

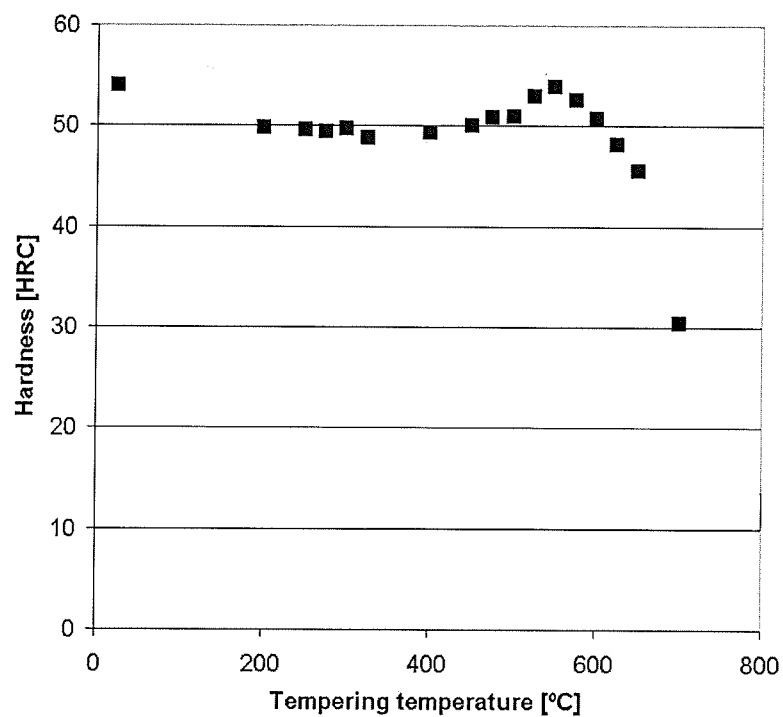
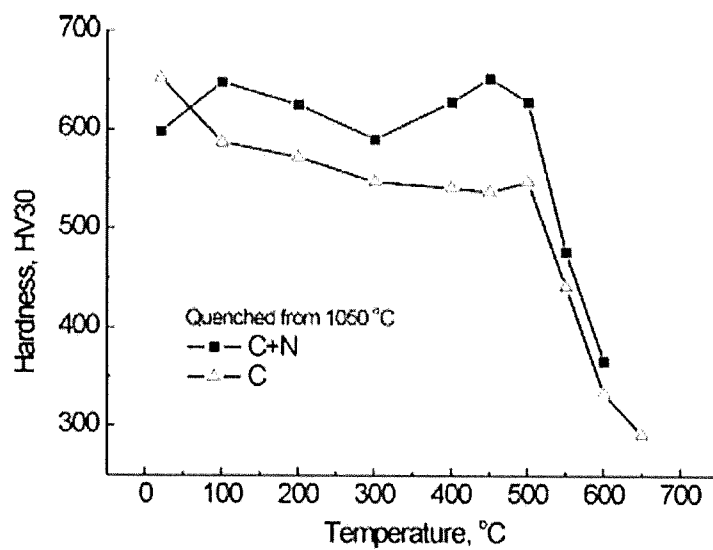


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Andersson et al.(10) **Pub. No.: US 2014/0056749 A1**(43) **Pub. Date: Feb. 27, 2014**(54) **HOT-WORK TOOL STEEL AND A PROCESS
FOR MAKING A HOT-WORK TOOL STEEL**(75) Inventors: **Jürgen Andersson**, Hagfors (SE);
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USPC **419/13**; 148/621; 148/653; 420/111;
420/106; 420/107; 420/109(57) **ABSTRACT**A low-chromium hot-work tool steel consisting of (in wt-%):
C 0.08-0.40, N 0.015-0.30, C+N 0.30-0.50, Cr 1-4, Mo 1.5-3,
V 0.8-1.3, Mn 0.5-2, Si 0.1-0.5, optionally Ni<3, Co≤5, B<0.
01, Fe balance apart from impurities, and a process for mak-
ing a low-chromium hot-work tool steel article having
increased tempering resistance.

**Fig. 1 (Prior art)****Fig. 2 (Prior art)**

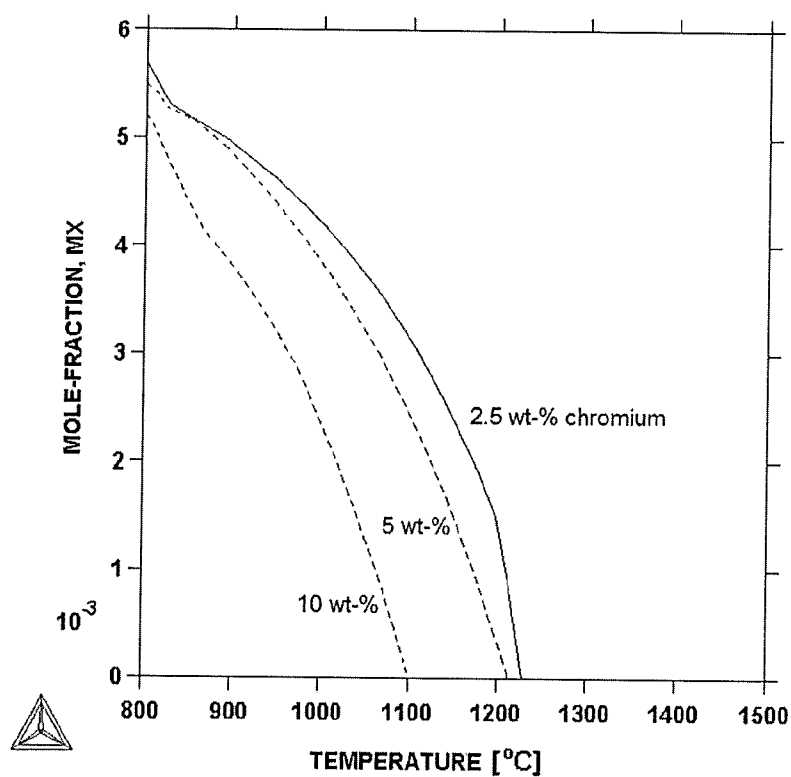


Fig. 3 (Prior art)

