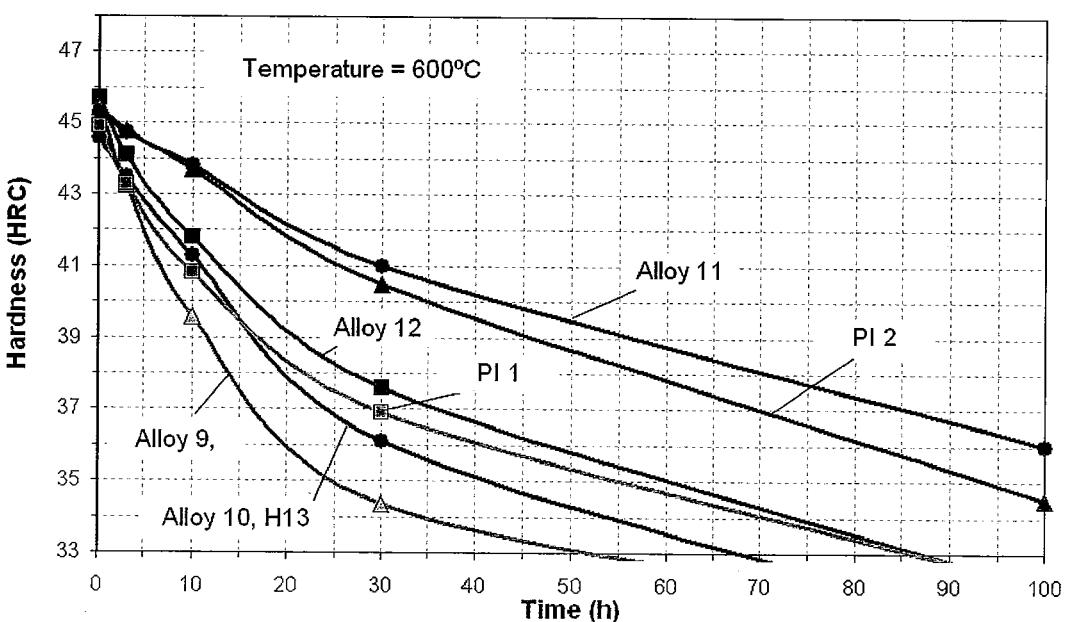


a)



b)

