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BA ME(71) Applicant: **Rovalma, S.A.****08228 Barcelona (ES)**(72) Inventor: **Valls Anglés, Isaac****08228, Barcelona (ES)**(74) Representative: **Elzaburu Marquez, Alberto****Elzaburu, S.L.P.****C/ Miguel Ángel, 21****28010 Madrid (ES)**(54) **High thermal diffusivity and high wear resistance tool steel**

(57) A tool steel family with outstanding thermal diffusivity, hardness and wear resistance has been developed, also exhibiting good hardenability. Also its mechanical strength, as well as its yield strength, at ambient and high temperature (superior to 600°C) are high, due to a high alloying level in spite of the high thermal conductivity. Because of its high thermal conductivity and good toughness, steels of this invention have also good resistance to thermal fatigue and thermal shock. This

steels are ideal for discontinuous processes where it is interesting to reduce cycle time and that require high hardness and/or wear resistance (plastic injection molding, other plastic forming processes and curing of thermosets, hot forming of sheet...). These tool steels are also appropriate for processes requiring high wear resistance and good resistance to thermal fatigue (forging, hot stamping, light-alloy injection...).

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DescriptionField of the invention

5 **[0001]** The present invention relates to a tool steel with very high thermal diffusivity and high wear resistance, mainly abrasive. This tool steel also shows good hardenability.

Summary

10 **[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 many metal shaping industrial applications in which there is a heat extraction from the manufactured product which is discontinuous, thermal diffusivity is of extreme importance. Traditionally, for tool steels, this property has been considered opposed to hardness and wear resistance. During plastic injection, hot stamping, even forging, metal injection, composite curing and other metal shaping processes, wear resistance and high or very
15 high thermal diffusivity are often simultaneously required. For many of these applications, big cross-section tools are required, for which hardenability of the material is also of extreme importance.

[0003] 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.
20 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),
25 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).

30 **[0004]** 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).

35 **[0005]** 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.

[0006] 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). Steels of the present invention prioritize wear resistance and diffusivity to CVN, although it is also considered very
40 important for some applications and, therefore, the intention is to try to also maximize it but without renouncing to the other two properties. Usually, increasing the hardness of the tool steel will decrease both toughness and thermal diffusivity and will increase wear resistance. A greater level of diffusivity for a given hardness level has been achieved for steels of the present invention, usually together with a good hardenability and, for some cases, with an excellent toughness compromise.

45 **[0007]** For many applications thick tools are used, especially when sufficient strength is required as for to require a thermal treatment. In this case, it is also very convenient to have a good hardenability to be able to achieve the desired hardness level on surface and, preferably, all the way to the nucleus. Hardenability is also very interesting for hot work steels, since it is much easier to achieve high toughness with a quenched martensite structure than with a quenched bainite. Thus, the higher the hardenability the less abruptly the quenching cooling will need to be. A sudden cooling is
50 more difficult to achieve and also more expensive and, since the forms of tools and components manufactured are often complex, can lead to breaking of the parts being heat treated or severe deformation.

[0008] Wear resistance and mechanical strength are often inversely proportional to the toughness. Thus, it is not easy to get a simultaneous increase in both properties. Thermal conductivity is a help in this case, since it allows a great increase of the thermal fatigue resistance, even if the CVN has been reduced to increase wear resistance or mechanical
55 strength.

[0009] There are many other desirable properties, if not necessary, for hot work steels that do not necessarily influence the longevity of the tool, but their production costs, like: ease of machining, welding or repair in general, support provided to the coating, costs...

[0010] The authors have discovered that the problem to simultaneously obtain high thermal diffusivity, wear resistance and hardenability, together with good levels of toughness, can be solved applying certain rules of composition and thermo-mechanical treatments within the following compositional range:

5	%C _{eq} = 0.31 - 0.9	%C = 0.31 - 0.9	%N = 0 - 0.6	%B = 0 - 0.6
	%Cr < 3.0	%Ni = 0 - 3.8	%Si = 0 - 1.4	%Mn = 0 - 3
	%Al = 0 - 2.5	%Mo = 0 - 10	%W = 0 - 12	%Ti = 0 - 2
	%Ta = 0 - 3	%Zr = 0 - 3	%Hf = 0 - 3	%V = 0 - 4
10	%Nb = 0 - 1.5	%Cu = 0 - 2	%Co = 0 - 6	%S = 0 - 1
	%Se = 0 - 1	%Te = 0 - 1	%Bi = 0 - 1	%As = 0 - 1
	%Sb = 0 - 1	%Ca = 0 - 1,		

the rest consisting of iron and unavoidable impurities, wherein

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

[0011] In the present invention it is always the case that:

$$\%Mo + \frac{1}{2} * \%W > 3.0$$

[0012] Some of the selection rules of the alloy within the range and thermo-mechanical treatments required to obtain the desired high thermal diffusivity to a high hardness level and wear resistance, are presented in the detailed description of the invention section. Obviously, a detailed description of all possible combinations is out of reach. The thermal diffusivity is regulated by the mobility of the heat energy carriers, which unfortunately can not be correlated to a singular compositional range and a thermo-mechanical treatment.