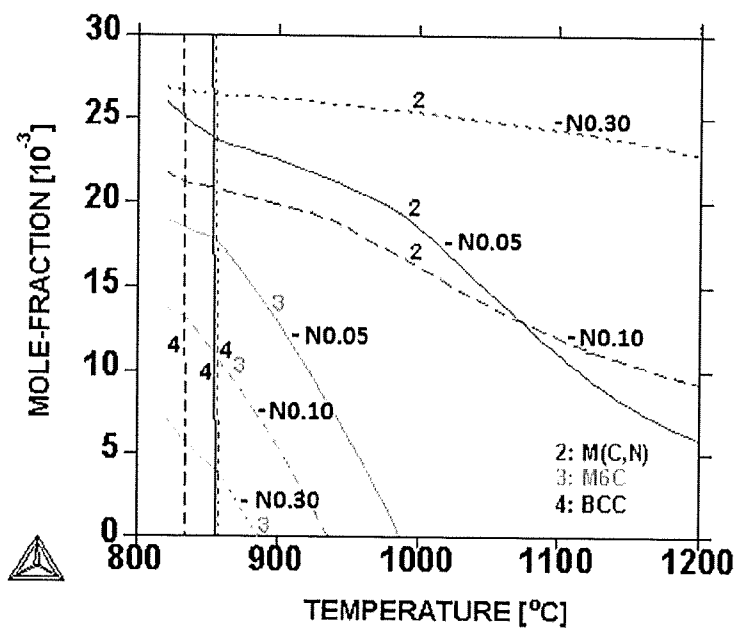


Fig. 4

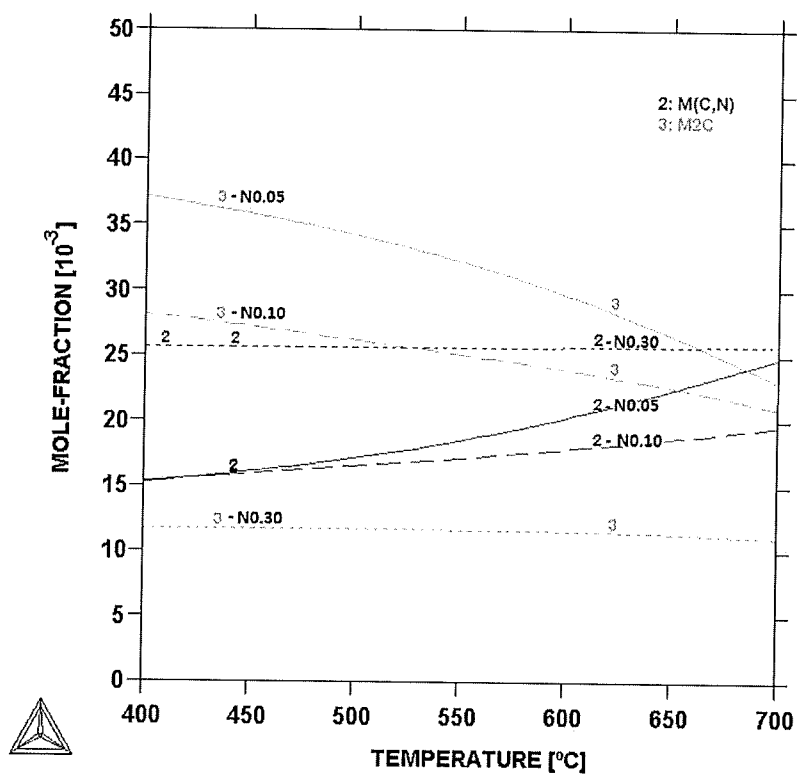


Fig. 5

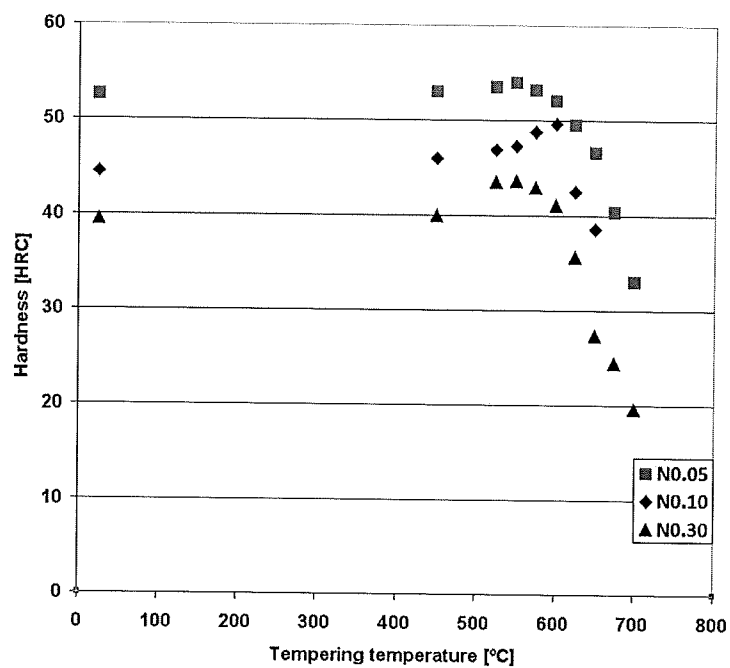


Fig. 6

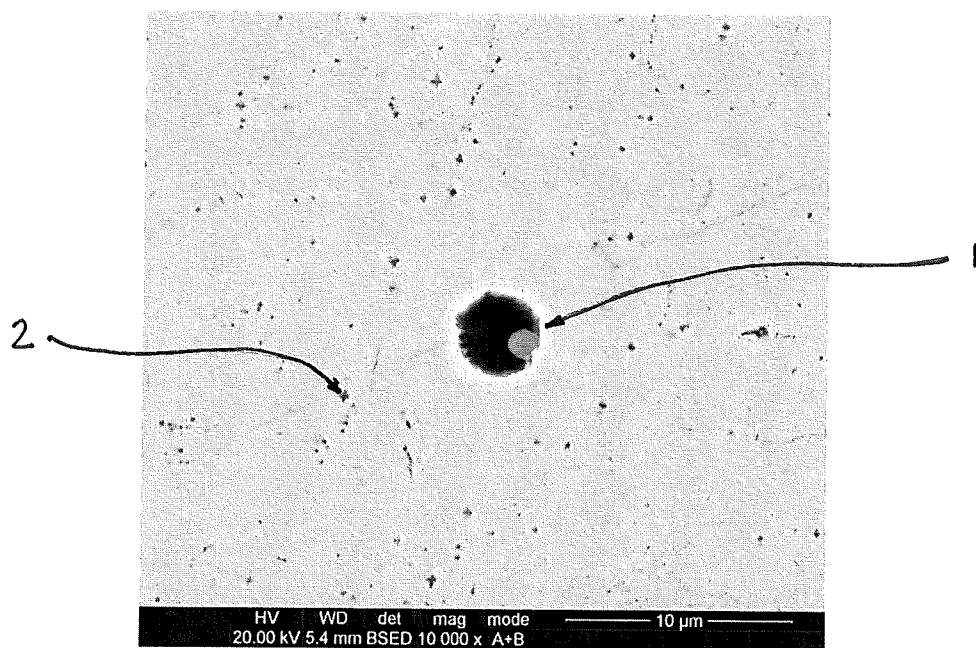


Fig. 7

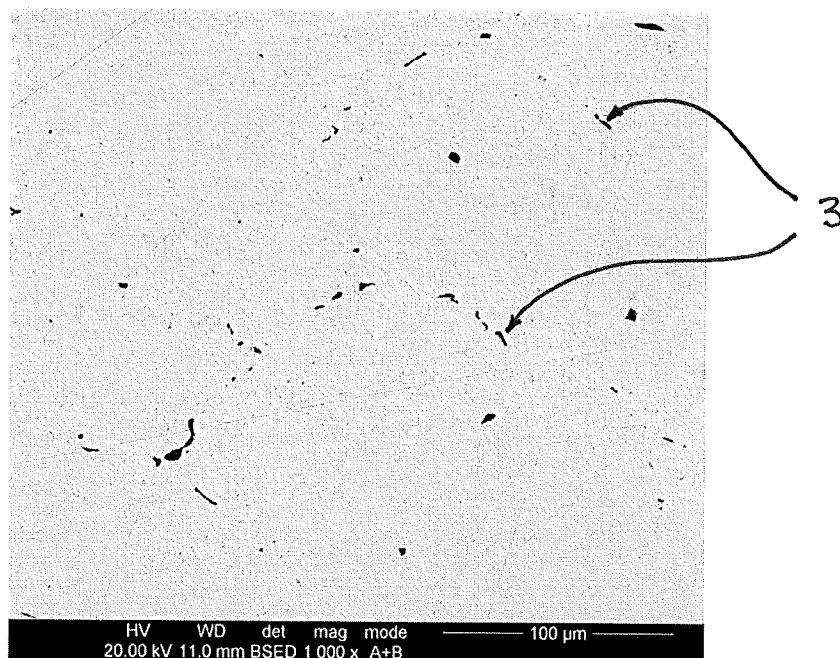


Fig. 8

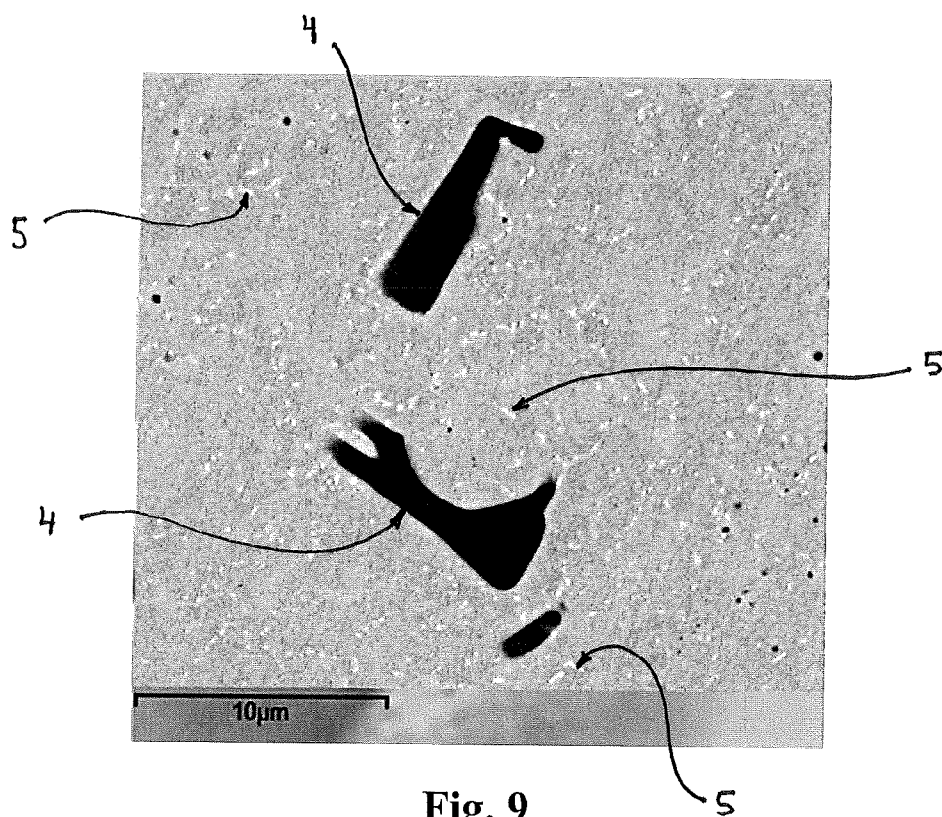


Fig. 9

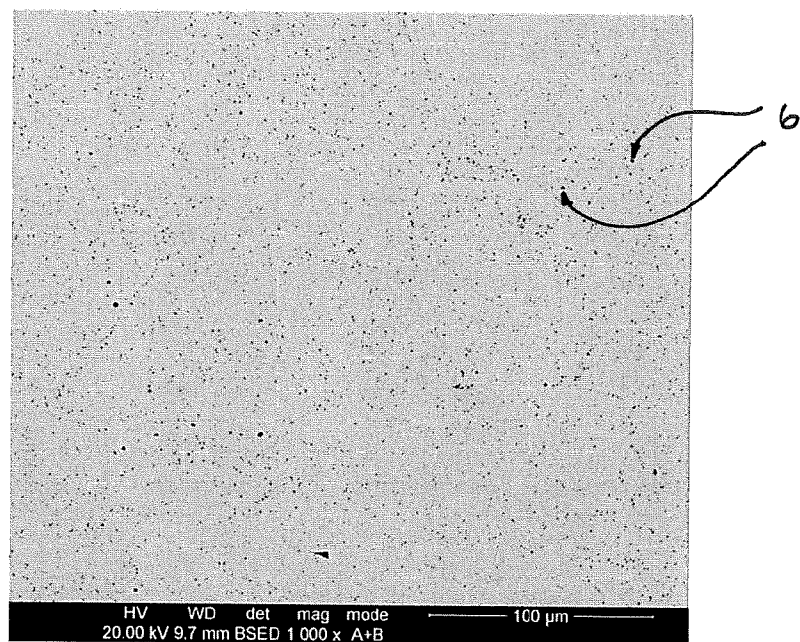


Fig. 10

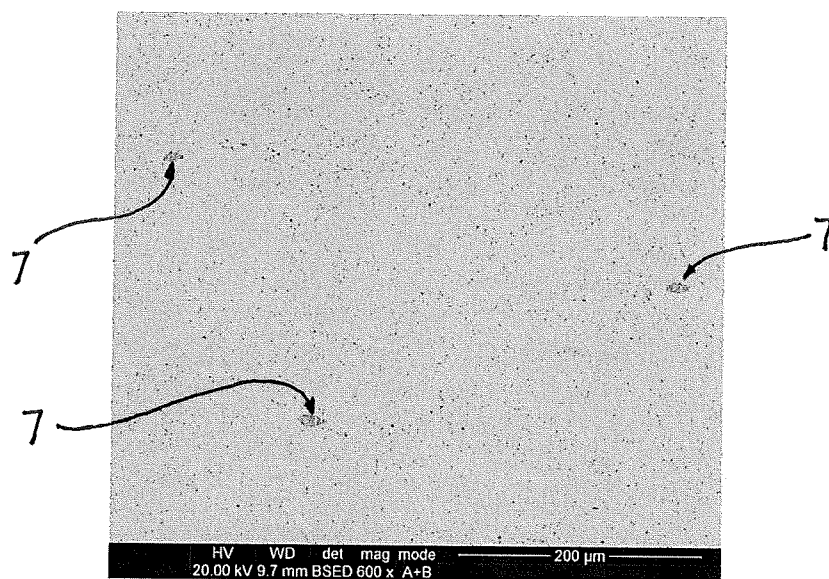


Fig. 11

HOT-WORK TOOL STEEL AND A PROCESS FOR MAKING A HOT-WORK TOOL STEEL

TECHNICAL FIELD

[0001] The present invention relates to a low-chromium hot-work tool steel and a process for making a low-chromium hot-work tool steel article.

BACKGROUND ART

[0002] The term 'hot-work tools' is applied to a great number of different kinds of tools for the working or forming of metals at comparatively high temperatures, for example tools for die casting, such as dies, inserts and cores, inlet parts, nozzles, ejector elements, pistons, pressure chambers, etc.; tools for extrusion tooling, such as dies, die holders, liners, pressure pads and stems, spindles, etc.; tools for hot-pressing, such as tools for hot-pressing of aluminium, magnesium, copper, copper alloys and steel; moulds for plastics, such as moulds for injection moulding, compression moulding and extrusion; together with various other kinds of tools such as tools for hot shearing, shrink-rings/collars and wearing parts intended for use in work at high temperatures. Low-alloyed hot-work tool steel is used in small to medium sized tools in