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(57) The invention relates to a method that has been developed to obtain good toughness and homogeneous properties through heavy sections in tool steels or likely highly alloyed steels. The microstructure attained is mostly bainitic. The method is especially good for hot work tool steels in applications demanding heavy sections and very high toughness. The method consists on the application of a low temperature bainitic transformation to tool steels presenting a low enough martensite transformation temperature (Ms). Additionally or alterna-

tively cementite is replaced from the bainite by other finer carbides, mainly mixed carbides containing elements with stronger affinity for carbon than iron. The method is especially simple if applied to steels with high contents of Si or Al (>1.3% and >0.4% respectively) where cementite growth is impaired. The method works also well for low cost plastic injection moulding and structural steels. Even some higher alloyed tool steels can benefit from the present method.

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**Description**Field of the invention

**[0001]** The present invention relates to the application of tough fully and partially bainitic heat treatments on certain steels, often alloyed tool steels or steels that can be used for tools and in particular hot work tool steels. This heat treatment strategy allows obtaining a fairly homogeneous distribution of properties through heavy sections. The resulting microstructures present high toughness. The present invention is also often applied to high toughness plastic injection moulding and structural steels and even to cold work and highspeed steels.

Summary

**[0002]** Tool steels often require a combination of different properties which are considered opposed. A typical example can be the yield strength and toughness. For most tool steels the best compromise of such properties is believed to be obtainable when performing a purely martensitic heat treatment followed by the adequate tempering, to attain the desired hardness.

**[0003]** For heavy sections it is often impossible to attain pure martensitic microstructure through the whole cross-section, and very often it is not even possible to attain such a microstructure at the surface. In some tool steels, mixed microstructures with bainite and martensite have a particularly low fracture toughness which is very detrimental for several applications, like for example those where thermal fatigue is a dominant failure mechanism.

**[0004]** For most tool steels to attain a martensitic microstructure through a heavy section implies the employment of very severe cooling that can easily lead to cracking.

**[0005]** In most applications, hardness (i.e mechanical resistance or yield strength) and toughness (resilience or fracture toughness) are not the only relevant material property for the tool steel, but some other properties are as relevant or at least relevant enough to be taken into account when designing the tooling solution. Such properties can be: resistance to working conditions (corrosion resistance, wear resistance, oxidation resistance at high temperatures,...), thermal properties (thermal diffusivity, thermal conductivity, specific heat, heat expansion coefficient,...), magnetic and/or electric properties, temperature resistance and many others. Often these properties are microstructure dependent and thus will be modified during heat treatment. So heat treatment is optimized to render the best property compromise for a given application.

**[0006]** Wear in material shaping processes is, primarily, abrasive and adhesive, although sometimes other wear mechanisms, like erosive and cavitative, are also present. To counteract abrasive wear hard particles are generally required in tool steels, these are normally ceramic particles like carbides, nitrides, borides or some combination of them. In this way, the volumetric fraction, hardness and morphology of the named hard particles will determine the material wear resistance for a given application. Also, the use hardness of the tool material is of great importance to determine the material durability under abrasive wear conditions. The hard particles morphology determines their adherence to the matrix and the size of the abrasive exogenous particle that can be counteracted without detaching itself from the tool material matrix. The best way to counteract the adhesive wear is to use FGM materials (functionally graded materials), normally in the form of ceramic coating on the tool material. In this case, it is very important to provide a good support for the coating which usually is quite brittle. To provide the coating with a good support, the tool material must be hard and have hard particles. In this way, for some industrial applications, it is desirable to have a tool material with high thermal diffusivity at a relatively high level of hardness and with hard particles in the form of secondary carbides, nitrides and/or borides and often also primary hard particles (in the case to have to counteract big abrasive particles).

**[0007]** In some applications the resistance to the working environment is more focused on corrosion or oxidation resistance than wear although both often co-exist. In such cases oxidation resistance at the working temperature or corrosion resistance against the aggressive agent are desirable. For such applications corrosion resistance tool steels are often employed, at different hardness levels and with different wear resistances depending on the application.

**[0008]** Thermal gradients are the cause of thermal shock and thermal fatigue. In many applications steady transmission states are not achieved due to low exposure times or limited amounts of energy from the source that causes a temperature gradient. The magnitude of thermal gradient for tool materials is also a function of their thermal conductivity (inverse proportionality applies to all cases with a sufficiently small Biot number).

**[0009]** Hence, in a specific application with a specific thermal flux density function, a material with a superior thermal conductivity is subject to a lower surface loading, since the resultant thermal gradient is lower. The same applies when the thermal expansion coefficient is lower and the Young's modulus is lower.

**[0010]** Traditionally, in many applications where thermal fatigue is the main failure mechanism, as in many casting or light alloy extrusions cases, it is desirable to maximize conductivity and toughness (usually fracture toughness and CVN).

**[0011]** Most forging applications use hardness in the 48-54 HRC range, plastic injection molding is preferably executed with tools having a hardness around 50-54 HRC, but for big plastic injection moulds often 30-45 HRC pre-hardened

materials are used, die casting of zinc alloys is often performed with tools presenting a hardness in the 47-52 HRc range, while brass and aluminium are more often cast in dies with 35-49 HRc, hot stamping of coated sheet is mostly performed with tools presenting a hardness of 48-54 HRc and for uncoated sheets 54-58 HRc. For sheet drawing and cutting applications the most widely used hardness lies in the 56-66 HRc range. For some fine cutting applications even higher hardness are used in the 64-69 HRc. In almost all instances of the different applications described in this paragraph, either resilience, fracture toughness or both are of great significance.

**[0012]** One additional advantage of bainitic heat treatments is that they can be attained with a less abrupt quenching rate. Also for some tool steels they can deliver a similar microstructure through a thicker section. For some tool steels with a retarded bainitic transformation it is possible to attain a perfectly homogeneous bainitic microstructure through an extremely heavy section.

**[0013]** Unfortunately, it is well known that tool steels with microstructures presenting a considerable portion of bainite in the martensitic intended microstructure present low toughness and in particular low fracture toughness.