State of the art

[0013] Until the developing of high thermal conductivity tool steels (EP 1887096 A1), the only known way to increase thermal conductivity of a tool steel was keeping its alloying content low and, consequently, showing poor mechanical properties, especially at high temperatures. Tool steels capable of surpassing 42 HRC after a tempering cycle at 600°C or more, were considered to be limited to a thermal conductivity of 30W/mK and thermal diffusivity of 8 mm²/s and 6.5 mm²/s for hardness above 42HRC and 52 HRC respectively. Tool steels of the present invention have a thermal diffusivity above 8 mm²/s and, often, above 12 mm²/s for hardness over 52 HRC, and even more than 16 mm²/s for hardness over 42 HRC, furthermore presenting a very good wear resistance and good hardenability. Thermal diffusivity is considered the most relevant thermal property since it is easier to measure accurately and because most of the tools are used in cyclic processes, so that the thermal diffusivity is much more important for evaluating performance of the tool than can be thermal conductivity.

[0014] Tool steels of the present invention have a wear resistance and hardness higher than steels described in EP2236639A1. The latter, on the contrary, show a higher hardenability in the perlite region and higher CVN compared to the tool steels with high thermal conductivity of the present invention. Hence, for applications where the main failure mechanism is thermal fatigue and no wear is present is better to use steels of EP2236639A1 but, for applications where wear resistance is important, tool steels of this invention have great advantage. Furthermore, the steels of the present invention exhibit higher thermal diffusivity for the same level of hardness. This is largely due to the fact that in EP2236639A1 carbides of the type of M₃Fe₃C, where M corresponds to Mo and/or W, are almost exclusively used, partly due to the presence of %Ni in the matrix that penalizes the thermal diffusivity in favour of hardenability, toughness (CVN) and lower linear thermal expansion coefficient. In the present invention there is lower %Ni and carbides are often partially replaced by harder carbides, even when the elements forming harder carbides tend to be solubilized in the Mo and/or W carbides, as is the case of %V.

[0015] There are other inventions that may have compositional range overlap but do not have anything to do with the present invention since rules for selecting the composition within the range and/or thermo-mechanical treatments required to achieve a structure with a matrix poor in elements in solid solution with great capacity to disperse heat energy carriers and having carbides with a high level of crystalline net perfection, and consequently a very low dispersion of heat energy carriers (mainly electrons and phonons), are not observed. This could be the case of JP04147706 here the inventors,

seeking an optimized superficial oxide coating, are using levels of %Cr lower than the normal ones (around 0.5%) to allow the mentioned oxidation with some specific treatments at high temperature. In the present invention %Cr has the tendency to dissolve in the W and/or Mo carbides causing the dispersion of the heat energy carriers and thus their presence is also undesirable. This is the only point of coincidence that also, in the case of JP04147706, does not lead to high thermal diffusivity in any of the examples described. At an even lower extent is the case of JP11222650, where the inventors look for the presence of large amounts of primary carbides to resist massive wear as is the case for high speed steel but with an exceptionally low content of %C to allow cold coining.

[0016] Other cases may be misleading because of not making special mention or having a generic reference levels of non-functional elements for the application mentioned, this is often the case for %Cr, %Si and %Mn. In fact, it is difficult to achieve a low level for some elements in steels. For instance, a steel supposedly lacking Cr (0%Cr in nominal composition), especially if it is an alloyed steel, will probably have %Cr > 0.3 if the steel is required, for some reason, to be made of selected scrap. In the case where normal scrap can be used, significantly cheaper, a %Cr > 0.5 would be expected. If, for a composition, the %Cr is not mentioned then it means that its presence is not considered important, but neither its absence. In this case, the content of %Cr does not compel the use of especial scraps and, if there are not other elements that require so, then a %Cr > 0.5 can be expected.

[0017] The case of %Si is slightly different, since it is possible to reduce its content through a refining process, such as ESR, although, due to the narrow window of the process in this case, it is technologically very difficult (and expensive, and therefore it is only carried out in the case of seeking a specific functionality) to reduce the %Si below 0.2 and, at the same time, to reach a low level of inclusions (especially oxides). All tool steels that with a normal range of composition could have high thermal conductivity and have not, is mainly due to the two following reasons:

- The ratio of %C and that of carbide formers are not well balanced to minimize solid solutions in the metal matrix, especially that of %C, and/or the thermo-mechanical treatments used do not pursue the maximization of mobility of the heat energy carriers. This is usually because the solid solution is used with the intention of increasing the mechanical strength.
- The nominal levels of %Si and %Cr, for instance, can be %Cr < 1 (or even without mentioning the %Cr, which can lead to the erroneous assumption that is 0%) and %Si < 0.4, which means that actually ends up by being %Cr > 0.3 and %Si > 0.25. This applies also for all trace elements with a strong influence on the conductivity of the matrix and even more those with a high solubility in carbides and great potential for distortion of the carbides structure. Usually, with the exception of %Ni and for some applications the %Mn, no element is desirable in solid solution with the matrix at a level higher than 0.5%. Preferably, the percentage of these, individually in solid solution, should not exceed 0.2%. If the main purpose of the application is to maximize the thermal conductivity, then any metallic element in solid solution with the matrix (obviously including transition metals), with the exception of %Ni and in some cases the %C and %Mn, should not exceed 0.1% or, even better, 0.05%.