applications where the demands on tempering resistance and thermal fatigue are high. Tempering resistance is the ability of a hot-work tool steel to keep its hardness at an elevated temperature for prolonged time. Hot-work tool steels are developed for strength and hardness during prolonged exposure to elevated temperatures and generally use a substantial amount of carbide forming alloys.

[0003] Another type of tool steels is the high speed steels, which are used for cutting tools where strength and hardness must be retained at temperatures up to or exceeding 760° C. To reduce the amount of tungsten and chromium required, e.g. 18 and 4 wt-%, respectively, variants using molybdenum (5-10 wt-%) were developed. High speed steel differs from hot-work steel in composition and price and cannot be used as a substitute for hot-work steel.

SUMMARY OF THE INVENTION

[0004] One object of the present invention is to provide a low-chromium hot-work tool steel having an improved property profile, in particular an improved tempering resistance.

[0005] The steels of the present invention is particular suitable for small tools which do not require a steel composition having a high hardenability for their manufacturing.

[0006] This object is obtained by providing a low-chromium hot-work tool steel as defined in claim 1, i.e. a steel consisting of (in wt-%):

C	0.08-0.40
N	0.015-0.30
C + N	0.30-0.50
Cr	1-4
Mo	1.5-3
V	0.8-1.3
Mn	0.5-2
Si	0.1-0.5
optionally	
Ni	<3
Co	≤5
B	<0.01
Fe balance apart from impurities.	