**[0014]** Nonetheless, bainite can be very fine and deliver high hardness and toughness if the transformation occurs at low enough temperatures. Many applications require high toughness, whether resilience or fracture toughness. In plastic injection applications often thin walls (in terms of resistant cross-section) are subjected to high pressures. When those walls are thin a big moment is generated on the base that often has a small radius, and thus high levels of fracture toughness are required. In hot working applications, the steels are often subjected to severe thermal cycling, leading to cracks on corners or heat checking on the surface. To avoid the fast propagation of such cracks it is also important for those steels to have as high as possible fracture toughness at the working temperature. Many efforts have been placed to attain purely martensitic structures in such applications, either through proper alloying to delay bainitic transformation kinetics, or through the development of methods to increase the cooling rate but avoiding cracking. The authors have observed that what is quite detrimental for toughness, and especially fracture toughness is the mixture of martensite and bainite, even for small quantities of the latter. But if bainite is the only phase present, or at least strongly dominant, and especially if the bainite is a fine lower bainite then very high values of toughness can be attained, also fracture toughness at high temperatures. The authors have also observed that even for higher and coarser bainite, when the alloying level is high enough and the proper tempering strategy is followed, then most of the coarse cementite can be replaced by finer carbides and good toughness values achieved especially at higher temperatures. As mentioned martensitic heat treatments are often difficult to attain for heavy sections, or they might involve alloying which is detrimental for other properties.

**[0015]** The inventors have observed that a possible way for attaining uniform high toughness values in tooling requiring heavy sections and high mechanical properties is through the achievement of an at least 70% bainitic microstructure (preferably more than 80% and even more than 90%) on tool steels, or likely highly alloyed steels, with a low enough martensite start of transformation temperature and attaining most of the bainitic transformation at a temperature close enough to the martensite start of transformation temperature as to have a fine bainitic microstructure. Alternatively for applications requiring the toughness at higher temperatures, the problem can be solved with the presence of enough alloying elements and the proper tempering strategy to replace most Fe<sub>3</sub>C with other carbides and thus attaining high toughness even for coarser bainite. Also the traditional way can be used in certain instances, consisting in avoiding coarse Fe<sub>3</sub>C and/or its precipitation on grain boundaries with the additions of elements that promote its nucleation like Al, Si.... It is also advantageous for most applications to use thermo-mechanical treatments leading to the refining of the final grain size.

#### State of the art

**[0016]** Super-bainitic or high strength bainitic steels are low alloy steels developed by H.K.D.H. Bhadeshia et al. where low temperature bainitic transformations are used to attain high mechanical properties (as an example can be taken: Very strong low temperature bainite, F.G. Caballero, H.K.D.H. Bhadeshia et al., in: Materials Science and Technology, March 2002, Vol. 18, Pg. 279-284 . DOI 10.1179/026708301225000725). They are steels with low martensite transformation start temperature mostly due to their high carbon contents, and with slow transformation kinetics for equilibrium phases (especially ferrite/perlite and upper bainite). The tool steels of the present invention rely on higher alloying for the attaining of the desirable mechanical properties, and normally lower %Ceq contents. As a consequence the transformation temperatures for the present invention are often higher leading to lower mechanical strength in the "as quenched" condition, which is not normally the condition of usage.

#### Detailed description of the invention

**[0017]** The present invention is based on a combination of alloying and heat treatments and how those heat treatments are applied. The preferred microstructure is predominantly bainitic since is normally the type of microstructure easier to attain in heavy sections and also because it can be very tough if properly attained. For some applications having some

ferrite and or perlite is not too detrimental, but for most applications no ferrite/perlite will be desirable or at the most 2% or eventually 5%. The applications more tolerant to ferrite/perlite can allow up to 10% or even 18%. In a bainitic microstructure generally the presence of martensite leads to a decrease in fracture toughness, for applications where fracture toughness is not so important there is no restrictions on the fraction of bainite and martensite, but the applications where fracture toughness matters on predominantly bainitic microstructures will prefer the absence of martensite or at most its presence up to 2% or eventually 4%. For some compositions 8% or even 17% of martensite might be tolerable and yet maintaining a high fracture toughness level. If high fracture toughness at lower temperatures is desirable, in heavy cross sections, there are two possible strategies to be followed for the steels of the present invention within the predominantly bainitic heat treatments. Either alloy the steel to assure the martensitic transformation temperature is low enough (normally lower than 400°C, preferably lower than 340°C, more preferably lower than 290°C and even lower than 240°C. For extremely fine bainite, but often associated to very slow transformation kinetics the transformation temperature should be below 220°C, preferably below 180°C and even below 140°C), and all transformation kinetics to stable not so desirable structures (ferrite/perlite, upper bainite) slowly enough (at least 600 seconds for 10% ferrite/perlite transformation, preferably more than 1200 seconds for 10% ferrite/perlite transformation, more preferably more than 2200 seconds for 10% ferrite/perlite transformation and even more than 7000 seconds for 10% ferrite/perlite transformation. Also more than 400 seconds for 20% transformation into bainite, preferably more than 800 seconds for 20% bainite, more preferably more than 2100 seconds for 20% bainite and even more than 6200 seconds for 20% bainite) to be able to make a predominantly fine bainite heat treatment. Alternatively the alloying content regarding elements with higher propensity than Fe to alloy with %C, %N and %B has to be chosen to be high enough. In this sense, most significant are the presence of %Mn, %V, %Nb, %Zr, %Ta, %Hf, to a lesser extend %Cr and all other carbide formers. Often more than a 4% in the sum of elements with higher affinity for carbon than iron will be present, preferably more than a 6.2%, more preferably more than 7.2% and even more than 8.4%. Additionally any thermo-mechanical treatment leading to a refining of the final grain size is advantageous, especially for predominantly bainitic heat treatments because then the effect is not only in the improvement of toughness but also in the increase of hardenability, the same can be said for treatments avoiding carbide precipitation on grain boundaries. Such a treatment can be, for example, a first step at high temperatures above 1.020 °C to coarsen the austenite grain size (since it is a diffusion process the higher the temperature the lower the time required, strain can also be introduced through mechanical deformation but recrystallization avoided at this point). Then the steel is cooled fast enough to avoid transformation into stable microstructures (ferrite/perlite, and also bainite as much as possible) and also to minimize carbide precipitation. Finally the steel is stress released at a temperature close to Ac1. This will promote the nucleation of very fine grains in the final heat treatment, especially if it is predominantly bainitic.

**[0018]** The present invention is especially well suited to obtain steels for the hot stamping tooling applications. The steels of the present invention perform especially well when used for plastic injection tooling. They are also well fitted as tooling for die casting applications. Another field of interest for the steels of the present document is the drawing and cutting of sheets or other abrasive components. Also forging applications are very interesting for the steels of the present invention, especially for closed die forging. Also for medical, alimentary and pharmaceutical tooling applications the steels of the present invention are of especial interest.