Detailed description of the invention

[0018] To obtain tool steels with high thermal diffusivity and wear resistance to high hardness levels with good hardenability, it has been observed that, within the compositional range specified above, a number of rules and general considerations in the selection of the composition within the range and the thermo-mechanical treatments to be used, some of which are described below, have to be taken into account.

[0019] Tool steels of the present invention excel mainly because of their high thermal diffusivity and wear resistance. Wear resistance and toughness tend to be inversely proportional, although different microstructures reach different relationships, i.e., as a function of microstructure different levels of toughness for the same elastic limit and hardness at a given temperature can be reached and, for a specific type of material, hardness tends to correlate with wear resistance unless the volume fraction or the morphology of wear resistant particles is significantly changed. In this vein, it is well known that for most tool steels with medium carbon content, pure microstructure of tempered martensite is the only one that offers the best compromise of mechanical properties. This means that it is important to avoid the formation of other microstructures like stable ferrite-perlite or metastable bainite during cooling after the process of austenitization of the heat treatment. Therefore, fast cooling rates will be needed and, if higher hardenability is required, some alloying elements to delay the kinetics of the formation of these more stable structures should be used. From all possible alternatives those with less negative effects on thermal diffusivity should be used.

[0020] A strategy to obtain wear resistance and higher elastic limit at high temperatures and, at the same time, obtain high thermal conductivity, is the use of carbides with high electron density, as secondary carbides of the M_3Fe_3C type and sometimes even primary carbides (M- should only be Mo or W for a greater thermal conductivity). There are other carbide types (Mo, W, Fe) with high electron densities and with tendency to solidify with a good crystalline perfection. Some elements like Zr and Hf and, at a less extent, Ta for instance comparing to Cr, when dissolving with this type of carbides do not provide much distortion to the crystalline structure and dispersion of charge carriers is small and so is

the effect on thermal conductivity. Moreover, these high carbide forming elements tend to form separate MC type carbides, due to its high affinity for C.

[0021] In fact, in the present invention it has been observed that the effect can be quite positive if a moderate quantity of %V is used and it is balanced with the presence of strong carbide former (preferably Zr and/or Hf). It has been seen that there can be amounts of %V up to 0.9 with practically no formation of primary carbides (obviously depending on the C_{eq} and the presence of other carbides, and for higher contents of C_{eq} is necessary to reduce the percentage of V at a maximum of 0.8 and even 0.5 or 0.4 to avoid the presence of primary carbides or massive dissolution in them) and with little dissolution in the carbides of (Fe, Mo, W), especially if used simultaneously with strong carbide forming elements, also there is a displacement of more carbon out of the matrix with the consequent benefit to the overall thermal diffusivity (in this case, the benefit is remarkable with %Hf+%Zr+%Ta greater than 0.1, and very significant if it exceeds 0.4 or 0.6, depending on the quantities of %Ceq and %V present). In fact, this combination is highly desirable as the percentage of V as the percentage of Zr, Hf and Ta tend to significantly improve the wear resistance compared to a steel that has only carbides (Fe, Mo, W), the same applied for %Nb. The effect becomes noticeable with %V = 0.1 and remarkable with %V = 0.3 or 0.5, depending on the level of %Ceq. If extreme wear resistance with the presence of primary carbides is to be achieved, as is the case in applications with large abrasive particles such as in hot stamping of uncoated sheet, then larger amounts of %V can be used, up to 1.5% or even 2% is possible while maintaining a good level of thermal diffusivity, especially if compensated with strong carbide forming elements. In this case, it can be convenient to have high levels of strong carbide forming elements combined with %V (%V+%Nb+%Hf+%Zr), above 1.2 or even 2.0 in weight percentage (for applications where a good wear resistance is needed, even 3.0, but then the cost of the alloy is increased). In this case, rarely any strong carbide forming element (%V, %Nb, %Ta, %Zr, %Hf) will individually exceed 3%, with the exception of %V where the upper limit is usually 4% in weight and Nb that, due to its negative effect on thermal diffusivity, tends to be used only to control grain size and when used as primary carbide former will rarely be above 1.5%. In general it is desired to mostly have Fe, Mo and W carbides (where obviously part of the C can be replaced by N or B), usually more than 60% and, optimally, more than 80% or even more than 90% of these type of carbides. The dissolution of other metallic elements of these types of carbides (obviously in the case of carbides metallic elements are mainly transition elements) can exist, but it is desired to be small to guarantee a high phononic conductivity. Normally no other metallic element, apart from the principal Fe, Mo and W, should exceed 20% of the weight of all metallic elements of the carbide, for this type of mainly desired carbides. Preferably should not be more than 15% and even better a 5%. This is because they tend to form structures with densities of solidification defects extremely low even for fast solidification kinetics (therefore less structural elements to cause dispersion of carriers).