[0007] Further objects may be obtained by the low-chromium hot-work tool steel according to the invention fulfilling one or more of the following conditions (in wt-%):

C	0.20-0.38	preferably 0.30-0.35
N	0.03-0.30	preferably 0.03-0.10
C + N	0.30-0.50	preferably 0.36-0.44
Cr	1-3	preferably 1.2-2.6
Mo	1.9-2.9	preferably 2.2-2.8
V	1.0-1.3	preferably 1.15-1.25
Mn	1-2	preferably 1.1-1.9
Si	0.1-0.5	preferably 0.2-0.4
Ni	<1	preferably <0.25
Co	<4	preferably <0.20
B	0.001-0.01	preferably 0.001-0.005

[0008] Preferred embodiments of the low-chromium hot-work tool steel may fulfill one or more of the following conditions (in wt-%):

C	0.25-0.35	preferably 0.27-0.34
N	0.04-0.30	preferably 0.04-0.10
C + N	0.38-0.42	
Cr	1.3-2.5	preferably 1.4-2.3.

[0009] More preferred embodiments of the low-chromium hot-work tool steel may fulfill one or more of the following conditions (in wt-%):

N	0.042-0.15	preferably 0.045-0.12
C + N	0.39-0.41	
Cr	1.3-2.3	preferably 1.4-2.1

[0010] Even more preferred embodiments of the low-chromium hot-work tool steel may fulfill one or more of the following conditions (in wt-%):

C	0.20-0.35	preferably 0.30-0.34
N	0.042-0.12	preferably 0.045-0.12
C + N	0.39-0.41	
Cr	1.4-1.9	preferably 1.5-1.7
Mo/V	1.8-2.3	preferably 1.9-2.1
Cr/V	<2	preferably <1.8

[0011] According to the inventive concept, the low-chromium hot-work tool steel may have a composition (in wt-%) according to the examples below:

C	0.20-0.40
N	0.03-0.30
C + N	0.30-0.50
Cr	1.2-2.3
Mo	1-3
V	0.8-1.3
Mn	1-2
Si	0.1-0.4
Ni	<1
optionally	
Co	3-5
B	0.001-0.01

-continued

	Mo/V	1.8-2.3
	Cr/V	<2
Fe balance apart from impurities, or		
	C	0.20-0.40
	N	0.03-0.30
	C + N	0.30-0.50
	Cr	1.2-2.3
	Mo	1.5-3
	V	0.8-1.3
	Mn	1-2
	Si	0.1-0.4
	Ni	<1
	optionally	
	Co	3-5
	B	0.001-0.01
	Mo/V	1.8-2.3
	Cr/V	<2
Fe balance apart from impurities, or		
	C	0.20-0.40
	N	0.04-0.30
	C + N	0.30-0.50
	Cr	1.2-2.3
	Mo	1-3
	V	0.8-1.3
	Mn	1-2
	Si	0.1-0.4
	Ni	<1
	Co	<0.2
	optionally	
	B	0.001-0.01
	Mo/V	1.8-2.3
	Cr/V	<2
Fe balance apart from impurities, or		
	C	0.20-0.38
	N	0.04-0.30
	C + N	0.36-0.44
	Cr	1.2-2.3
	Mo	1.9-2.9
	V	0.8-1.3
	Mn	1-2
	Si	0.1-0.4
	Ni	<0.25
	Co	<0.20
	optionally	
	B	0.001-0.01
	Mo/V	1.8-2.3
	Cr/V	<2
Fe balance apart from impurities, or		
	C	0.30-0.34
	N	0.04-0.09
	C + N	0.37-0.43
	Cr	1.4-1.9
	Mo	2.2-2.8
	V	1.0-1.3
	Mn	1-2
	Si	0.2-0.4
	Ni	<0.25
	Co	<0.20
	optionally	
	B	0.001-0.005
	Mo/V	1.8-2.3
	Cr/V	<2

Fe balance apart from impurities.

[0012] Another object is to provide a low-chromium hot-work tool steel article having an improved property profile, in particular an improved tempering resistance.

[0013] In accordance with the present invention this object is obtained by a process as defined in claim 11, ie. A process which comprises the steps of:

[0014] a) providing a low-chromium hot-work tool steel as defined in any of the claims;

[0015] b) forming a steel article from the steel composition;

[0016] c) austenitizing the steel article obtained in step b) at a temperature of at most 1200° C. for a time on the order of half an hour followed by quenching; and

[0017] d) tempering the quenched steel article at least twice at a temperature between 500 and 700° C. for a time on the order of 2 hours.

[0018] Preferred embodiments of the process are set out in the dependent claims 12-15.

[0019] In a creep resistant steel having a high chromium content, i.e. 9-12 wt-%, it is possible to dissolve vanadium carbide-nitrides already at relatively low temperatures, i.e. 1020-1050° C. However, if the chromium content is low, less than about 4-5 wt-%, primary vanadium carbide-nitrides will be formed in the melt, and they are virtually impossible to dissolve afterwards.

[0020] In the steel of the present invention, the total amount of carbon and nitrogen shall be regulated to $0.30 \leq (C+N) \leq 0.50$, preferably $0.36 \leq (C+N) \leq 0.44$. The nominal content shall be in the order of 0.40 wt-%. At the same time, it is advantageous to regulate the nitrogen content to between 0.015 and 0.30 N, preferably 0.015 and 0.15 N, and even more preferred 0.015-0.10 and carbon may preferably be regulated to at least 0.20 wt-%. The preferred ranges are set out in the product claims.

[0021] When the nitrogen content is balanced to about 0.05 to 0.10 wt-% vanadium carbonitrides will form, which will be partly dissolved during the austenitizing step and then precipitated during the tempering step as particles of nanometer size. The thermal stability of vanadium carbonitrides is better than that of vanadium carbides, and consequently the tempering resistance of the low-chromium hot-work tool steel article will be much improved. Further, by tempering at least twice, the tempering curve (showing hardness as a function of tempering temperature) will have a higher, secondary peak.

[0022] In the most preferred embodiment of the invention the nitrogen content preferably is on the order of 0.05 wt-%. This value gives a better performance than higher values. A nitrogen content on the order of 0.05 wt-% gives a higher potential for secondary hardening during quenching than higher contents do, thus giving the steel a high hardness. However, an amount in the order of 0.10 wt-% has shown to give a shift of the secondary hardening peak to somewhat higher tempering temperatures which is positive. The preferred ranges of are set out in the product claims.

[0023] Additionally, the performed tests and modelling calculations indicate that an increased austenitizing temperature is required in connection with increased nitrogen contents.

[0024] Chromium promotes the hardenability and corrosion resistance of steels. At too low contents the corrosion resistance will be adversely affected. A minimum chromium content in the steel, therefore, is set to 1 wt-%. The maximum content is set to 4 wt-% in order to avoid undesired formation of chromium rich carbides/carbonitrides, e.g. $M_{23}C_6$. The chromium content preferably shall not exceed 3 wt-%, and even more preferred preferably not exceed 2.6 wt-%. In one embodiment of the invention, the chromium content is 1.5-1.7 wt-%. The preferred ranges of are set out in the product claims. A low chromium content delays the precipitation of chromium carbides in the microstructure in favour of the more thermally stable vanadium-rich carbo-nitride. Thus the recovery is slowed down in the material and the tempering resistance becomes improved

[0025] The steel shall contain vanadium in an amount of at least 0.8 wt-% in order to provide a sufficient precipitation

potential and thus an adequate tempering resistance and desired high temperature strength properties. In order to avoid excessive formation of M(C,N) precipitates which would increase the risk of large undissolved precipitates remaining in the matrix after heat treatment and further risk a depletion of carbon and nitrogen in the matrix, the upper limit of vanadium is 1.3 wt-%. Preferably vanadium is between 1.0 and 1.3 wt-%. The preferred ranges of are set out in the product claims.

[0026] The ration Cr/V should preferably be less than 2, more preferably less than 1.8 in order to get the desired MC phase. The reason is that Cr can be considered as a poison for the MC phase.

[0027] Silicon shall be present in the steel in an amount of between 0.1-0.5 wt-%, preferably 0.2-0.4 wt-%. By keeping the content of silicon low it is possible to obtain an initial precipitation of meta-stable M_3C carbides. These carbides will act as a reservoir for carbon for subsequent precipitation of the desired M(C,N) particles. Also, precipitation of undesired chromium-rich $M_{23}C_6$ particles in the grain boundaries and lattice boundaries is avoided. The preferred ranges of are set out in the product claims.