**[0019]** The present invention suits especially well when using steels presenting high thermal conductivity (thermal conductivity above 35 W/mK, preferably 42 W/mK, more preferably 48 W/mK and even 52 W/mK), since their heat treatment is often complicated especially for large or complex in geometry dies. In such cases the usage of the present invention can lead to very significant costs savings, due to the levels of toughness not attainable in any other way, at least at high hardness levels and for heavy sections. The present invention is well indicated in particular when using high thermal conductivity steels, within the following composition range, all percentages being indicated in weight percent:

%C <sub>eq</sub> = 0.16—1.9	%C = 0.16-1.9	%N = 0-1.0	%B = 0-0.6
%Cr < 3.0	%Ni = 0—6	%Si = 0-1.4	%Mn = 0-3
%Al = 0-2.5	%Mo = 0-10	%W = 0-10	%Ti = 0-2
%Ta = 0-3	%Zr = 0-3	%Hf = 0-3	%V = 0-4
%Nb = 0-1.5	%Cu = 0-2	%Co = 0—6,	

any other element except iron not present in an amount of more than 1%,  
the rest consisting of iron, wherein

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

characterized in that

$\%Mo + \frac{1}{2} \cdot \%W > 2.0$ .

**[0020]** Some smaller ranges within the above mentioned compositional range are of special significance for certain applications. For example when it comes to the %Ceq content it is preferably to have a minimum value of 0.22% or even 0.33%. On the other hand for very high conductivity applications it is better to keep %C below 1.5% and preferably below 0.9%. %Ceq has a strong effect in reducing the temperature at which martensitic transformation starts, thus higher values of %Ceq will be desirable for either high wear resistance applications or applications where a fine bainite is desirable. In such cases it is desirable to have a minimum of 0.4% of Ceq often more than 0.5% and even more than 0.8%. If some other elements that reduce the martensite transformation temperature are present (like for example %Ni) then the same effect can be obtained with lower %Ceq (same levels as described before). Also the %Moeq ( $\%Mo + \frac{1}{2} \cdot \%W$ ) levels should be higher for maximum thermal conductivity, normally above 3.0% often above 3.5%, preferably above 4% or even 4.5%. But high levels of %Moeq do tend to shorten the bainitic transformation time. Also if thermal conductivity needs to be maximized is better to do so within a compositional range with lower %Cr, normally less than 2.8% preferably less than 1.8% and even less than 0.3%. A special attention has to be placed in elements that increase hardenability by slowing the kinetics of the austenite decomposition into ferrite/perlite. Very effective in this sense is %Ni and somewhat less %Mn. Thus for heavy sections it is often desirable to have a minimum %Ni content normally 1%, preferably 1.5% and even 3%. If %Mn is chosen for this goal higher amounts are required to attain the same effect. About double as much quantity is required as is the case for %Ni. For applications where the steel is to attain temperatures in excess of 400 °C during service it might be very interesting to have %Co present which tends to increase tempering resistance amongst others and presents the odd effect of affecting the thermal diffusivity positively for high temperatures. Although for some compositions an amount of 0.8% might suffice, normally it is desirable to have a minimum of 1.0% preferably 1.5% and for some applications even 2.7%. Also for applications where wear resistance is important it is advantageous to use strong carbide formers, then  $\%Zr + \%Hf + \%Nb + \%Ta$  should be above 0.2%, preferably 0.8% and even 1.2%. Also %V is good carbide former that tends to form quite fine colonies but has a higher incidence on thermal conductivity than some of the former, but in applications where thermal conductivity should be high but is not required to be extremely high and wear resistance and toughness are both important, it will generally be used with a content above 0.1%, preferably 0.3% and even more than 0.55%. For very high wear resistance applications it can be used with a content higher than 1.2% or even 2.2%.

**[0021]** So, for such kind of steels, unusually high final tempering temperatures end up being used, often above 600°C, even when hardness over 50 HRC are chosen. In steels of the present invention it is usual to achieve hardness of 47 HRC, even more than 52 HRC, and often more than 53 HRC and with the embodiments regarded as particularly advantageous due to their wear resistance, hardness above 54 HRC, and often more than 56 HRC are possible with even one tempering cycle above 590°C, giving a low scattering structure characterized by a thermal diffusivity greater than 8 mm<sup>2</sup>/s and, generally, more than 9 mm<sup>2</sup>/s, or even more than 10 mm<sup>2</sup>/s, when particularly well executed then greater than 11 mm<sup>2</sup>/s, even greater than 12 mm<sup>2</sup>/s an occasionally above 12,5 mm<sup>2</sup>/s. As well as achieving hardness greater than 46 HRC, even more than 50 HRC with the last tempering cycle above 600°C, often above 640°C, and sometimes even above 660 °C, presenting a low scattering structure characterized by a thermal diffusivity higher than 10 mm<sup>2</sup>/s, or even than 12 mm<sup>2</sup>/s, when particularly well executed then greater than 14 mm<sup>2</sup>/s, even greater than 15 mm<sup>2</sup>/s and occasionally above 16 mm<sup>2</sup>/s. Those alloys can present even higher hardness with lowering tempering temperatures, but for most of the intended applications a high tempering resistance is very desirable. Actually the bainitic microstructure presents a markedly higher tempering resistance in this kind of steels. As can be seen in the examples with some very particular embodiments with high carbon and high alloying, leading to a high volume fraction of hard particles, hardness above 60 HRC with low scattering structures characterized by thermal diffusivity above 8mm<sup>2</sup>/s and generally more than 9mm<sup>2</sup>/s are possible in the present invention.

**[0022]** The present invention can be particularly interesting for applications requiring a steel with improved ambient resistance, especially when high levels of mechanical characteristics are desirable for big cross sections. The present invention is then especially good indicated when using ambient resistant steels within the following compositional range, all percentages being indicated in weight percent:

$\%C_{eq} = 0.15-3.0$	$\%C = 0.15-3.0$	$\%N = 0-1.6$	$\%B = 0-2.0$
$\%Cr > 4.0$	$\%Ni = 0-6.0$	$\%Si = 0-2.0$	$\%Mn = 0-3$
$\%Al = 0-2.5$	$\%Mo = 0-15$	$\%W = 0-15$	$\%Ti = 0-2$
$\%Ta = 0-3$	$\%Zr = 0-3$	$\%Hf = 0-3$	$\%V = 0-12$
$\%Nb = 0-3$	$\%Cu = 0-2$	$\%Co = 0-6,$	

any other element except iron not present in an amount of more than 1%, the rest consisting of iron, wherein