[0022] As discussed before, the only exception is the presence of a limited quantity of strong carbide forming elements, although the formation of independent carbides is preferable. In this case, Mo and W provide sufficient obstacles for the formation of stable structures (perlite and ferrite), although the formation of bainite is very fast. In some steels superbainitic structures can be formed applying a martempering heat treatment, which consists in the complete solubilisation of alloying elements followed of a rapid cooling to a specific temperature (to avoid ferrite formation) in the range of lower bainitic formation and an extended temperature maintenance to obtain a 100% bainitic structure. For the majority of the steels a pure martensitic structure is desirable, so that in this system some bainitic transformation delaying elements must be added, since Mo and W are very inefficient in this respect. Generally, for this purpose Cr is commonly used, but has an extremely negative effect on the thermal conductivity for this system because it dissolves in the M_3Fe_3C carbides and causes a great distortion, so it's much better to use strong carbide forming elements and non soluble elements in carbides. These last elements will reduce the conductivity of the matrix and, thus, the ones with the minimum negative effect should be used. Accordingly, the natural candidate is Ni, but at the same time others can be used. Since in the present invention carbide formers with great affinity to C are tend to be used for their positive effect on wear resistance, the necessary and desirable quantity of delaying elements of the transformation kinetics to stable structures during quenching is lower. Usually, a quantity up to 1% in weight, and for large sections up to 3.0%, will be enough to get sufficient hardenability and contribute to the increase of toughness without an excessive detriment of conductivity. Higher %Ni quantities provide more toughness and a reduction in the linear thermal expanded coefficient, but the priority of the present invention is a combination of wear resistance with thermal diffusivity, thus, only for some special applications the strategy of using high contents of %Ni, with a maximum of 3.8., can be used. There are applications where lower amounts of %Ni already lead to the desired effect, especially if the contents of %Mn and/or %Si are a bit higher (%Mn usually does not exceed 3%) or sections of the material used are smaller.

[0023] The use of %Mo as a single carbide former (obviously together with Fe), is advantageous when maximising thermal conductivity, but it has the disadvantage to provide a higher thermal expansion coefficient and, thus, it decreases the thermal fatigue resistance. Hence it is preferable to have a relation of 1.2 to 3 times more Mo than W, but not the absence of W. The exception are the applications where only thermal conductivity is to be maximised together with toughness, but not particularly thermal fatigue resistance. Hardenability and the alloy cost, due to the high volatility of Mo and W prices, can lead to changing preferences regarding the %W being the main element in %Mo_{eq}, (where %Mo_{eq} = %Mo + $\frac{1}{2}$ · %W).

[0024] High contents of Mo_{eq} can be used with high levels of C_{eq} , resulting in an increased cost alloy, low toughness, very difficult to weld, complicated hardenability for large parts and limited machinability. But very high levels of wear resistance with good thermal diffusivity can be achieved. For applications where the highlighted drawbacks are not determinant these can be alloys of interest. This can be the case for some cutting applications. Here, levels of C_{eq} usually

superiors to 0.5% are used and, often, even over 0.6%. Levels of % Mo_{eq} are often above 5 and frequently above 6 or even 9. Also the limits of the Mo_{eq}/C_{eq} ratio are shifted to superior levels compared to the rest of the alloys of the present invention. Values higher than 14 are possible and, higher than 11, are probable.

[0025] In all document the term carbide is referring to the primary carbides as well as the secondary, unless otherwise specified.

[0026] The more restrictive the %Si and %Cr the higher the thermal conductivity, although the solution is more expensive (also, some properties, that could be important for some applications, and thus would be desirable to be maintained, could get worse with the reduction of these elements below certain levels as, for instance, for toughness due to oxide inclusions in the case Al, Ti, Si and any other deoxidizing, are used in insufficient quantities or, in some cases of corrosion resistance, if %Cr or %Si are too low). Thus, often there must be a compromise between increase of costs, toughness reduction, wear resistance or other relevant properties for certain applications and the benefit of higher thermal conductivity. Maximum thermal conductivity can be obtained only if levels of %Si and %Cr are below 0.1 % or, even better, if below 0.05%. To maximise thermal diffusivity, also levels of the rest of the elements, with the exception of %C, %Mo, %W, %V, %Zr, %Hf, %Ta, %Nb and in some instances %Mn and %Ni, must be as low as possible (below 0.05 is technically possible with an acceptable cost for most of the applications, although a maximum of 0.1 is, of course, less expensive). For some applications in which toughness is especially important less restrictive levels of %Si must be employed (is the least detrimental to the thermal conductivity of all iron deoxidants elements) and thus give up to some thermal conductivity, to ensure the inclusion level is not too high. Depending on the levels of %C, %Mo and %W used, there can be sufficient hardenability, especially in the perlitic zone. For cases of large components, where it is not possible to avoid the formation of bainite during quenching, the use of elements in solid solution to prevent the formation of coarse cementite precipitates (Fe_3C) that entail very low toughness, such as %Al and %Si, may be interesting. Generally below 0.4, exceptionally with levels of around 1% and, very exceptionally, above 2% and for the %Al, up to a maximum of 2.5%. The levels of %Mo, %W and %C used to obtain the desired mechanical properties must be balanced to achieve a high thermal conductivity, so that within the matrix remain the least amount of these elements in solid solution. The same applies for the rest of carbide formers that could be used to obtain a certain tribological response (like %V, %Zr, %Hf, %Ta,...).

