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(54) Corrosion and wear resistant alloy

(57) A powder metallurgy corrosion and wear resistant tool steel article, and alloy thereof. The article is manufactured by hot isostatic compaction of nitrogen atomized, prealloyed high-chromium, high-vanadium, high-niobium powder particles. The alloy is characterized by very high wear and corrosion resistance, making it particularly useful for use in the manufacture of components for advanced bearing designs as well as machinery parts exposed to severe abrasive wear and corrosion conditions, as encountered, for example, in the plastic injection molding industry and food industry.

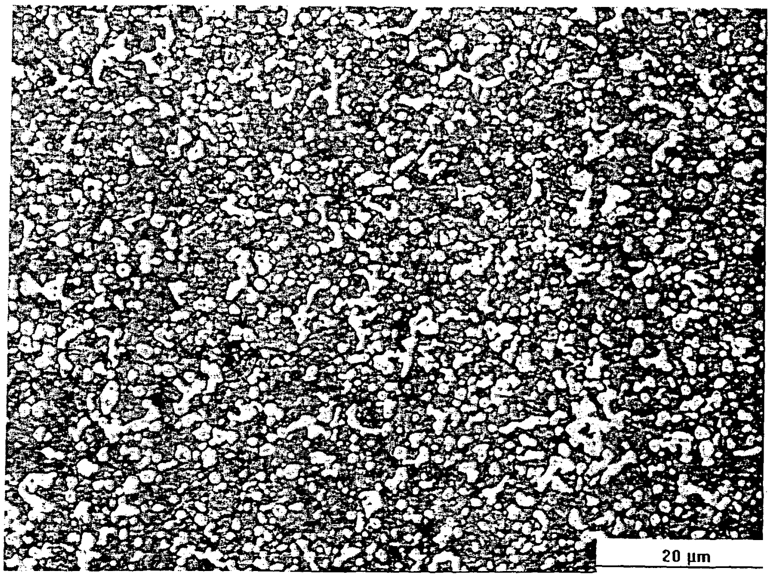

Figure 3. Microstructure of the alloy of the invention (04-099) hardened from 2150°F in oil and tempered at 975°F for 2h+2h+2h. Etched with Vilella's reagent for 90 seconds.

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Description

DESCRIPTION OF THE INVENTION

Field of the Invention

[0001] The invention relates to powder metallurgy corrosion and wear resistant tool steel alloy article, manufactured by hot isostatic compaction of nitrogen atomized, prealloyed high-chromium, high-vanadium, high-niobium powder particles. The alloy of the article of the invention is characterized by very high wear and corrosion resistance, making it in particular useful as a material from which to make components for advanced bearing designs as well as machinery parts exposed to severe abrasive wear and corrosion conditions such as those, among many others, in the plastic injection molding industry and the food industry.

Background of the Invention

[0002] To perform satisfactorily, the alloys that are used in a number of demanding applications—such as screws and barrels in the plastic injection molding industry, for example—must be resistant to wear and corrosion attack. The trend in the industry is to keep increasing processing parameters (e.g., temperature and pressure), which in turn imposes ever-increasing demands on the alloys and their ability to successfully withstand corrosion attack and wear of the materials being processed. In addition, the corrosiveness and abrasiveness of those materials are constantly increasing.

[0003] The wear resistance of tool steels depends on the amount, the type, and the size distribution of primary carbides, as well as the overall hardness. The main function of primary alloy carbides, due to their very high hardness, is to provide wear resistance. Of all types of primary carbides commonly found in tool steels, V-rich and V-Nb-rich MC primary carbides possess the highest hardness.

[0004] The corrosion resistance of tool steels depends primarily on the amount of "free" chromium in the matrix, i.e., the amount of chromium that is not "tied up" into carbides. For good corrosion resistance, through-hardening tool steel must contain at least about 12 wt. % "free" chromium in the martensitic matrix after heat treatment. However, corrosion and wear resistant tool steels must also contain a relatively high level of carbon for heat treatment response. As chromium has a high affinity for carbon with which it forms chromium-rich carbides, a corrosion and wear resistant tool steel must contain excess chromium.