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

**[0023]** Some smaller ranges within the above mentioned compositional range are of special significance for certain

applications. For example when it comes to the %Ceq content it is preferably to have a minimum value of 0.22%, preferably 0.28% more preferably 0.34% and when wear resistance is important preferably 0.42% and even more preferably 0.56%. Very high levels of %Ceq are interesting due to the low temperature at which martensite transformation starts, such applications favor %Ceq maximum levels of 1.2%, preferably 1.8% and even 2.8%. Applications where toughness is very important favor lower %Ceq contents, and thus maximum levels should remain under 0.9% preferably 0.7% and for very high toughness under 0.57%. Although a noticeable ambient resistance can be attained with 4% Cr, usually higher levels of %Cr are recommendable, normally more than 8% or even more than 10%. For some special attacks like those of chlorides it is highly recommendable to have %Mo present in the steel, normally more than 2% and even more than 3.4% offer a significant effect in this sense. Also for applications where wear resistance is important it is advantageous to use strong carbide formers, then %Zr+%Hf+%Nb+%Ta should be above 0.2%, preferably 0.8% and even 1.2%. Also %V is good carbide former that tends to form quite fine colonies but has a higher incidence on thermal conductivity than some of the former, but in applications where thermal conductivity should be high but is not required to be extremely high and wear resistance and toughness are both important, it will generally be used with a content above 0.1%, preferably 0.54% and even more than 1.15%. For very high wear resistance applications it can be used with content higher than 6.2% or even 8.2%.

**[0024]** The present invention can be particularly interesting for applications requiring a steel with corrosion or oxidation resistance, especially when high levels of mechanical characteristics are desirable throughout heavy sections. The present invention is then especially good indicated when using corrosion resistant steels within the following compositional range, all percentages being indicated in weight percent:

%C <sub>eq</sub> = 0.15-2.0	%C = 0.15-0.9	%N = 0-0.6	%B = 0-0.6
%Cr > 11.0	%Ni = 0-12	%Si = 0-2.4	%Mn = 0-3
%Al = 0-2.5	%Mo = 0-10	%W = 0-10	%Ti = 0-2
%Ta = 0-3	%Zr = 0-3	%Hf = 0-3	%V = 0-12
%Nb = 0-3	%Cu = 0-2	%Co = 0-12,	

any other element except iron not present in an amount of more than 1%, the rest consisting of iron, wherein

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

**[0025]** Some smaller ranges within the above mentioned compositional range are of special significance for certain applications. For example when it comes to the %Ceq content it is preferably to have a minimum value of 0.22%, preferably 0.38% more preferably 0.54% and when wear resistance is important preferably 0.82%, more preferably 1.06% and even more than 1.44%. Very high levels of %Ceq are interesting due to the low temperature at which martensite transformation starts, such applications favor %Ceq maximum levels of 0.8%, preferably 1.4% and even 1.8%. Applications where toughness is very important favor lower %Ceq contents, and thus maximum levels should remain under 0.9% preferably 0.7% and for very high toughness under 0.57%. Although corrosion resistance for martensitic microstructure can be attained with 11 % Cr, usually higher levels of %Cr are recommendable, normally more than 12% or even more than 16%. For some special attacks like those of chlorides and to enhance hardness gradient at the secondary hardness peak it is highly recommendable to have %Moeq present in the steel, often more than 0.4%, preferably more than 1.2% and even more than 2.2% offer a significant effect in this sense. Also for applications where wear resistance or thermal conductivity are important it is advantageous to use strong carbide formers, then %Zr+%Hf+%Nb+%Ta should be above 0.1%, preferably 0.3% and even 1.2%. Also %V is good carbide former that tends to form quite fine colonies but has a higher incidence on thermal conductivity than some of the former, but in applications where thermal conductivity should be high but is not required to be extremely high and wear resistance and toughness are both important, it will generally be used with a content above 0.1%, preferably 0.24% and even more than 1.15%. For very high wear resistance applications it can be used with content higher than 4.2% or even 8.2%.

**[0026]** The present invention can be particularly interesting for applications requiring a steel with very high wear resistance, especially when high levels of hardness are desirable throughout heavy sections. The present invention is then especially good indicated when using high wear resistant steels within the following compositional range, all percentages being indicated in weight percent:

%C <sub>eq</sub> = 0.5-3.0	%C = 0.5-3.0	%N = 0-2.2	%B = 0-2.0
%Cr = 0.0-14	%Ni = 0-6.0	%Si = 0-2.0	%Mn = 0-3
%Al = 0-2.5	%Mo = 0-15	%W = 0-15	%Ti = 0-4

(continued)

%Ta = 0-4      %Zr = 0-12      %Hf = 0-4      %V = 0-12  
 %Nb = 0-4      %Cu = 0-2      %Co = 0-6,

any other element except iron not present in an amount of more than 1%, the rest consisting of iron, wherein

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

**[0027]** Some smaller ranges within the above mentioned compositional range are of special significance for certain applications. For example when it comes to the %Ceq content it is preferably to have a minimum value of 0.62%, preferably 0.83% more preferably 1.04% and when extreme wear resistance is important preferably 1.22%, more preferably 1.46% and even more than 1.64%. Very high levels of %Ceq are interesting due to the low temperature at which martensite transformation starts, such applications favor %Ceq maximum levels of 1.8%, preferably 2.4% and even 2.8%. %Cr has two ranges of particular interest: 3.2%-5.5% and 5.7%-9.4%. To enhance hardness gradient at the secondary hardness peak it is highly recommendable to have %Moeq present in the steel, often more than 2.4%, preferably more than 4.2% and even more than 10.2% offer a significant effect in this sense. Also for applications where wear resistance or thermal conductivity are important it is advantageous to use strong carbide formers, then %Zr+%Hf+%Nb+%Ta should be above 0.1%, preferably 1.3% and even 3.2%. Also %V is good carbide former that tends to form quite fine colonies of very hard carbides, thus when wear resistance and toughness are both important, it will generally be used with a content above 1.2%, preferably 2.24% and even more than 3.15%. For very high wear resistance applications it can be used with content higher than 6.2% or even 10.2%.