[0027] For some applications some environmental resistance can be of interest and, thus, be desirable to have some %Cr or %Si in solid solution (oxidation resistance to high temperature). The negative effect on thermal diffusivity can be moderated through carbon fixing with stronger carbide formers elements. Without the later, %Cr should not exceed 2% and, preferable, 1.5%. Although in the presence of V, %Nb, %Ta, %Zr and %Hf, and preferably the last two or three, levels of 3% of Cr can be achieved maintaining a good thermal diffusivity, and even 1.4% for the case of Si.

[0028] Generally, to solely maximise thermal diffusivity (i.e. there are not other properties of great importance), it is convenient to observe the following alloying rule (to minimize the %C in solid solution), if a tempered martensite or bainite microstructure withstanding mechanical requirements wants to be obtained. The formula must be corrected if carbide formers with high affinity for the %C (like Hf, Zr or Ta, even Nb) are used. It must be also modified if %Cr>0.2 or $Mo_{eq} > 7$:

$$0.02 < xC_{eq} - solC - AC \cdot [(xMo - solMo) / (3 \cdot A_{Mo}) + (xW - solW) / (3 \cdot A_W) + (xV - solV) / A_V] > 0.265$$

where:

xC_{eq} - carbon weight percentage;
 xMo - molybdenum weight percentage;
 xW - tungsten weight percentage;
 xV - vanadium weight percentage;
 AC - carbon atomic mass (12.0107 u);
 A_{Mo} - molybdenum atomic mass (95.94 u);
 A_W - tungsten atomic mass (183.84 u);
 A_V - vanadium atomic mass (50.9415 u);
 $solC$ - carbon percentage in solid solution;
 $solMo$ - molybdenum percentage in solid solution;
 $solW$ - tungsten percentage in solid solution;

solV - vanadium percentage in solid solution.

[0029] For an even higher thermal conductivity it is even more desirable to have:

$$0.04 < xC_{eq} - solC - AC \cdot [(xMo-solMo) / (3 \cdot AMo) + (xW-solW) / (3 \cdot AW) + (xV-solV) / AV] > 0.22$$

[0030] And still better:

$$0.09 < xC_{eq} - solC - AC \cdot [(xMo-solMo) / (3 \cdot AMo) + (xW-solW) / (3 \cdot AW) + (xV-solV) / AV] > 0.18$$

[0031] To compensate the presence of other %C avid carbide formers an extra term must be added to the formula for each type of %C avid carbide former:

$$-AC \cdot xM / (R \cdot AM)$$

where:

xM - carbide former weight percentage;

AC - carbon atomic mass (12.0107 u);

R - number of carbide former units per carbide unit (for example: 1 if the carbide type is MC, 23/7 if the carbide type would be $M_{23}C_7$...)

AM - carbide former atomic mass.

[0032] This balance provides an extraordinary thermal conductivity if the reinforcing ceramic particles formers, including the non metallic part (%C, %B and %N), are taken into the carbides (as an alternative nitrides, borides and intermediate substances). Then, the appropriated thermal treatment must be applied. This thermal treatment will have a phase in which most of the elements will be dissolved (austenitization to sufficiently high temperature, usually around 1080°C for moderated Mo_{eq} levels, 1120°C for medium levels of Mo_{eq} and 1240°C for high levels of Mo_{eq} , exceptionally, if distortion of the heat treatment is of great importance for the application, lower austenitization temperatures can be used). An abrupt cooling will follow, its intensity will be determined by the desired mechanical properties, although stable structures should be avoided since phases with big quantities of %C and carbide formers in solid solution are implied. Metastable microstructures are even worse, since the microstructure distortion caused by carbon is even greater, hence thermal conductivity is lower, although once these metastable structures have relaxed the carbide formers place themselves in the desired position. Martensite and bainite tempered following this procedure will be the desired microstructures for this case. The largest possible carbide substitution of Fe by Mo, W and all carbide forming elements with greater affinity for carbon other than Cr are desired, so the tempering strategy selected has a great influence in the final thermal conductivity, with particular relevance to the final tempering temperature and minimum tempering temperature. For hardness over 40 HRc, the highest possible temperature is desirable for the last tempering if thermal diffusivity is to be maximized, and this approach is used to set the intermediate tempering strategy. That is, the same final hardness level can be achieved with different sequences of tempering and the one using a higher final tempering temperature is chosen, if the only objective is to maximize the thermal diffusivity at a certain level of hardness. So, usually, 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, with the last tempering cycle above 590°C giving a diffusivity greater than 8 mm²/s and, generally, more than 9 mm²/s. As well as achieving hardness greater than 42 HRc, with the last tempering cycle above 600°C, often above 640°C, showing a diffusivity higher than 10 mm²/s, or even than 12 mm²/s.