[0028] Manganese is present in order to give the steel an adequate hardenability, particularly given the relatively low content of chromium and molybdenum in the steel. The content of manganese in the steel is between 0.5 and 2 wt-%, preferably between 1.0 and 2.0 wt-%. The preferred ranges of are set out in the product claims.

[0029] Molybdenum shall be present in the steel in an amount of between 1.5 and 3 wt-%, preferably 2.2-2.8 wt-%, in order to provide a secondary hardening during tempering and to give a contribution to the hardenability. The preferred ranges of are set out in the product claims.

[0030] Part of the molybdenum may be substituted for tungsten in a manner known per se but the steel shall preferably not contain any intentionally added amounts of tungsten, i.e. shall not contain tungsten in amounts exceeding impurity level, because of certain drawbacks related to the presence of that element.

[0031] The ratio Mo/V should preferably lie in the range of 1.8-2.3, more preferably 1.9-2.1 in order to get the desired precipitation sequence and precipitation potential of the secondary carbides. It is known that Mo stabilizes the M_2C phase and by adjusting the contents of Mo and V to fall within the range of 1.8-2.3 also the molybdenum rich M_2C will form, which phase has a higher coarsening rate as compared to the vanadium rich MC phase.

[0032] Nickel and cobalt are elements that may be included in the steel in amounts up to 3 wt-% and 5 wt-% respectively. Cobalt may increase the hardness at high temperatures which may be advantageous for some applications of the steel. If cobalt is added, an effective amount is about 4 wt. %. Nickel may increase the corrosion resistance, hardenability and toughness of the steel. The preferred ranges of are set out in the product claims.

[0033] In principle, austenitizing may be carried out at a temperature between the soft annealing temperature 820° C. and the maximum austenitizing temperature 1200° C., but the austenitizing of the steel article preferably is carried out at a temperature on the order of 1050-1150° C., preferably at 1080-1150° C., typically at 1100° C. In-house tests indicate that higher austenitizing temperatures shift the tempering hardness to higher temperatures, i.e. the secondary hardening peak will be shifted to higher temperatures, which means that

the desired hardness will be reached at a higher initial tempering temperature. Thus the material will obtain an improved tempering resistance and the work temperature of the tools could be elevated.

[0034] The tempering of the quenched steel article preferably is carried out at least twice at a retention time of 2 hours at a temperature between 500 and 700° C., preferably 550 and 680° C. In the most preferred embodiment of the steel composition, the tempering is carried out at a temperature between 600 and 650° C., preferably between 625 and 650° C.

[0035] Nitrogen contents in the range of 0.05-0.10 wt-% may be obtained by incorporating the nitrogen by conventional casting methods to form a melt, casting the melt to form an ingot, and homogenizing the ingot by heat treatment. Nitrogen additions will produce large primary vanadium-rich M(C,N) precipitates, which in turn will give the material uneven hardness. However, the large primary carbo-nitrides will not occur if the nitrogen content is lowered and there is a homogenizing heat treatment prior to a subsequent forging.

[0036] In a variant of the steel, higher nitrogen contents than indicated for the preferred embodiment is also conceivable. In this variant, nitrogen may amount to up to 0.30 wt-%. To obtain higher nitrogen contents, conventional casting methods are insufficient. Instead, the nitrogen could be incorporated by first manufacturing a steel powder of essentially the desired composition, except for the nitrogen, then nitriding this powder in solid state by nitrogen containing fluid, e.g. nitrogen gas, thereafter hot pressing the powder isostatically at a temperature on the order of 1150° C. and a pressure on the order of 76 MPa to form an ingot. By manufacturing the tool steel by powder metallurgy, the problem of large primary carbide occurrence is avoided.

[0037] The ingot is preferably forged at a temperature on the order of 1270° C., and then soft annealed at a temperature on the order of 820° C., followed by cooling at a rate of 10° C. per hour to a temperature of 650° C. and then free cooling in air to make it ready for austenitizing.

[0038] The steel of the present invention has a much improved tempering resistance permitting a longer article life in hot-work applications. As already indicated above, the nitrogen content preferably is on the order of 0.05 wt-% and the chromium content is preferably less than 3 wt-%, i.e. 1.2-2.6 or 1.3-2.3.

[0039] The steel article of the present invention shall preferably also satisfy some of the following demands:

- [0040] good tempering resistance,
- [0041] good high-temperature strength,
- [0042] good thermal conductivity,
- [0043] not have an unacceptably large coefficient of heat expansion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0044] In the following, the invention will be described in more detail with reference to preferred embodiments and the appended drawings.

[0045] FIG. 1 is a diagram showing hardness vs. tempering temperature of an exemplary prior art low-chromium hot-work tool steel containing no nitrogen.

[0046] FIG. 2 is a diagram showing hardness of prior art steels (contents in wt-%) Cr 15, Mo 1, C 0.6 and Cr 15, Mo 1, C 0.29, N 0.35 at different tempering temperatures.

[0047] FIG. 3 is a diagram illustrating the effect of low chromium content on the stability of M(C,N) in austenite.

[0048] FIG. 4 is a diagram showing the mole fraction of M_6C , $M(C,N)$ and the bcc matrix as a function of temperature. (Balance phase: austenitic matrix.)

[0049] FIG. 5 is a diagram showing the amount of $M(C,N)$ phase and meta-stable M_2C as function of temperature. (Balance phase: ferrite.)

[0050] FIG. 6 is a diagram showing hardness vs. tempering temperature curves for trial alloys N0.05, N0.10 and N0.30

[0051] FIG. 7 is a back-scattered SEM image showing small undissolved $M(C,N)$ precipitates and a globular mixed oxide-sulphide particle in N0.05.

[0052] FIG. 8 is a back-scattered SEM image revealing undissolved, primary $M(C,N)$ at former austenite grain boundaries in alloy N0.10.

[0053] FIG. 9 is a back-scattered SEM image depicting primary particles in soft annealed N0.10.

[0054] FIG. 10 is a back-scattered SEM image revealing an even distribution of undissolved $M(C,N)$ particles in N0.30.

[0055] FIG. 11 is a back-scattered SEM image revealing some clusters of undissolved $M(C,N)$ found in N0.30.

MODE(S) FOR CARRYING OUT THE INVENTION

[0056] Molybdenum and vanadium medium alloyed hot-work tool steels have good resistance to thermal fatigue, softening and high-temperature creep. An exemplary nominal chemical composition of such a prior art steel is presented in Table 1 (wt-%).

TABLE 1

C	Cr	Mo	V	Mn	Si	Fe
0.38	2.6	2.3	0.9	0.75	0.3	92.8

[0057] It has been suggested that the steel of Table 1 owes its high-temperature properties to the precipitation of nanometre-sized vanadium carbides during tempering. These hard carbides of MC type (2900 HV) give a secondary hardening of the material. FIG. 1 presents a tempering curve (hardness vs tempering temperature) for the exemplary prior art tool steel. The samples were austenitized at 1030° C., and then tempered two times at different temperatures; from 200° C. up to 700° C. for a tempering time of 2+2 hours. As can be seen, in the interval 500 to 650° C. there is a pronounced secondary hardening peak at 550° C. Later work has also shown that there is a significant precipitation of the meta-stable molybdenum-rich M_2C in the exemplary prior art tool steel during tempering at 625° C., which contributes to the secondary hardening effect. The ability of a hot-work tool steel to keep its hardness at an elevated temperature for prolonged time, the tempering resistance, can normally be connected to the initial tempering temperature; if the material is held at a temperature well below the initial tempering temperature it will not soften. At holding temperatures closer to or above the initial tempering temperature the softening will be more pronounced.

[0058] If the secondary hardening peak could be shifted to higher temperatures, this would mean that the desired hardness (e.g. 44-46 HRC) could be reached at a higher initial tempering temperature. Thus the material would get an improved tempering resistance, and the work temperature of the tools could be raised.