**[0028]** The present invention can be also applied for the manufacturing of big plastic injection tools particularly interesting for applications requiring very low cost steel with high mechanical resistance and toughness. This particular application of the present invention is also interesting for other applications requiring inexpensive steels with high toughness and considerable yield strength throughout heavy sections. The present invention is then applied to low cost steels within the following compositional range, all percentages being indicated in weight percent:

%Ceq = 0.2-0.9    %C = 0.2-0.9    %N = 0-0.6    %B = 0-0.6  
 %Cr = 0.0-4.0    %Ni = 0-6.0    %Si = 0.2-2.8    %Mn = 0.2-3  
 %Al = 0-2.5    %Mo = 0-6    %W = 0-8    %Ti = 0-2  
 %Ta = 0-2    %Zr = 0-2    %Hf = 0-2    %V = 0-4  
 %Nb = 0-2    %Cu = 0-2    %Co = 0-6,

any other element except iron not present in an amount of more than 2%,  
 the rest consisting of iron, wherein

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

characterized in that

%Si + %Mn + %Ni + %Cr > 2.0, or

%Mo > 1.2, or

%B > 2 ppm

**[0029]** It should be clear that from all the possible compositions within the range only those where the microstructure described in the present invention is attainable are of interest. Some smaller ranges within the above mentioned compositional range are of special significance for certain applications. For example when it comes to the %Ceq content it is preferably to have a minimum value of 0.22%, preferably 0.28%, more preferably 3.2% and even 3.6%. Very high levels of %Ceq are interesting due to the low temperature at which martensite transformation starts, such applications favor %Ceq maximum levels of 0.6%, preferably 0.8% and even 0.9%. %Cr has two ranges of particular interest: 0.6%-1.8% and 2.2%-3.4%. To enhance hardness gradient at the secondary hardness peak it is highly recommendable to have %Moeq present in the steel, often more than 0.4%, preferably more than 1.2%, more preferably more than 1.6% and even more than 2.2% offer a significant effect in this sense. In this particular application of the invention the elements that mostly remain in solid solution, the most representative being %Mn, %Si and %Ni are very critical. It is desirable to have the sum of all elements which primarily remain in solid solution exceed 0.8%, preferably exceed 1.2%, more

preferably 1.8% and even 2.6%. As can be seen both %Mn and %Si need to be present. %Mn is often present in an amount exceeding 0.4%, preferably 0.6% and even 1.2%. The case of %Si is even more critical since when present in significant amounts it strongly contributes to the retarding of cementite coarsening. Therefore %Si will often be present in amounts exceeding 0.4%, preferably 0.6% and even 0.8%. When the effect on cementite is pursued then the contents are even bigger, often exceeding 1.2%, preferably 1.4% and even 1.65%. Also for applications where wear resistance or thermal conductivity are important it is advantageous to use strong carbide formers, then %Zr+%Hf+%Nb+%Ta should be above 0.1%, preferably 1.3% and even 2.2%. Also %V is good carbide former that tends to form quite fine colonies of very hard carbides, thus when wear resistance and toughness are both important, it will generally be used with a content above 0.2%, preferably 0.4% and even more than 0.8%. For very high wear resistance applications it can be used with content higher than 1.2% or even 2.2%. Other elements may be present, especially those with little effect on the objective of the present invention. In general it is expected to have less than 2% of other elements (elements not specifically cited), preferably 1%, more preferably 0.45% and even 0.2%. As can be seen the critical elements for attaining the mechanical properties desired for such applications need to be present and thus it has to be %Si+%Mn+%Ni+%Cr greater than 2.0%, preferably greater than 2.2%, more preferably greater than 2.6% and even greater than 3.2%. For some applications it is interesting to replace %Cr for %Mo, due to the higher effect on the secondary hardness peak and the improved thermal conductivity potential it impairs the steel, and then the same limits apply. Alternatively to %Si+%Mn+%Ni+%Mo > 2.0%.... the presence of %Mo can be dealt alone when present in an amount exceeding 1.2%, preferably exceeding 1.6%, and even exceeding 2.2%. For the applications where cost is important it is specially advantageous to have the expression %Si + %Mn + %Ni + %Cr replaced by %Si + %Mn and then the same preferential limits can apply, but in presence of other alloying elements, also lower limits can be used like %Si+%Mn > 1.1%, preferably 1.4% or even 1.8%. For this kind of steels tough bainite treatments at temperatures close to martensite start of transformation (Ms) are very interesting (often 70% or more, preferably 70% and more, or even 82% or more of the transformation of austenite should take place below 520 °C, preferably 440 °C, more preferably 410 °C or even 380 °C, but not below 50 °C below martensite start of transformation [Ms]).

**[0030]** A contribution to the increase in toughness in the bainitic microstructures of the present invention can be made through the dissolution of the cementite and the carbon that goes into solid solution can contribute to the separation or precipitation of carbides containing carbide-forming elements. (Cr, Mo, W, V, Nb, Zr, Ta, Hf...) often mixed carbides containing those elements and others like for example iron. Those carbides often precipitate as M7C3, M4C3, MC, M6C, M2C and others carbides. The temperature at which this happens is often above 400 °C, preferably 450 °C, more preferably 480 °C and even 540 °C.

**[0031]** For applications where mechanical strength more than wear resistance are important, and it is desirable to attain such mechanical strength without compromising all too much toughness, the volume fraction of small secondary hard particles is of great importance. Small secondary hard particles, in this document, are those with a maximum equivalent diameter (diameter of a circle with equivalent surface as the cross section with maximum surface on the hard particle) below 7.5 nm. It is then desirable to have a volume fraction of small secondary hard particles for such applications above 0.5%. It is believed that a saturation of mechanical properties for hot work applications occurs at around 0.6%, but it has been observed by the inventors that for some applications requiring high plastic deformation resistance at somewhat lower temperatures it is advantageous to have higher amounts than these 0.6%, often more than 0.8% and even more than 0.94%. Since the morphology (including size) and volume fraction of secondary carbides change with heat treatment, the values presented here describe attainable values with proper heat treatment.

**[0032]** Cobalt has often been used in hot work tool steels principally due to the increase in mechanical strength, and in particular the increase of yield strength maintained up to quite high temperatures. This increase in yield strength is attained through solid solution and thus it has a quite negative effect in the toughness. The common amounts of Co used for this propose is 3%. Besides the negative effect in toughness it is also well known the negative effect in the thermal conductivity. The inventors have seen that within the compositional ranges of the present invention it is possible to use Co, and attain an improved yield strength/ toughness relation since Co can promote the nucleation of secondary hard particles and thus keep their size small. It has also been seen that for some compositions of the present invention, when adding Co the Thermal diffusivity does indeed decrease at room temperature, but then can actually increase at higher temperatures (normally above 400 °C) if the correct thermo-mechanical treatment is applied. The inventors have seen that the best results are encountered when %Co is above 1.3%, preferably above 1.5% and optimally above 2.4%. Also %C should exceed 3.2%, preferably 3.4% and optimally 3.6%. If thermal conductivity at high temperatures is of outmost importance for the application a special care has to be taken not to have excessive %V, it should be kept below 2.8%, preferably below 2.3% and optimally below 1.7%. Finally %Mo should normally exceed 3.3% often 3.5% and even 4.0%. Heat treatment has to be selected with a rather high austenitization temperature and an abnormally high tempering temperatures, actually more than 55 HRC commonly achieved with at least one tempering cycle at 630 °C or even above, 50 HRC can be maintained even with one tempering cycle at 660 °C or more. Proper thermo-mechanical processing together with the compositional rules just explained have to be implemented to minimize scattering at high temperatures, the optimized arrangements is characterized by providing diffusivities of more than 5.8 mm<sup>2</sup>/s, often more than 6.1 mm<sup>2</sup>/s



and even more than 6.5mm<sup>2</sup>/s at measuring temperatures as high as 600 °C.