[0005] The corrosion resistance of tool steels is further improved by the presence of molybdenum in the martensitic matrix. Some tool steels that contain about 10 wt. % "free" chromium in the martensitic matrix are corrosion resistant because they also contain a sufficient amount of "free" molybdenum. An example is Crucible 154 CM grade, which is based on the Fe-1.05C-14Cr-4Mo system.

[0006] In order to withstand the stresses imposed during operation, the tool steel must also possess sufficient mechanical properties, such as hardness, bend fracture strength, and toughness. In addition, the tool steel must possess sufficient hot workability, as well as machinability and grindability, to ensure that parts with the required shape and dimensions can be manufactured. In general, the higher the volume fraction of primary carbides, the higher the wear resistance of the tool steel, and the lower its toughness and hot workability.

[0007] The corrosion and wear resistant martensitic tool steels currently used include grades such as CPM S90V, M390, Elmax, Anval 10V-12, HTM X235, for example. Despite the fact that the overall chromium content of some of these alloys is as high as 20 wt. % (e.g., M390), the corrosion resistance is not necessarily as high as one might expect. Depending on the overall chemical composition and the heat treatment parameters, a large amount of chromium, which is a strong carbide former, is pulled out of the matrix and tied up into chromium-rich carbides. This tied up chromium does not contribute toward the corrosion resistance.

[0008] One of the practices that has been used to improve the combination of resistance to corrosion and wear, as exemplified by CPM S90V, is to add vanadium. This alloying addition forms hard’vanadium-rich MC primary carbides and ties up a part of the carbon. Due to the fact that the affinity of vanadium toward carbon is higher than that of chromium, the presence of vanadium in tool steels decreases the amount of chromium-rich primary carbides, all other conditions being equal (i.e., the overall chromium and carbon content, the heat treatment parameters, for example). In the alloy of the invention, in addition to vanadium, niobium is used as well in order to further increase the amount of MC primary carbides, and in turn decrease the amount of chromium-rich primary carbides, due to the fact that niobium has even a higher affinity toward carbon than vanadium.

[0009] A primary object of the invention is to provide wear and corrosion resistant, high chromium, high vanadium, high niobium, powder metallurgy tool steel article with significantly improved corrosion and wear resistance.

SUMMARY OF THE INVENTION

[0010] It has been discovered that the improved balance between wear resistance, the corrosion resistance, and the hardness of the high-chromium, high-vanadium, powder metallurgy martensitic stainless steel article of the invention is affected by adding niobium. The alloy article of the invention possesses a unique combination of corrosion and wear properties that are achieved by balancing its overall chemical composition as well as selecting an appropriate heat treatment.

[0011] It has been discovered that the addition pf niobium decreases the solubility of chromium in V-Nb-rich MC primary carbides, which in turn increases the amount of "free" chromium in the martensitic matrix. According to thermodynamic calculations, the carbon sublattice of the V-Nb-rich MC primary carbides that precipitate in the alloy of the invention has less vacancies compared to the carbon sublattice of the comparable V-rich MC primary carbides: $(V, Nb)C_{0.83}$ versus $VC_{0.79}$.

[0012] It has been discovered that the presence of niobium in the alloy of the invention also lowers the amount of chromium that dissolves in MC primary carbides. This in turn increases the amount of "free" chromium in the matrix, which further improves the corrosion resistance.

[0013] The major alloying elements used in the alloy of the invention (chromium, molybdenum, vanadium, and niobium) are ferrite stabilizers. High amounts of these ferrite stabilizers can lead to the presence of ferrite in the heat-treated microstructure. It has been discovered, however, that the presence of about 2 wt. % cobalt in the ,alloying system of the invention is a necessary and sufficient measure to eliminate ferrite in the heat-treated microstructure.

[0014] Finally, in order to obtain a desired combination of wear and corrosion resistance, along with good mechanical properties, such as bend fracture strength, toughness, and grindability, it is necessary to control closely the atomization process (to obtain fine spherical powder) and the hot isostatic parameters of the prealloyed powders as is well-known in the art. The alloy of the invention is to be preferably hot isostatically pressed at the temperature of 2150°F (±25°F) and the pressure of at least 14.5 ksi.