[0059] Earlier work on high-chromium steels suggests that when nitrogen is added to the steel, it is possible to achieve higher hardness during tempering. Samples of Cr 15, Mo 1, C 0.6 and Cr 15, Mo 1, C 0.29, N 0.35 were solution treated at 1050° C. followed by water quenching and cooling to liquid nitrogen, and then they were tempered at different temperatures for 2 hours. As can be seen in FIG. 2, the peak hardness became significantly higher when adding nitrogen. The initial hardness of the martensite is lower for the nitrogen containing steel, but during tempering this steel achieves a higher hardness than the steel containing no nitrogen.

[0060] The explanation for this is that nitrogen makes the chromium more homogeneously distributed in the matrix, due to increased solubility of chromium in the austenitic phase. After quenching the martensitic phase inherited the evenly distributed chromium from the austenite, and during tempering a very finely distributed precipitation of chromium nitrides takes place, thus giving a stronger hardening effect in the material.

[0061] Furthermore, the substitution of nitrogen for part of the carbon is used to achieve a higher hardness of the martensitic steel matrix. The nitrogen addition initially causes a larger amount of retained austenite. However, this austenite can later be transformed to martensite by cold work, and it is possible to achieve hardness as high as 68 HRC in this manner.

[0062] A low chromium content appears to have a positive effect on the tempering resistance. A comparison of two different hot-work tools steels with 1.5 and 5.0 wt-% chromium shows that the lower chromium content delays the precipitation of chromium carbides in the microstructure in favour of the more thermally stable vanadium-rich MC. Thus the recovery is slowed down in the material and the tempering resistance becomes improved.

[0063] However, studies made on a typical creep resistant 9-12 wt-% chromium steel containing 0.06 wt-% N indicate that low chromium contents stabilize the MX (X being C+N) particles dramatically, see FIG. 3. If the austenitizing were to be performed at 1100° C., then all of the $M(C,N)$ particles would be dissolved in the steel containing 10 wt % chromium. If the chromium content were lowered to 2.5 wt % (cf. the exemplary low-chromium tool steel of FIG. 1), then large amounts of $M(C,N)$ would still be present in the austenite. Apparently, the consequence of a low chromium content is that only small amounts of interstitials will be dissolved into the austenite during austenitizing treatment.

[0064] According to the present invention a low-chromium hot-work tool steel article having increased tempering resistance is made by carrying out the following process steps:

[0065] a) incorporating nitrogen in a low-chromium hot-work tool steel melt composition and thereby providing a steel composition as defined in any of the process claims;

[0066] b) forming a steel article from the steel composition;

[0067] c) austenitizing the steel article obtained in step b) at a temperature of at most 1200° C. for a time on the order of half an hour followed by quenching; and

[0068] d) tempering the quenched steel article at least twice at a temperature between 500 and 700° C. for a time on the order of 2 hours.

[0069] Considering the conventional understanding in the present technical field, these results are surprising since the prevalent teaching is that lowering of the chromium content will result in a reduced hardenability and difficulties to dissolve primary $M(C,N)$ particles

[0070] In a creep resistant steel having a high chromium content, i.e. 9-12% by weight, it is possible to dissolve vanadium carbo-nitrides already at relatively low temperatures, i.e. 1020-1050° C. However, if the chromium content is low, less than about 4-5% by weight, primary vanadium carbo-nitrides will be formed in the melt, and they are virtually impossible to dissolve afterwards.

[0071] The inventors have found that when the nitrogen content is balanced to about 0.015 to 0.30 wt-% in a low-chromium steel, vanadium carbo-nitrides will form, which will be partly dissolved during the austenitizing step and then precipitated during the tempering step as particles of nanometer size. The particles are in the order of about 1 µm to about 10 µm. In some cases, where the nitrogen content is low, typically at 0.05 wt-% the average size of the particles are less than 1 µm. The thermal stability of vanadium carbo-nitrides is better than that of vanadium carbides, and consequently the tempering resistance of the low-chromium hot-work tool steel article will be much improved. Further, by tempering at least twice, the tempering curve (showing hardness as a function of tempering temperature) will have a higher, secondary peak.

[0072] In a preferred embodiment of the steel, the nitrogen content preferably is on the order of 0.05 percent by weight. This value gives a better performance than higher values. A nitrogen content on the order of 0.05 percent by weight gives a higher potential for secondary hardening during quenching than higher contents do.

[0073] In the preferred embodiment, the chromium content preferably is 1.5-1.7 percent by weight. A low chromium content delays the precipitation of chromium carbides in the microstructure in favour of the more thermally stable vanadium-rich carbo-nitrides. Thus the recovery is slowed down in the material and the tempering resistance becomes improved.

[0074] In principle, austenitizing may be carried out at a temperature between the soft annealing temperature 820° C. and the maximum austenitizing temperature 1200° C. In a preferred embodiment, i.e. in a composition having a nitrogen content in the order of 0.05 percent by weight and a chromium content in the order of 1.5 to 1.7 percent by weight, the austenitizing of the steel article preferably is carried out at a temperature on the order of 1050-1150° C., preferably at 1100° C. In-house tests indicate that higher austenitizing temperatures shift the tempering hardness to higher temperatures, i.e. the secondary hardening peak will be shifted to higher temperatures, which means that the desired hardness will be reached at a higher initial tempering temperature. Thus the material will get an improved tempering resistance and the work temperature of the tools will be raised.

[0075] The tempering of the quenched steel article preferably is carried out at least twice at a retention time of 2 hours at a temperature between 500 and 700° C., preferably 550 and 680° C. In the most preferred embodiment of the steel composition, the tempering is carried out at a temperature between 600 and 650° C., preferably between 625 and 650° C.

[0076] Nitrogen contents in the range of 0.05-0.10 percent by weight may be obtained by incorporating the nitrogen by conventional casting methods to form a melt, casting the melt to form an ingot, and homogenizing the ingot by heat treatment. Nitrogen additions will produce large primary vanadium-rich M(C,N) precipitates, which in turn will give the material uneven hardness. However, large primary carbo-

nitrides will not occur if the nitrogen content is lowered and there is a homogenizing heat treatment prior to a subsequent forging.

[0077] In the preferred embodiment of the invention the nitrogen content preferably is on the order of 0.05 wt-%. This value gives a better performance than higher values. A nitrogen content on the order of 0.05 wt-% gives a higher potential for secondary hardening during quenching than higher contents do, thus giving the steel a high hardness. However, an amount in the order of 0.10 wt-% has shown to give a shift of the secondary hardening peak to somewhat higher tempering temperatures which is positive. Additionally, the performed tests and modelling calculations indicate that an increased austenitizing temperature is required in connection with increased nitrogen contents.

[0078] In a variant of the steel, higher nitrogen contents than indicated for the preferred embodiment is also conceivable. In this variant, nitrogen may amount to up to 0.30 wt-%. To obtain higher nitrogen contents, conventional casting methods are insufficient. Instead, the nitrogen then is incorporated preferably by first manufacturing a steel powder of essentially the desired composition, except for the nitrogen, then nitriding this powder in solid state by nitrogen gas, thereafter hot pressing the powder isostatically at a temperature on the order of 1150° C. and a pressure on the order of 76 MPa to form an ingot. By manufacturing the tool steel by powder metallurgy, the problem of primary carbide occurrence is avoided.

[0079] The ingot is preferably forged at a temperature on the order of 1270° C., and then soft annealed at a temperature on the order of 820° C., followed by cooling at a rate of 10° C. per hour to a temperature of 650° C. and then free cooling in air to make it ready for austenitizing.

EXAMPLE 1

[0080] In Table 2 below the chemical compositions in percent by weight of three different alloys N0.05; N0.10 and N0.30. are presented. N0.05 designates a material having a nitrogen content of 0.05 wt-%, and so on. Note that these are the actual compositions of the trial ingots.

[0081] The aim was to keep the level of all alloying elements except carbon and nitrogen constant. Compared to the standard low chromium hot-work tool steel of Table 1, chromium was also slightly decreased. There was a small decrease in molybdenum content and an increase in manganese content. For carbon and nitrogen, the aim was to have a constant sum of around 0.40 wt-% of these elements, and this was relatively well achieved.