**[0033]** To increase machinability S, As, Te, Bi or even Pb, Ca, Cu, Se, Sb or others can be used, with a maximum content of 1%, with the exception of Cu, than can even be of 2%. The most common substance, sulfur, has, in comparison, a light negative effect on the matrix thermal conductivity in the normally used levels to increase machinability. However, its presence must be balanced with Mn, in an attempt to have everything in the form of spherical manganese bisulphide, less detrimental for toughness, as well as the least possible amount of the remaining two elements in solid solution in case that thermal conductivity needs to be maximized.

**[0034]** Another hardening mechanism can be used in order to search for some specific combination of mechanical properties or environmental degradation resistance. It is always the intention to maximize the desired property, but trying to have minimal possible adverse impact on thermal conductivity. Solid solution with Cu, Mn, Ni, Co, Si, etc... (including some carbide formers with less affinity to carbon, like Cr) and interstitial solid solution (mainly with C, N and B). For this purpose, precipitation can also be used, with an intermetallic formation like Ni<sub>3</sub>Mo, NiAl, Ni<sub>3</sub>Ti... (also of Ni and Mo, small quantities of Al and Ti can be added, but special care must be taken for Ti, since it dissolves in M<sub>3</sub>Fe<sub>3</sub>C carbides and a 2% should be used as a maximum). Finally, other carbide types can also be used, but it is usually difficult to maintain high levels of thermal conductivity, unless carbide formers present a very high affinity with carbon, as it has been described throughout this document. Co can be used as a hardener by solid solution or as a catalyst of Ni intermetallic precipitation, rarely in contents higher than 6%. Some of these elements are also not as harmful when dissolved in M<sub>3</sub>Fe<sub>3</sub>C carbides, or other carbides of (Fe, Mo, W), this is specially the case for Zr and Hf and, to a lesser extent, for Ta, these can also limit V and Nb solubility.

**[0035]** When amounts are measured in weight percentage, atomic mass and the formed type of carbide determine if the quantity of a used element should be big or small. So, for instance, 2%V is much more than 4%W. V tends to form MC carbides, unless it dissolves in other existing carbides. Thus, to form a carbide unit only a unit of V is needed, and the atomic mass is 50.9415. W tends to form M<sub>3</sub>Fe<sub>3</sub>C carbides in hot work steels. So three units of W are needed to form a carbide unit, and the atomic mass is 183.85. Therefore, 5.4 more times carbide units can be formed with 2%V than with 4%W.

**[0036]** Tool steel of the present invention can be manufactured with any metallurgical process, among which the most common are sand casting, lost wax casting, continuous casting, melting in electric furnace, vacuum induction melting. Powder metallurgy processes can also be used along with any type of atomization and eventually subsequent compacting as the HIP, CIP, cold or hot pressing, sintering (with or without a liquid phase and regardless of the way the sintering process takes place, whether simultaneously in the whole material, layer by layer or localized), laser cusing, spray forming, thermal spray or heat coating, cold spray to name a few of them. The alloy can be directly obtained with the desired shape or can be improved by other metallurgical processes. Any refining metallurgical process can be applied, like VD, ESR, AOD, VAR... Forging or rolling are frequently used to increase toughness, even three-dimensional forging of blocks. Tool steel of the present invention can be obtained in the form of bar, wire or powder (amongst others to be used as solder or welding alloy). Even, a low-cost alloy steel matrix can be manufactured and applying steel of the present invention in critical parts of the matrix by welding rod or wire made from steel of the present invention. Also laser, plasma or electron beam welding can be conducted using powder or wire made of steel of the present invention. The steel of the present invention could also be used with a thermal spraying technique to apply in parts of the surface of another material. Obviously the steel of the present invention can be used as part of a composite material, for example when embedded as a separate phase, or obtained as one of the phases in a multiphase material. Also when used as a matrix in which other phases or particles are embedded whatever the method of conducting the mixture (for instance, mechanical mixing, attrition, projection with two or more hoppers of different materials...).

**[0037]** Tool steel of the present invention can also be used for the manufacturing of parts under high thermo-mechanical loads and wear resistance or, basically, of any part susceptible to failure due to wear and thermal fatigue, or with requirements for high wear resistance and which takes advantage of its high thermal conductivity. The advantage is a faster heat transport or a reduced working temperature. As an example: components for combustion engines (such as rings of the engine block), reactors (also in the chemical industry), heat exchange devices, generators or, in general, any power processing machine. Dies for forging (open or closed die), extrusion, rolling, casting and metal thixoforming. Dies for plastic forming of thermoplastics and thermosets in all of its forms. In general, any matrix, tool or part can benefit from increased wear resistance and thermal fatigue. Also dies, tools or parts that benefit from better thermal management, as is the case of material forming or cutting dies with release of large amounts of energy (such as stainless steel or TRIP steels) or working at high temperatures (hot cutting, hot forming of sheet).

**[0038]** Additional embodiments are described in the dependent claims.

## EXAMPLES

**[0039]** All values are given in weight percentage.

**[0040]** The following examples show properties that can be obtained:

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Other	Maintenance T°/time °C/h	Hardness / CVN HRc/J
0.40	0.09	0.27	0.05	2.1	1.4	1.53	-	263 72*	42 40
0.39	0.05	0.2	0.02	<0.01	1.5	1.6	Ni,B	300 72*	35 34
0.38	0.05	0.26	0.4	<0.01	1.5	1.56	-	310 72	38 >450**
0.27	3.76	1.39	0.5	<0.01	<0.05	<0.01	Ni=3.5 Zr, Hf	230 120*	41 14
0.37	3.46	1.01	<0.01	<0.01	<0.05	<0.01	Ni=2.8	RT slow cool*	45 >450**
0.33	3.8	1.22	0.4	1.06	0.1	<0.01	Hf, Zr, Nb	360 72*	52 250**
0.38	3.74	1.36	0.02	<0.01	<0.05	<0.01	Zr, Hf, Nb	280 72*	50 102**
1.02	1.78	0.92	2.4	8.01	1.12	0.28		250 200*	60 148**
* Tempering cycles have been applied with at least one tempering in the 520- 680 °C range.									
**Charpy pendulum resilience was evaluated on a 10x10x55 mm unnotched sample.									