**Figure 2:****Figure 3:****a) Alloy 1 (0.05% Si)****b) Alloy 4 (2.0% Si)**

**Figure 4:****a) Logarithmic scale****b) Linear scale**

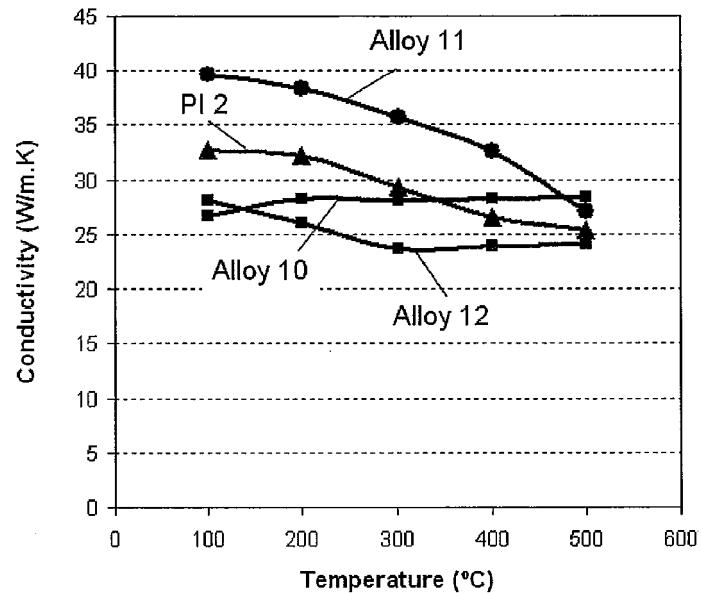
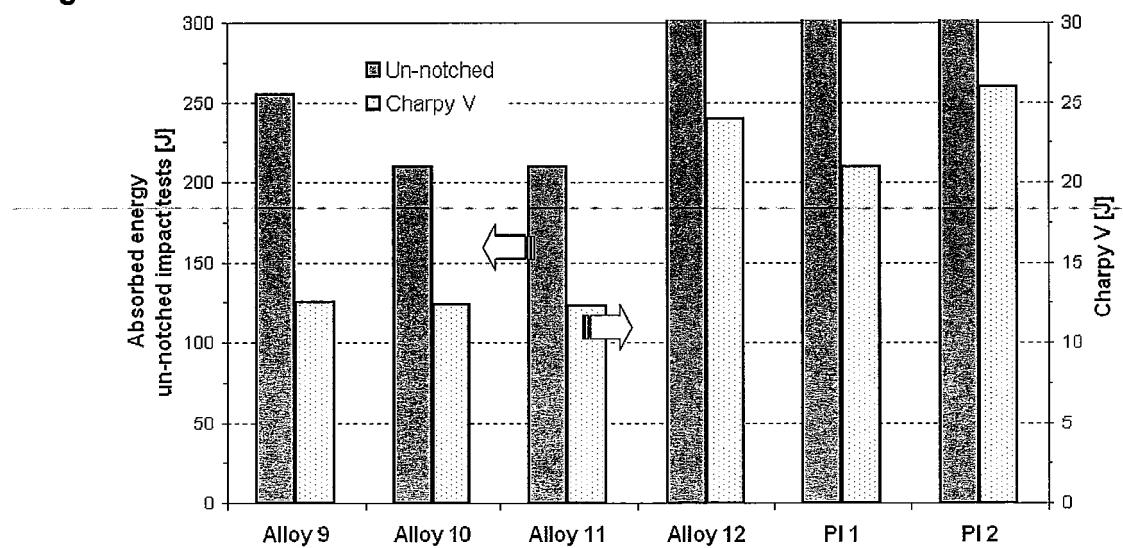
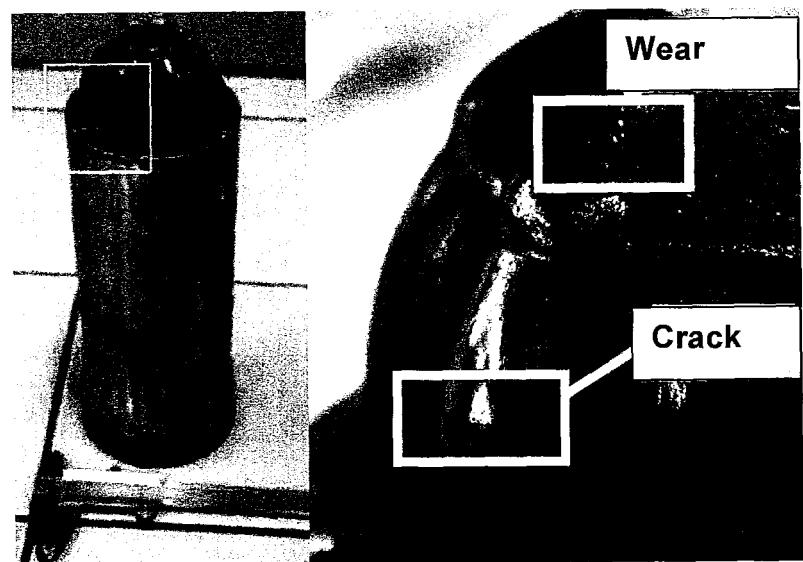
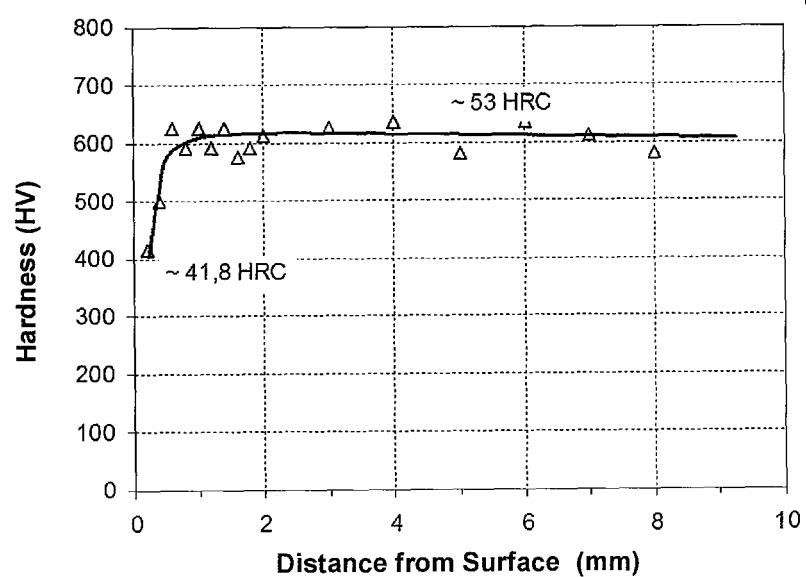
**Figure 5:****Figure 6:**

Figure 7:



a)



b)