[0015] In accordance with the invention, there is provided a corrosion and wear resistant article produced by hot isostatic compaction of nitrogen gas atomized prealloyed powder particles within the following composition limits, in weight percent, carbon, 2.0 to 3.5, preferably 2.7 to 3.0; silicon 1.0 max.; chromium 12.0 to 16.0, preferably 13.5 to 14.5; molybdenum 2.0 to 5.0 preferably 3.0 to 4.0; vanadium 6.0 to 11.0, preferably 8.5 to 9.5; niobium 2.0 to 6.0, preferably 3.0 to 4.0; cobalt 1.5 to 5.0, preferably 2.0 to 3.0; nitrogen 0.05 to 0.30, preferably 0.10 to 0.20; and balance iron and incidental impurities.

[0016] Preferably, carbon is balanced with chromium, molybdenum, vanadium, and nitrogen in accordance with

$$C_{min} = 0.4 + 0.099\times(\%Cr - 11) + 0.063\times\%Mo + 0.177\times\%V + 0.13\times\%Nb - 0.85\times\%N$$

$$C_{max} = 0.6 + 0.099\times(\%Cr - 11) + 0.063\times\%Mo + 0.177\times\%V + 0.13\times\%Nb - 0.85\times\%N$$

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] **Figure 1** shows a vertical section of the Fe-C-Cr-Mo-V-Nb-N system at 14 wt % Cr, 3.5 wt % Mo, 9 wt % V, 3.5 wt % Nb, and 0.13 wt % N;

[0018] **Figure 2** is a vertical section of the Fe-C-Cr-Mo-V-Nb-Co-N system at 14 wt % Cr, 3.5 wt % Mo, 9 wt % V, 3.5 wt % Nb, 2 wt % Co, and 0.13 wt % N;

[0019] **Figure 3** shows the etched microstructure (magnification of 1500X) of the alloy of the invention (04-099) hardened from 2150°F in oil and tempered at 975°F for 2h+2h+2h; and

[0020] **Figure 4** shows the etched microstructure (magnification of 1500X) of the hardened alloy (04-100) with no cobalt present.

DESCRIPTION OF THE EMBODIMENTS

Chemical Compositions Tested

[0021] Table 1 gives the chemical compositions that were examined experimentally and that led to the alloy of the article of the invention that achieves an improved combination of corrosion and wear resistant properties. The reported alloys 03-192 through 04-099 are alloys in accordance with the invention.

[0022] All examined compositions were prepared using the Crucible Particle Metallurgy (CPM) technology. Prealloyed tool steel grades of the various reported chemical compositions were melted in a nitrogen atmosphere, atomized by nitrogen gas, and hot-isostatically-pressed (HIP) at the temperature of 2150°F and the pressure of 14.5 ksi for four hours.

[0023] With respect to the various alloying elements in the wear and corrosion resistant tool steel are concerned, the following applies.

[0024] Carbon is present in an amount of at least 2.0 %, while the maximum content of carbon may amount to 3.5 %, and preferably in the range of 2.7-3.0 %. It is important to carefully control the amount of carbon in order to obtain a desired combination of corrosion and wear resistance, as well as to avoid forming either ferrite or unduly large amounts of retained austenite during heat treatment. The carbon in the articles of the invention may preferably be balanced with the chromium, molybdenum, vanadium, and nitrogen contents of the alloy of the invention according to the following formulae:

$$C_{min} = 0.4 + 0.099\times(\%Cr - 11) + 0.063\times\%Mo + 0.177\times\%V + 0.13\times\%Nb - 0.85\times\%N$$

$$C_{max} = 0.6 + 0.099\times(\%Cr - 11) + 0.063\times\%Mo + 0.177\times\%V + 0.13\times\%Nb - 0.85\times\%N$$

[0025] **Nitrogen** is present in an amount of 0.05-0.30 %, and preferably in the range of 0.10-0.20 %. The effects of nitrogen in the alloy of the invention are rather similar to those of carbon. In tool steels, where carbon is always present, nitrogen forms carbonitrides with vanadium, niobium, tungsten, and molybdenum. Unlike carbon, nitrogen improves the corrosion resistance of the alloy of the invention when dissolved in the martensitic matrix.