## Claims

1. A method to manufacture a steel, casting die or tool, comprising providing a steel with both a bainite and a martensite domain of existence, **characterized in that** the steel is subjected to a thermal treatment comprising austenitization followed by a cooling rapid enough to avoid the massive formation of stable phases with a transformation temperature higher than bainite, and maintaining the temperature high and long enough to minimize the transformation of austenite to martensite, so that at least 60% of the transformation takes place below the martensite start of transformation temperature(Ms)+200°C but above Ms-50°C;  
in such manner that at least 70% bainitic microstructure with fine carbide-like constituents is attained, so that a CVN higher than 8 Joule is achieved within at least 20mm from the surface of the thermally treated steel.
2. The method according to claim 1, wherein the steel has a martensite start (Ms) of transformation equal or lower than 480°C
3. The method according to claims 1 or 2, wherein the steel contains at least 3% carbide formers stronger than iron and the thermal treatment is followed by at least one tempering cycle above 500°C to separate the alloy cementite, to dissolve the cementite in solid solution, and to separate the carbide formers stronger than iron.
4. The method according to any of claims 1 to 3, wherein the steel contains at least 1.3% Si and/or 0.4% Al to retard the cementite growth.
5. The method according to any of claims 1 or 4 wherein, upon formation of the bainite, the steel is tempered with at least one tempering cycle at a temperature above 500°C to ensure that a significant portion of the cementite is replaced by carbide-like structures containing carbide formers stronger than iron.
6. The method according to any of claims 1 to 5, wherein the steel is a high thermal conductivity steel and that at the least one tempering cycle is carried out at a temperature above 540°C, so that a low scattering structure **characterized by** a thermal diffusivity higher than 8 mm<sup>2</sup>/s is obtainable.
7. The method according to any one of claims 1 to 6, wherein the steel has a composition within the following compositional range, all percentages being indicated in weight percent:

%C <sub>eq</sub> = 0.16-1.9	%C = 0.16-1.9	%N = 0-1.0	%B = 0-0.6
%Cr < 3.0	%Ni = 0—06	%Si = 0-1.4	%Mn = 0-3
%Al = 0-2.5	%Mo = 0-10	%W = 0-10	%Ti = 0-2

(continued)

%Ta = 0-3      %Zr = 0-3      %Hf = 0-3      %V = 0-4  
 %Nb = 0-1.5      %Cu = 0-2      %Co = 0-6

any other element except iron not being present in an amount of more than 2%,  
 the rest consisting of iron, wherein

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

and

$$\%Mo + \frac{1}{2} \cdot \%W > 2.0.$$

8. The method according to anyone of claims 1 to 6, wherein the steel has a composition within the following compositional range, all percentages being indicated in weight percent:

%C<sub>eq</sub> = 0.15-3.0      %C = 0.15-3.0      %N = 0-1.6      %B = 0-2.0  
 %Cr > 4.0      %Ni = 0-6.0      %Si = 0-2.0      %Mn = 0-3  
 %Al = 0-2.5      %Mo = 0-15      %W = 0-15      %Ti = 0-2  
 %Ta = 0-3      %Zr = 0-3      %Hf = 0-3      %V = 0-12  
 %Nb = 0-3      %Cu = 0-2      %Co = 0-6

any other element except iron not being present in an amount of more than 2%,  
 the rest consisting of iron, wherein

$$\%C_{eq} = \%C + 0.86 \cdot \%N + 1.2 \cdot \%B.$$

9. The method according to anyone of claims 1 to 6, wherein the steel has a composition within the following compositional range, all percentages being indicated in weight percent:

%C<sub>eq</sub> = 0.5-3.0      %C = 0.5-3.0      %N = 0-2.2      %B = 0-2.0  
 %Cr = 0.0-14      %Ni = 0-6.0      %Si = 0-2.0      %Mn = 0-3  
 %Al = 0-2.5      %Mo = 0-15      %W = 0-15      %Ti = 0-4  
 %Ta = 0-4      %Zr = 0-12      %Hf = 0-4      %V = 0-12  
 %Nb = 0-4      %Cu = 0-2      %Co = 0-6

any other element except iron not being present in an amount of more than 2%,  
 the rest consisting of iron, wherein

$$\%C_{eq} = \%C + 0.86 \cdot \%N + 1.2 \cdot \%B.$$

10. The method according to anyone of claims 1 to 6, wherein the steel has a composition within the following compositional range, all percentages being indicated in weight percent:

%C<sub>eq</sub> = 0.2-0.9      %C = 0.2-0.9      %N = 0-0.6      %B = 0-0.6  
 %Cr = 0.0-4.0      %Ni = 0-6.0      %Si = 0.2-2.8      %Mn = 0.2-3  
 %Al = 0-2.5      %Mo = 0-6      %W = 0-8      %Ti = 0-2  
 %Ta = 0-2      %Zr = 0-2      %Hf = 0-2      %V = 0-4  
 %Nb = 0-2      %Cu = 0-2      %Co = 0-6,

any other element except iron not present in an amount of more than 2%,  
 the rest consisting of iron, wherein

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

**characterized in that**

$$\%Si + \%Mn + \%Ni + \%Cr > 2.0, \text{ or}$$

$$\%Mo > 1.2, \text{ or } \%B > 2 \text{ ppm}$$

11. The method according to any of claims 1 to 10, wherein at least 70% of the bainitic transformation is made at temperature below 400°C, so that most of the attained microstructure is a fine bainite **characterized by** a hardness

above 45 HRc without tempering.

12. The method according to any of claims 1 to 11, wherein at least 70% of the bainitic transformation is made at temperatures below 400°C and/or the thermal treatment includes at least one tempering cycle at a temperature above 500°C to ensure separation of stronger carbide formers carbides, so that most of the attained microstructure, with the exception of the eventual presence of primary carbides, is **characterized by** the minimization of rough secondary carbides, in particular at least 60% in volume of the secondary carbides has a size of 250 nm or less, such that a toughness of 10 J CVN or more is attained.

13. The method according to any of claims 1 to 12, wherein the composition and tempering strategy is chosen so that high temperature separation secondary carbide types such as types MC, MC-like type as M4C3, M6C and M2C are formed, in such a manner that a hardness above 47 HRc is obtainable even after holding the material for 2h at a temperature of 600 °C.