[0033] When remaining in the carbide system $Mo_xW_{3-x}Fe_3C$, Cr levels are kept as low as possible, and the only goal for the chosen application is the maximization of the thermal diffusivity to the highest possible level of hardness. One of the preferred ways to balance the contents of %W, %Mo and %C in the present invention is through the adhesion to the following alloying rule:

$$\%C_{eq} = 0.4 + (\%Mo_{eq(real)} - 4) \cdot 0.04173$$

where: $Mo_{eq(real)} = \%Mo + (AMo/AW) \cdot \%W$.

with :

AMo - molybdenum atomic mass (95.94 u);

AW - tungsten atomic mass (183.84 u);

[0034] If the expression is normalized in a parameter $K = (\%C_{eq} / 0.4 + (\%Mo_{eq(real)} - 4) \cdot 0.04173)$, the desirable values for this parameter are, for the present invention:

Optimally: 0.94 / 1.3;

preferably: 0.8 / 1.5;

desirable: 0.6 / 2.5;

[0035] This alloying rule can be reformulated to better adapting to different levels of %C alloying, and thus, to different applications, since the given formulation is interesting for values of $\%C_{eq} > 0.33$.

[0036] 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.

[0037] 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_3Mo , $NiAl$, Ni_3Ti ... (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_3Fe_3C 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_3Fe_3C 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.

[0038] 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_3Fe_3C 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.

[0039] 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 subsequent compacting as the HIP, CIP, cold or hot pressing, sintering (with or without a liquid phase), thermal spray or heat coating, 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 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 for use as solder 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...).

[0040] 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).

EXAMPLES

[0041] Some examples indicate the way in which the steel composition of the invention can be specified with higher precision for different hot working applications:

Example 1

[0042] Dies for the stamping or press hardening of sheet. In this case maximum possible thermal diffusivity is desired at high hardness. The desired wear resistance depends on the sheet coating.

- Sheets coated with Zn, AlSi or other inorganic coatings (the same compositions are optimized for the manufacture of injection molds for thermoplastics, especially when steels described below are made by powder metallurgy):

For this purpose in the context of the present invention the following compositional range can be used:

C_{eq} : 0.3 - 0.6 Cr < 3.0% (preferably Cr < 0.1 %)

V: 0 - 0.9% (preferably 0.3 - 0.8%)

Si: < 0.15% (preferably %Si < 0.1, but with an acceptable level of oxide inclusions)

Mn: < 0.5% Mo_{eq} : 3.5 - 5.5

where $Mo_{eq} = \%Mo + 1/2 \%W$ and

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

The rest of the elements should be kept as low as possible and, in any case, always be below 0.15%, with the exception of strong carbide formers (%Ta, %Zr, %Hf).

All values are given in weight percentage.

The following three examples show properties that can be obtained:

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Other	Hardness HRc	Therm. Diff. mm ² /s
0.40	3.6	1.4	0.3	<0.01	<0.05	<0.01	-	52	11.47
0.45	1.6	4.5	0.4	<0.01	<0.05	<0.01	-	52-53	10.96
0.41	3.5	1.4	0.8	1.3	<0.05	<0.01	-	50	9.32

* In all cases heat treatment which maximizes diffusivity at the indicated hardness has been applied, minimizing the presence of elements in solution with the matrix, except for % Cr, especially minimizing the presence of %C and, to a lesser extent, %V in the matrix. In all cases this means very high austenitization temperatures, from 3 to 5 tempering cycles, with the latest in the range 600-640 °C.

An advanced optimization is obtained when elements strongly reacting with %C to form carbides (also %N and %B are employed). Five examples show the properties that can be obtained:

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Otros	Hardness HRc	Therm. diff. mm ² /s
0.50	3.6	1.4	0.5	<0.01	<0.05	<0.01	Hf, Zr, Nb	56-57	12.73
0.50	3.6	1.4	0.5	<0.01	<0.05	<0.01	Hf, Zr, Nb	54	13.93
0.33	3.36	1.91	<0.01	<0.01	<0.05	0.4	Hf, Zr, Nb, B=0.16	50	13.04

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(continued)

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Otros	Hardness HRc	Therm. diff. mm ² /s
0.33	3.36	1.91	<0.01	<0.01	<0.05	0.4	Hf, Zr, Nb, B=0.16	43	16.62
0.42	3.45	1.4	0.6	2.2	<0.05	<0.01	Hf=0.3, Zr=0.2	52	10.42
* In all cases heat treatment which maximizes diffusivity at the indicated hardness has been applied, minimizing the presence of elements in solution with the matrix, except for % Cr, especially minimizing the presence of %C and, to a lesser extent, %V in the matrix. In all cases this means very high austenitization temperatures, from 3 to 5 tempering cycles, with the latest in the range 610-680 °C. Being %Hf: 0.10 - 0.22, %Zr: 0.05 - 0.18 y %Nb: about 0.07, unless specifically indicated.									