[0026] **Silicon** may be present in an amount of up to 1 %, and preferably up to 0.5 %. Silicon functions to deoxidize the prealloyed materials during the melting phase of the gas-atomization process. In addition, silicon improves the tempering response. Excessive amounts of silicon are undesirable, however, as it decreases toughness and promotes the formation of ferrite in the microstructure.

[0027] **Manganese** may be present in an amount of up to 1 %, and preferably up to 0.5%. Manganese functions to control the negative effects of sulfur on hot workability. This is achieved through the precipitation of manganese sulfide. In addition, manganese improves hardenability and increases the solubility of nitrogen in the liquid prealloyed materials during the melting phase of the gas-atomization process. Excessive amounts of manganese are undesirable, however, as it can lead to the formation of unduly large amounts of retained austenite during the heat treatment.

[0028] **Chromium** is present in an amount of 12.0-16.0 %, and preferably in the range of 13.5-14.5 %. The main purpose of chromium is to increase the corrosion resistance, and, to a lesser degree, to increase hardenability and secondary-hardening response.

[0029] **Molybdenum** is present in an amount of 2.0-5.0 %, and preferably in the range of 3.0-4.0 %. Like chromium, molybdenum increases the corrosion resistance, hardenability, and secondary-hardening response of the alloy of the invention. Excessive amounts of molybdenum, however, reduce hot workability.

[0030] **Vanadium** is present in an amount of 6.0-11.0 %, and preferably in the range of 8.5-9.5 %. Vanadium is critically important for increasing wear resistance. This is achieved through the formation of vanadium-rich MC type primary carbonitrides.

[0031] **Niobium** is present in an amount of 2.0-6.0 %, and preferably in the range of 3.0-4.0 %. Every percent of niobium is equivalent to the amount of vanadium calculated as follows:

$$\%V = (50.9 / 92.9) \times \%Nb$$

where 50.9 and 92.9 are atomic weights of vanadium and niobium, respectively. Niobium and vanadium are equivalent elements when it comes to the wear resistance. However, these two elements do not have the same effect on the corrosion resistance. The presence of niobium decreases the solubility of chromium in MC primary carbides, i.e., niobium-vanadium-rich MC primary carbides contain a smaller amount of chromium compared to vanadium-rich MC primary carbides. This in turn increases the amount of "free" chromium in the matrix, which in turn increases the corrosion resistance.

[0032] To illustrate the effect of niobium on the alloy of the invention, Thermo-Calc software, coupled with TCFE3 steel thermodynamic database, was used to model two alloys that have the equivalent amount of vanadium; one with niobium (Fe-2.8C-14Cr-3.5Mo-9V-3.5Nb-2Co-0.13N) and the other one without niobium (Fe-2.8C-14Cr-3.5Mo-11V-2Co-0.13N). The two alloys have the same vanadium equivalency (11 % V). Thermodynamic calculations were performed for the following two austenitization temperatures: 2050°F and 2150°F. The results are given in Tables 2 and 3. The amount of "free" chromium in the matrix is higher in the alloy that contains niobium. Based on thermodynamic calculations, it has been discovered that the presence of niobium decreases the solubility of chromium in MC primary carbides (see Table 3), which in turn results in a higher level of "free" chromium in the matrix.

[0033] **Cobalt** is present in an amount of 1.5-5.0 %, and preferably in the range of 2.0-3.0 % in order to prevent the undesirable presence of ferrite (α) in the heat-treated microstructure of the alloy of the invention.

[0034]

Table 1. Chemical compositions that were experimentally examined as well as modeled with Thermo-Calc software.