14. The method according to any of claims 1 to 13, wherein the steel has a composition within the following range:

$$\% \text{Cr} < 3.0$$

$$\% \text{Si} < 0.8$$

wherein

$$\% \text{Mo} + \frac{1}{2} \cdot \% \text{W} > 2.0.$$

and the tempering strategy is chosen to minimize carriers scattering, such that a low scattering structure **characterized by** a diffusivity of 8 mm<sup>2</sup>/s or more is obtainable even for a hardness of 45 HRc or more.

15. The method according to any of claims 1 to 13, wherein the steel has the following composition:

$$\% \text{Ni} > 0.8$$

16. The method according to anyone of claims 1 to 15, **characterized in that** the steel presents at least two of the following features:

- it contains retained austenite;
  - its cementite is not wholly dissolved in the solid solution;
  - its cementite has not fully coalesced; and
  - carbide formers stronger than iron are present in the solid solution,
- so that the hardness of the steel can be raised in an amount of at least 4 HRc upon application of a later thermal treatment below austenitizing temperature.



## EUROPEAN SEARCH REPORT

Application Number  
EP 12 16 6949

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 2000 226635 A (SUMITOMO METAL IND) 15 August 2000 (2000-08-15) * abstract; tables 2, ex. 37,41 * -----	1-7, 11-16	INV. C21D6/00 C22C38/02 C22C38/04 C22C38/22 C22C38/24
X	JP 11 269603 A (SUMITOMO METAL IND) 5 October 1999 (1999-10-05) * tables 2, ex. 23, 24 * -----	1-7, 11-16	
X	EP 2 065 483 A1 (HITACHI METALS LTD [JP]) 3 June 2009 (2009-06-03) * paragraphs [0022] - [0027]; claims 1-17; figures 1-5 * -----	1-7, 11-16	
X	GB 999 866 A (BROCKHOUSE J & CO LTD) 28 July 1965 (1965-07-28) * column 2; claims 1-6 * -----	1-6,8, 11-16	
A	JP 2006 104519 A (DAIDO STEEL CO LTD) 20 April 2006 (2006-04-20) * abstract * -----	1-6,8, 11-16	
A	EP 2 270 245 A1 (DAIDO STEEL CO LTD [JP]) 5 January 2011 (2011-01-05) * the whole document * -----	1-6,9, 11-16	TECHNICAL FIELDS SEARCHED (IPC)
A	JP 2008 095190 A (HITACHI METALS LTD) 24 April 2008 (2008-04-24) * abstract; claims 1-17 * -----	1-6, 10-16	C21D C22C
<p>5 <del>The present search report has been drawn up for all claims</del></p>			
Place of search		Date of completion of the search	Examiner
The Hague		13 March 2013	Chebelev, Alice
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04C01)



Application Number

EP 12 16 6949

**CLAIMS INCURRING FEES**

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☒ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

1-8, 11-16

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).



# **LACK OF UNITY OF INVENTION** **SHEET B**

Application Number

EP 12 16 6949

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

## 1. claims: 7(completely); 1-6, 11-16(partially)

Method of manufacturing a tool steel or casting die steel with at least 70% bainitic microstructure with fine carbide-like constituents wherein the steel is subjected to a thermal treatment of austenitization, cooling, maintaining and tempering; the method wherein the steel composition is: %Ceq=0.16-1.9, %C=0.16-1.9, %N=0-1.0, %B= 0-0.6, %Cr<3.0, %Ni=0-6.0, %Si=0-1.4, %Mn=0-3, %Al=0.2.5, %Mo=0-10, %W=0-10, %Ti=0-2, %Ta=0-3, %Zr=0-3, %Hf=0-3, %V=0-4, %Nb=0-1.5, %Cu=0-2, %Co=0-6, %Ceq=%C+0.86x%N+1.2x%B, %Mo+1/2%W>2.0

---

## 2. claims: 8(completely); 1-6, 11-16(partially)

Method of manufacturing a tool steel or casting die steel with at least 70% bainitic microstructure with fine carbide-like constituents wherein the steel is subjected to a thermal treatment of austenitization, cooling, maintaining and tempering, the method wherein the steel composition is: %Ceq=0.15-3.0, %C=0.15-3.0, %N=0-1.6, %B= 0-2.0, %Cr>4.0, %Ni=0-6.0, %Si=0-.2.0 %, Mn=0-3, %Al=0-2.5, %Mo=0-15, %W=0-15, %Ti=0-2, %Ta=0-3, %Zr=0-3, %Hf=0-3, %V=0-12, %Nb=0-3.0, %Cu=0-2, %Co=0-6, %Ceq=%C+0.86x%N+1.2x%B.

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## 3. claims: 9(completely); 1-6, 11-16(partially)

Method of manufacturing a tool steel or casting die steel with at least 70% bainitic microstructure with fine carbide-like constituents wherein the steel is subjected to a thermal treatment of austenitization, cooling, maintaining and tempering, the method wherein the steel composition is: %Ceq=0.5-3.0, %C=0.5-3.0, %N=0-2.2, %B= 0-2.0, %Cr=0.0-14, %Ni=0-6.0, %Si=0-.2.0 %, Mn=0-3, %Al=0-2.5, %Mo=0-15, %W=0-15, %Ti=0-4, %Ta=0-4, %Zr=0-12, %Hf=0-4, %V=0-12, %Nb=0-4, %Cu=0-2, %Co=0-6, %Ceq=%C+0.86x%N+1.2x%B.

---

## 4. claims: 10(completely); 1-6, 11-16(partially)

Method of manufacturing a tool steel or casting die steel with at least 70% bainitic microstructure with fine carbide-like constituents wherein the steel is subjected to a thermal treatment of austenitization, cooling, maintaining and tempering, the method wherein the steel composition is: %Ceq=0.2-0.9 %C=0.2-0.9, %N=0-0.6, %B= 0-0.6, %Cr=0.0-4.0, %Ni=0-6.0, %Si=0.2-.2.8 %, Mn=0.2-3, %Al=0-2.5, %Mo=0-6, %W=0-8, %Ti=0-2, %Ta=0-2, %Zr=0-2, %Hf=0-2, %V=0-4, %Nb=0-2, %Cu=0-2, %Co=0-6, %Ceq=%C+0.86x%N+1.2x%B, %Si+%Mn+%Ni+%Cr>2.0 or %M>1.2 or %B>2ppm



**LACK OF UNITY OF INVENTION  
SHEET B**

Application Number  
EP 12 16 6949

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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