TABLE 2

	Material							
	C	N	Cr	Mo	V	Mn	Si	Fe
N0.05	0.38	0.05	1.70	2.77	1.20	1.09	0.30	92.5
N0.10	0.27	0.10	1.53	2.32	1.20	1.85	0.26	92.5
N0.30	0.08	0.32	1.51	2.20	1.20	1.88	0.29	92.5

[0082] The tempering stage concerns mainly meta-stable phases, and previous electron microscopy work has shown that they exist in standard low chromium hot-work tool steel at tempering temperature intervals, i.e. 400 to 700° C. These carbide phases are mainly vanadium-rich MC (FCC) and

molybdenum-rich M_2C (HCP). Some amount of chromium-rich M_7C_3 has also been found in the standard low chromium hot-work tool steel.

[0083] The following calculations were made in order to decide whether or not these nitrogen containing alloys were possible to harden, i.e. if enough alloying elements could be dissolved into the austenitic matrix at the austenitizing temperature, so that martensite would form during quenching. The interesting temperature interval thus was between the soft annealing temperature, 820° C. and the set practically usable maximum austenitizing temperature, 1200° C.

[0084] The results of these equilibrium calculations are presented in FIG. 4. Here the mole fraction of M_6C , $M(C,N)$ and the bcc matrix is shown as a function of temperature. The balance phase is austenite. The full curves represent N0.05; the dashed curves represent N0.10 and the dotted curves represent N0.30. Note the high content of $M(C,N)$ in the N0.30 alloy even up to 1200° C. As expected, the bcc phase is unstable above 850° C. It is interesting to see that the slope of the equilibrium curve, representing the amount of $M(C,N)$, decreases as the nitrogen content increases. This means that it is more difficult to dissolve $M(C,N)$ in N0.30 compared to N0.05. Thus, it is expected that the amount of carbon, nitrogen and vanadium would be lower in the N0.30 matrix after austenitizing at 1100° C. than in the N0.05 matrix.

[0085] Since the molybdenum-rich M_6C phase only dissolves carbon and no nitrogen, it suffers from the lower carbon content in N0.10 and N0.30, thus the amount of M_6C decreases with decreasing carbon content. It should also be noted that all M_6C is dissolved at the austenitizing temperatures used.

[0086] The calculations performed in the tempering temperature region were only done in order to estimate the potential for secondary precipitation in N0.05, N0.10 and N0.30. The equilibria found can at best show what phases would be present in the material after a sufficiently long time. Previous work has shown that in practice there is some auto-tempering in the standard low chromium hot-work tool steel. This means that M_3C (cementite) will precipitate after the austenitizing process.

[0087] The results from the calculations in the tempering temperature region are presented in FIG. 5. The full curves represent N0.05; the dashed curves represent N0.10 and the dotted curves represent N0.30. Secondary hardening normally takes place between 500 and 650° C., and in this temperature interval there is no big difference between N0.05 and N0.10 regarding the amount of $M(C,N)$. N0.30 on the other hand has a high and almost constant amount of $M(C,N)$, probably due to the high vanadium and nitrogen contents.

[0088] The higher carbon content in N0.05 produces more M_2C phase in equilibrium with the matrix compared to N0.10. In N0.30 there is much less M_2C .

[0089] Based upon the previous calculations it should be possible to estimate the potential for secondary precipitation in these alloys after austenitizing at a certain temperature. This potential depends on the difference in amount of $M(C,N)$ phase and M_2C phase between the meta-stable equilibrium at tempering temperature and the equilibrium at austenitizing temperature. In Table 3, these differences are presented as the secondary precipitation potential for the three different alloys. The values are given in mole percent.

TABLE 3

	Phases, mole percent		
	M (C,N)	M_2C	Total
<u>Alloy N0.05</u>			
Tempering, 625° C	2.1	2.8	
Austenitizing, 1100° C.	1.1	0.0	
Precipitation Potential	1.0	2.8	3.8
<u>Alloy N0.10</u>			
Tempering, 625° C.	1.8	2.3	
Austenitizing, 1100° C.	1.2	0.0	
Precipitation Potential	0.6	2.3	2.9
<u>Alloy N0.30</u>			
Tempering, 625° C.	2.6	1.2	
Austenitizing, 1100° C.	2.4	0.0	
Precipitation Potential	0.2	1.2	1.4

[0090] The results presented in Table 3 indicate that N0.05 would have the best hardening response due to the low amount of $M(C,N)$ phase present at 1100° C., i.e. a lot of alloying elements can be dissolved into the austenitic matrix. It also indicates that N0.05 has the best potential for a good secondary hardening during tempering at 625° C.

EXAMPLE 2

[0091] The two alloys N0.05 and N0.10 were conventionally cast as small ingots of 50 kg. N0.10 was the first trial and there was no homogenizing treatment done on this ingot before the forging process. The second trial, N0.05, a homogenizing treatment at 1300° C. for 15 hours was applied before forging. The third alloy, N0.30 had a too high nitrogen content to be manufactured by conventional casting. Therefore this alloy was produced using powder metallurgy. First the steel powder was manufactured and then this powder was nitrided in solid state by pressurized N_2 -gas. The powder was then hot isostatically pressed (HIP) at 1150° C. with the pressure of 76 MPa.

[0092] All three ingots were forged at 1270° C. and then samples were cut out with the dimensions: 15×15×8 mm. The samples were heat treated by first soft annealing at 820° C.; the sequence for cooling after annealing is 10° C. per hour to 650° C. and then free cooling in air. After soft annealing, N0.05 was austenitized at 1100° C. for 30 minutes. In order to compensate for the poorer potential for precipitation, N0.10 was austenitized at 1150° C. for 30 minutes, and N0.30 was austenitized at 1200° C. for 30 minutes. Nine samples from each of the three alloys were tempered at following temperatures: 450, 525, 550, 575, 600, 625, 650, 675 and 700° C. The soaking time was two hours and it was a double tempering, i.e. the total tempering time was four hours. After heat treatment, the hardness of the samples was measured. Scanning electron microscopy (SEM) was performed in order to further investigate the morphology, distribution and size of the undissolved particles in the samples. The SEM instrument used was a FEI Quanta 600 F.

Hardness Measurements

[0093] The results from the hardness measurements are presented in FIG. 6. As can be seen, all three alloys have a secondary hardening peak in the temperature interval 500 to 650° C. All tempering was done for 2+2 hours. N0.05 has the highest hardness in the as-quenched condition (53HRC), while N0.10 and N0.30 had somewhat lower hardness. However, all three alloys are regarded as hardenable. The hardness

curve of N0.05 is very similar to that of the standard low-chromium hot-work tool steel with a maximum of around 54 HRC as shown in FIG. 1.

[0094] The secondary hardening peak of N0.10 seems to be somewhat shifted to a higher temperature with peak hardness at 600° C. The peak hardness for both N0.05 and N0.30 was at 550° C.

Scanning Electron Microscopy

[0095] The undissolved M(C,N) particles in the conventionally cast N0.05, the alloy with the lowest nitrogen content, have an average size smaller than 1 μm . This is comparable with ordinary undissolved carbides in steel. Another phase that is easily found in N0.05 is the mixture of aluminium-oxide and manganese-sulphide, see FIG. 7, which is a SEM image (back-scattered) showing small undissolved M(C,N) precipitates 2 and a globular mixed oxide-sulphide particle 1 in N0.05. The sample was austenitized at 1100° C. for 30 min and tempered at 625° C. for 2+2 hours.

[0096] The reason for the many non-metallic inclusions in N0.05 (and N0.10) is that all trial ingots were manufactured and cast in open atmosphere.

[0097] The most common size of the M(C,N) particles in N0.10 is between 5 and 10 μm Equivalent Circle Diameter (ECD) after austenitizing at 1150° C. for 30 minutes and tempering at 625° C. for 2+2 hours. Larger, primary carbides 3 (precipitated in the melt) are frequently found in former austenite grain boundaries, see FIG. 8, which is a back-scattered SEM image revealing undissolved, primary M(C,N) at former austenite grain boundaries in alloy N0.10. The sample was austenitized at 1150° C. for 30 min and tempered at 625° C. for 2+2 hours.