- Uncoated sheets and, therefore, with iron oxides that can be large:

For this purpose, in the context of the present invention, the following compositional range can be used:

C_{eq} : 0.4 - 0.9 Cr < 3.0% (preferably Cr < 0.1 %)

V: 0 - 2.0% (preferably 0.4 - 0.8%)

Si: < 0.5%

Mn:<1.0% Mo_{eq} : 3.5 - 9

where $Mo_{eq} = \%Mo + 1/2 \%W$ y

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

[0043] The rest of the elements should be kept as low as possible and, in any case, always be below 0.15%, with the exception of strong carbide formers (%Ta, %Zr, %Hf). All values are indicated in weight percentages.

[0044] The following examples show the properties that can be obtained:

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Other	Hardness HRc	Therm. diff. mm ² /s
0.60	3.6	1.2	0.62	<0.01	0.14	0.54	-	58	11.17
0.60	3.6	1.2	0.62	<0.01	0.14	0.54	-	47.5	12.47
0.85	6.48	4.0	<0.01	0.02	0.2	0.22	-	52.5	10.96
0.85	6.48	4.0	<0.01	0.02	0.2	0.22	-	45	12.87
0.79	6.42	3.78	0.41	<0.01	0.1	0.1	Hf,Zr	54	11.42
0.79	6.42	3.78	0.41	<0.01	0.1	0.1	Hf,Zr	46	12.38
0.45	3.87	1.67	0.49	<0.01	0.45	<0.01	-	51	10.65

* In all cases heat treatment which maximizes diffusivity at the indicated hardness has been applied, minimizing the presence of elements in solution with the matrix, especially minimizing the presence of %C and, to a lesser extent, %V in the matrix. In this case, also seeking the highest possible presence of primary carbides. In all cases this means very high austenitization temperatures, from 2 to 4 tempering cycles, with the latest in the range 550-620 °C. Being %Hf: 0.10 - 0.22, %Zr: 0.05 - 0.18 y %Nb: about 0.07, unless specifically indicated.

Example 2

[0045] For closed-die forging. In this case, a simultaneous optimization of wear resistance and thermal fatigue has to be achieved, therefore, maximum thermal diffusivity and wear resistance are desirable (presence of primary carbides) maintaining also maximized CVN. For dies or large parts subject to thermal shock or thermal fatigue a good CVN should be maintained, even when the treatment cannot be fully martensitic, in which case Si or Al are used to hinder the precipitation of thick cementite (Fe₃C), or %Ni is used to improve the hardenability in the ferritic-perlitic zone and decrease the linear thermal expansion coefficient. In this case, tool steels in the following range can be used (powder metallurgy

steels except for applications where the present abrasive particles are very large). Steels of the present invention are particularly attractive for applications where wear is the predominant failure mechanism:

For this purpose, in the context of this invention, a compositional range of the following type can be used:

C_{eq} : 0.3 - 0.6 Cr < 0.1% (preferably Cr < 0.05%)

Si: < 1.4%

Al: 0 - 2%

Mn: < 1.5% Mo_{eq} : 3.0 - 7.0

where $Mo_{eq} = \%Mo + 1/2 \%W$

[0046] The rest of the elements should be kept as low as possible and, in any case, always be below 0.15%, with the exception of strong carbide formers (%Ta, %Zr, %Hf). All values are given in weight percentages.

[0047] Five examples show the properties that can be obtained:

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Other	Hardness HRc	Therm. diff. mm ² /s at 400°C
0.37	3.3	1.01	<0.01	<0.01	<0.05	<0.01	Hf, Zr, Ni=2,9	45.5	11.14
0.31	3.08	0.86	<0.01	<0.01	<0.05	0.16	Hf, Zr, Ni=2,3	44	12.69
0.5	3.65	1.27	0.45	<0.01	0.1	<0.01	Al=0.7	53	10.12
0.5	3.73	1.52	0.17	<0.01	0.8	<0.01	Hf,Zr, S	51	9.74
0.53	3.61	1.35	0.44	<0.01	<0.05	0.6	Al=0.8	55	9.62

* In all cases heat treatment which maximizes diffusivity at the indicated hardness has been applied, minimizing the presence of elements in solution with the matrix, especially minimizing the presence of %C and, to a lesser extent, %V in the matrix. In this case, also seeking the highest possible presence of primary carbides. In all cases this means very high austenitization temperatures, from 3 to 5 tempering cycles, with the latest in the range 590-660 °C. Being %Hf: 0.10 - 0.22, %Zr: 0.05 - 0.18 y %Nb: about 0.07, unless specifically indicated.