<b>INTERNATIONAL SEARCH REPORT</b>		International application No. PCT/BR2010/000375															
<p><b>A. CLASSIFICATION OF SUBJECT MATTER</b></p> <p><b>C22C 38/22 C22C 38/18</b></p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																	
<p><b>B. FIELDS SEARCHED</b></p> <p>Minimum documentation searched (classification system followed by classification symbols)</p> <p><b>C22C 38/--</b></p>																	
<p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p><b>SINPI (INPI DATABASE)</b></p>																	
<p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p> <p><b>EPODOC, ESPACENET, SCIENCE DIRECT, GOOGLE</b></p>																	
<p><b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b></p> <table border="1" style="width: 100%;"> <thead> <tr> <th style="text-align: left;">Category*</th> <th style="text-align: left;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="text-align: left;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>CN 101240401 A (CENTRAL IRON STEEL RES INST [CN]) 13th August 2008 (2008-08-13)</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>US 6365096 B1 (UDDEHOLM TOOLING AB [SE]) 2nd April 2002 (2002-04-02)</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>EP 0632139 A1 (THYSSEN STAHL AG [DE]) 4th January 1995 (1995-01-04)</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>BR 9909160 A (UDDEHOLM TOOLING AB [SE]) 5th December 2000 (2000-12-05)</td> <td>1-10</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	CN 101240401 A (CENTRAL IRON STEEL RES INST [CN]) 13th August 2008 (2008-08-13)	1-10	A	US 6365096 B1 (UDDEHOLM TOOLING AB [SE]) 2nd April 2002 (2002-04-02)	1-10	A	EP 0632139 A1 (THYSSEN STAHL AG [DE]) 4th January 1995 (1995-01-04)	1-10	A	BR 9909160 A (UDDEHOLM TOOLING AB [SE]) 5th December 2000 (2000-12-05)	1-10
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.															
A	CN 101240401 A (CENTRAL IRON STEEL RES INST [CN]) 13th August 2008 (2008-08-13)	1-10															
A	US 6365096 B1 (UDDEHOLM TOOLING AB [SE]) 2nd April 2002 (2002-04-02)	1-10															
A	EP 0632139 A1 (THYSSEN STAHL AG [DE]) 4th January 1995 (1995-01-04)	1-10															
A	BR 9909160 A (UDDEHOLM TOOLING AB [SE]) 5th December 2000 (2000-12-05)	1-10															
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		<input checked="" type="checkbox"/> See patent family annex.															
<p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p> <p>“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</p> <p>“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>“&amp;” document member of the same patent family</p>																	
Date of the actual completion of the international search 25th January 2011 (25.01.2011)		Date of mailing of the international search report 8th February 2011(08.02.2011)															
Name and mailing address of the ISA/ BR Facsimile No.		Authorized officer  Telephone No.															

INTERNATIONAL SEARCH REPORT		International application No. PCT/BR2010/000375
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to claim No.
X	<p>MESQUITA, RA, BARBOSA, CA. Novo aço ferramenta de alta resistência a quente. <i>Tecnologia em Metalurgia e Materiais</i> Vol. 3, No. 3 January-March 2007, pages 63-68 retrieved on 2011-01-24 retrieved from <a href="http://www.abmbrasil.com.br/materias/download/811205.pdf">http://www.abmbrasil.com.br/materias/download/811205.pdf</a> the whole document</p> <p>MESQUITA, RA et al. Casos de aplicação de novos aços ferramenta para trabalho a quente. <i>Tecnologia em Metalurgia e Materiais</i> Vol. 2, No. 1 July-September 2005, pages 70-75 retrieved on 2011-01-24 retrieved from <a href="http://www.abmbrasil.com.br/materias/download/35115.pdf">http://www.abmbrasil.com.br/materias/download/35115.pdf</a> the whole document</p>	1-10

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

PCT/BR2010/000375

CN 101240401 A	2008-08-13	None	
US 6365096 B1	2002-04-02	AT 241023 T AU 740442 B2 AU 3282899 A BR 9909160 A CA 2324499 A1 CN 1295624 A CN 1097641 C DE 1084282 T1 DE 69908124 D1 DK 1084282 T3 ES 2198147 T3 HK 1033966 A1 JP 2002509986 T JP 4516211 B2 PT 1084282 E SE 511758 C2 SE 9801044 D0 TW 524860 B WO 9950468 A1	2003-06-15 2001-11-01 1999-10-18 2000-12-05 1999-10-07 2001-05-16 2003-01-01 2002-11-28 2003-06-26 2003-07-07 2004-01-16 2003-12-05 2002-04-02 2010-08-04 2003-08-29 1999-11-22 1998-03-27 2003-03-21 1999-10-07
EP 0632139 A1	1995-01-04	AT 156865 T DE 4321433 C1 DE 59403705 D1 EP 0632139 B1	1997-08-15 1994-12-08 1997-09-18 1997-08-13
BR 9909160 A	2000-12-05	AT 241023 T AU 740442 B2 AU 3282899 A CA 2324499 A1 CN 1295624 A CN 1097641 C DE 1084282 T1 DE 69908124 D1 DK 1084282 T3 ES 2198147 T3 HK 1033966 A1 JP 2002509986 T JP 4516211 B2 PT 1084282 E SE 511758 C2 SE 9801044 D0 TW 524860 B US 6365096 B1 WO 9950468 A1	2003-06-15 2001-11-01 1999-10-18 1999-10-07 2001-05-16 2003-01-01 2002-11-28 2003-06-26 2003-07-07 2004-01-16 2003-12-05 2002-04-02 2010-08-04 2003-08-29 1999-11-22 1998-03-27 2003-03-21 2002-04-02 1999-10-07

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