[0098] FIG. 9 is a detail SEM micrograph of primary M(C,N) particles 4 in N0.10. They were discovered automatically in SEM using the INCA Feature software from Oxford Instruments. Their sharp edges indicated that they had precipitated from the melt. The white areas in the image are molybdenum-rich M_6C particles 5. Note that in this case the sample was soft annealed N0.10.

[0099] In the powder metallurgically manufactured N0.30, the undissolved M(C,N) particles 6 had a size distribution (ECD) between 1 to 5 μm with the most common size 2 μm , thus the particles were small even though the nitrogen content was high. The particles were homogeneously distributed in the microstructure, see FIG. 10. However, as shown in FIG. 11, some clusters 7 of M(C,N) were found.

[0100] The chemical composition of the undissolved particles of the M(C,N) phase in all three alloys was measured by EDS and the result is presented in Table 4, which shows the chemical composition of the M(C,N) particles in alloys N0.05, N0.10 and N0.30. The values are given in atomic percent. Note that, even though the accuracy in EDS regarding light elements such as carbon and nitrogen is not so high, one can see that the balance of carbon and nitrogen in the M(C,N) phase is what can be expected based upon the nominal compositions. The $\pm$ values given in the table are the ones given in the INCA program (Oxford instruments). Some of the iron recorded probably comes from the surrounding matrix, especially for the alloy N0.05.

TABLE 4

Alloy	C	N	V	Fe	Cr	Mo
N0.05	39.4 $\pm$ 0.34	—	15.4 $\pm$ 0.14	42.1 $\pm$ 0.29	1.18 $\pm$ 0.08	—
N0.10	26.4 $\pm$ 0.28	27.6 $\pm$ 0.42	32.4 $\pm$ 0.33	11.0 $\pm$ 0.17	1.3 $\pm$ 0.10	1.0 $\pm$ 0.12
N0.30	12.1 $\pm$ 0.24	41.9 $\pm$ 0.32	21.4 $\pm$ 0.2	21.5 $\pm$ 0.5	2.1 $\pm$ 0.09	0.38 $\pm$ 0.1

INDUSTRIAL APPLICABILITY

[0101] The process and the low-chromium hot-work tool steel of the present invention are applicable where it is desired to get hot-work steel tools, which can be utilized at increased temperatures for an extended period of time.

1. A low-chromium hot-work tool steel consisting of (in wt-%):

C	0.08-0.40
N	0.015-0.30
C + N	0.30-0.50
Cr	1-4
Mo	1.5-3
V	0.8-1.3
Mn	0.5-2
Si	0.1-0.5
optionally	
Ni	<3
Co	$\leq$ 5
B	<0.01

Fe balance apart from impurities.

2. A low-chromium hot-work tool steel according to claim 1 fulfilling one or more the following conditions (in wt-%):

C	0.20-0.38	preferably 0.30-0.35
N	0.03-0.30	preferably 0.03-0.10
C + N	0.30-0.50	preferably 0.36-0.44
Cr	1-3	preferably 1.2-2.6
Mo	1.9-2.9	preferably 2.2-2.8
V	1.0-1.3	preferably 1.15-1.25
Mn	1-2	preferably 1.1-1.9
Si	0.1-0.5	preferably 0.2-0.4
Ni	<1	preferably <0.25
Co	<4	preferably <0.20
B	0.001-0.01	preferably 0.001-0.005

3. A low-chromium hot-work tool steel according to claim 1 fulfilling more of the following conditions (in wt-%):

C	0.25-0.35	preferably 0.27-0.34
N	0.04-0.30	preferably 0.04-0.10
C + N	0.38-0.42	
Cr	1.3-2.5	preferably 1.4-2.3

4. A low-chromium hot-work tool steel according to claim 3 fulfilling one or more of the following conditions (in wt-%):

N	0.042-0.15	preferably 0.045-0.12
C + N	0.39-0.41	
Cr	1.3-2.3	preferably 1.4-2.1

5. A low-chromium hot-work tool steel according to claim 1 fulfilling one or more of the following conditions (in wt-%):

C	0.20-0.35	preferably 0.30-0.34
N	0.042-0.12	preferably 0.045-0.12
C + N	0.39-0.41	
Cr	1.4-1.9	preferably 1.5-1.7
Mo/V	1.8-2.3	preferably 1.9-2.1
Cr/V	<2	preferably <1.8

6. A low-chromium hot-work tool steel according to claim 1 consisting of (in wt-%):

C	0.20-0.40
N	0.03-0.30
C + N	0.30-0.50
Cr	1.2-2.3
Mo	1-3
V	0.8-1.3
Mn	1-2
Si	0.1-0.4
Ni	<1
optionally	
Co	3-5
B	0.001-0.01
Mo/V	1.8-2.3
Cr/V	<2

Fe balance apart from impurities.

7. A low-chromium hot-work tool steel according to claim 1 consisting of (in wt-%):

C	0.20-0.40
N	0.03-0.30
C + N	0.30-0.50
Cr	1.2-2.3
Mo	1.5-3
V	0.8-1.3
Mn	1-2
Si	0.1-0.4
Ni	<1
optionally	
Co	3-5
B	0.001-0.01
Mo/V	1.8-2.3
Cr/V	<2

Fe balance apart from impurities.

8. A low-chromium hot-work tool steel according to claim 1 consisting of (in wt-%):

C	0.20-0.40
N	0.04-0.30
C + N	0.30-0.50
Cr	1.2-2.3
Mo	1-3
V	0.8-1.3
Mn	1-2
Si	0.1-0.4
Ni	<1
Co	<0.2
optionally	
B	0.001-0.01

-continued

Mo/V	1.8-2.3
Cr/V	<2

Fe balance apart from impurities.

9. A low-chromium hot-work tool steel according to claim 1 consisting of (in wt-%):

C	0.20-0.38
N	0.04-0.30
C + N	0.36-0.44
Cr	1.2-2.3
Mo	1.9-2.9
V	0.8-1.3
Mn	1-2
Si	0.1-0.4
Ni	<0.25
Co	<0.20
optionally	
B	0.001-0.01
Mo/V	1.8-2.3
Cr/V	<2

Fe balance apart from impurities.

10. A low-chromium hot-work tool steel according to claim 1 consisting of (in wt-%):

C	0.30-0.34
N	0.04-0.09
C + N	0.37-0.43
Cr	1.4-1.9
Mo	2.2-2.8
V	1.0-1.3
Mn	1-2
Si	0.2-0.4
Ni	<0.25
Co	<0.20
optionally	
B	0.001-0.005
Mo/V	1.8-2.3
Cr/V	<2

Fe balance apart from impurities.

11. A process for making a low-chromium hot-work tool steel article having increased tempering resistance, comprising:

- providing a steel as defined in any of the preceding claims;
- forming a steel article from the steel;
- austenitizing the steel article obtained in step b) at a temperature of at most 1200° C. for a time on the order of half an hour followed by quenching; and d) tempering the quenched steel article for a time of 2 hours at least twice at a temperature between 500 and 700° C.

12. A process as claimed in claim 11, comprising carrying out the austenitizing of the steel article at a temperature of 1050-1150° C., preferably at 1080-1150° C.

13. A process as claimed in claim 11, comprising carrying out the tempering of the quenched steel article at a temperature of 550-680° C., preferably 600-650° C. and even more preferred at 625-650° C.

14. A process as claimed in claim 11, further comprising incorporating the nitrogen by first manufacturing a steel powder of essentially the desired composition, except for the nitrogen, then nitriding this powder in solid state by nitrogen

gas to provide the desired composition, and thereafter hot pressing the powder to form an ingot.

15. A process as claimed in claim **11**, further comprising the steps of homogenizing, forging and soft annealing the ingot before austenitizing.

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