Example 3

[0048] For hot cutting of sheet. In this case wear resistance must be maximized with a good hardenability and toughness (fracture toughness, in this case). Thermal conductivity is very important to maintain the temperature at the cutting edge as low as possible. Weldability is less important in this case, and small inserts are often used, so compositions with high content of alloying elements can be used. For this purpose, in the context of the present invention, the following compositional range can be used:

C_{eq} : 0.5 - 0.9 Cr < 0.1% (preferably Cr < 0.05%)

Si: < 0.15% (preferably Si < 0.1%)

V: 0 - 2% for cases with $Mo_{eq} > 5$ and V: 0 - 4% for cases with $Mo_{eq} < 5$

Mo_{eq} : 5-10

where $Mo_{eq} = \%Mo + 1/2 \%W$

[0049] The rest of the elements should be kept as low as possible and, in any case, always be below 0.15%, with the exception of strong carbide formers (%Ta, %Zr, %Hf). All values are given in weight percentages.

[0050] Three examples show the properties that can be obtained:

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Other	Hardness HRc	Therm. diff. mm ² /s at 400°C
0.59	6.7	4.6	<0.01	<0.01	<0.05	<0.01	-	55	12.39

(continued)

%C	%Mo	%W	%V	%Cr	%Si	%Mn	Other	Hardness HRc	Therm. diff. mm ² /s at 400°C
0.69	7.89	3.95	0.7	<0.01	<0.05	<0.01	-	55	10.76
0.62	8.01	3.75	0.1	<0.01	<0.05	<0.01	Ni=0.28	57	10.10
* In all cases heat treatment which maximizes diffusivity at the indicated hardness has been applied, minimizing the presence of elements in solution with the matrix, especially minimizing the presence of %C and, to a lesser extent, %V in the matrix. In this case, also seeking the highest possible presence of primary carbides. In all cases this means very high austenitization temperatures (1120°C in the first two cases and 1240°C in the last one), from 2 to 4 tempering cycles, with the latest in the range 600-640 °C.									

Claims

1. A steel, in particular a hot work tool steel, with the following composition, being all percentages indicated weight percentages:

%C _{eq} = 0.3 - 0.9	%C = 0.3 - 0.9	%N = 0 - 0.6	%B = 0 - 0.6
%Cr < 3.0	%Ni = 0 - 3.8	%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	%S = 0 - 1
%Se = 0 - 1	%Te = 0 - 1	%Bi = 0 - 1	%As = 0 - 1
%Sb = 0 - 1	%Ca = 0 - 1,		

the rest consisting of iron and unavoidable impurities, wherein

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

characterized in that

$$\%Mo + \frac{1}{2} \cdot \%W > 3.0.$$

2. A steel according to claim 1, wherein:

$$\%V + \%Nb + \%Hf + \%Zr > 0.1$$

3. A steel according to claim 1, wherein:

$$\%V + \%Nb + \%Hf + \%Zr > 1.2$$

4. A steel according to any one of claims 1 to 3, wherein:

$$\%C_{eq} > 0.36$$

5. A steel according to any one of claims 1 to 4, wherein:

$$\%C > 0.4$$

6. A steel according to any one of claims 1 to 5, wherein:

$$\%Mo + \frac{1}{2} \cdot \%W < 10.0$$

7. A steel according to any one of claims 1 to 5, wherein:

$$\%Mo + \frac{1}{2} \cdot \%W < 4.5 \text{ with } \%Mo = 0 - 4.5 \text{ and } \%W = 0 - 9$$

8. A steel according to any one of claims 1 to 7, wherein:

$$\%V < 2.0$$

9. A steel according to any one of claims 1 to 8, wherein:

$$\%Nb < 0.1$$

10. A steel according to any one of claims 1 to 9, wherein:

$$\%Ni < 2.99$$

11. A steel according to any one of claims 1 to 9, wherein:

$$\%Ni < 1.0$$

12. A steel according to any one of claims 1 to 11, wherein:

$$\text{when } \%Cr > 2, \text{ then } \%Nb + \%Ta + \%Zr + \%Hf > 0.2$$

13. A steel according to any one of claims 1 to 12, wherein:

$$3 < \%C_{eq} / \%Mo_{eq} < 14,$$

where

$$\%Mo_{eq} = \%Mo + \frac{1}{2} \cdot \%W$$

14. A steel according to any one of claims 1 to 13 where when doing a martensitic, bainitic or martensitic-bainitic quench with at least one tempering cycle at high temperature, above 590°C, a hardness above 47 HRC with a diffusivity above 9 mm²/s is obtained.

15. A die, tool or piece at least partially comprising a tool steel according to any one of claims 1 to 14.



EUROPEAN SEARCH REPORT

Application Number
EP 11 38 2004

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