Alloy	C	Cr	Mo	W	V	Nb	Co	N
02-354	1.64	16.89	2.85	2.78	-	3.66	5.25	0.206
02-355	1.77	16.85	2.85	2.78	-	3.66	5.23	0.207
02-356	1.88	16.87	2.86	2.79	-	3.66	5.23	0.205
02-357	1.90	17.00	2.91	2.69	-	3.68	5.34	0.183
02-358	2.14	17.05	2.92	2.69	-	3.68	5.34	0.182
02-359	2.33	17.08	2.92	2.70	-	3.68	5.35	0.182
03-192	2.61	14.23	3.02	-	8.10	3.08	1.95	0.157
03-193	2.66	14.23	3.02	-	8.10	3.08	1.95	0.157
03-194	2.71	14.23	3.02	-	8.10	3.08	1.95	0.157
03-195	2.81	14.23	3.02	-	8.10	3.08	1.95	0.157
03-199	2.49	14.20	2.97	-	7.78	3.13	1.99	0.115
03-200	2.59	14.20	2.97	-	7.78	3.13	1.99	0.115
03-201	2.64	14.20	2.97	-	7.78	3.13	1.99	0.115
04-098	2.76	13.76	3.49	-	8.98	3.50	1.96	0.127
04-099	2.83	13.76	3.49	-	8.99	3.51	1.96	0.134
04-100	2.68	13.89	3.35	-	9.03	3.42	-	0.125

[0035]

Table 2. Chemical composition of austenitic matrix at 2050°F and 2150°F.

Alloy	[°F]	Chemical Composition of Austenitic Matrix [wt. %]							
		C	Cr	Mo	V	Nb	Co	N	Fe
9V-3.5Nb	2050	0.42	13.39	2.45	1.19	0.008	2.48	0.0042	bal.
11V-0Nb		0.43	12.55	2.29	1.43	-	2.46	0.0024	bal.
9V-3.5Nb	2150	0.55	13.95	2.60	1.45	0.012	2.45	0.0062	bal.
11V-0Nb		0.56	13.08	2.46	1.75	-	2.42	0.0038	bal.

[0036]

Table 3. Chemical composition of MC primary carbides at 2050°F and 2150°F.

Alloy	[°F]	Chemical Composition of MC Primary Carbides [at. %]							
		C	Cr	Mo	V	Nb	Co	N	Fe
9V-3.5Nb	2050	43.19	5.12	3.62	36.41	9.12	0.0028	2.19	0.35
11V-0Nb		41.95	7.44	3.84	43.84	-	0.0036	2.18	0.75
9V-3.5Nb	2150	43.15	5.86	3.33	35.91	9.09	0.0039	2.16	0.49
11V-0Nb		41.82	8.44	3.49	43.06	-	0.0049	2.15	1.05

[0037]

Table 4. Heat treatment response of alloys hardened from 2150°F in oil and tempered for 2h+2h+2h.

Bar No.	Tempering Temperature							
	500	750	975	1000	1025	1050	1100	1200
04-098	59.4	59.7	62.5	60.7	59.7	58.3	53.1	46.7
04-099	60.1	60.7	63.5	61.4	60.7	58.6	53.3	47.4
04-100	49.3	51.8	54.2	51.9	50.8	49.0	47.0	40.2
S90V	58.5	60.5		60.5				

[0038]

Table 5. Pin-abrasion wear resistance of alloys.

Alloy	Austenitization Temperature	Temper	Hardness [HRC]	Pin Abrasion
04-098	2150°F	500°F	59.5	49.5 mg
		975°F	62.5	33.7 mg
04-099	2150°F	500°F	60.0	45.4 mg
		975°F	63.5	29.4 mg
04-100	2150°F	500°F	49.5	65.0 mg
		975°F	54.0	49.1 mg
CPM S90V	2150°F	500°F	59.0	52.0 mg
		975°F	61.5	37.3 mg
Elmax	1975°F	500°F	57.0	70.0 mg
		975°F		
M390	2100°F	500°F	58.0	62.0 mg
		975°F		
X235	2100°F	500°F		
		986°F/1022°F	59.5	52.5

[0039]

Table 6. Calculated matrix chemical compositions of corrosion and wear resistant tool steels.

Alloy	[°F]	Chemical Composition of Austenitic Matrix [wt. %]								**PRE**
		C	Cr	Mo	V	W	Nb	Co	N	
440C	1900	0.43	11.57	0.06	-	-	-	-	0.065	**12.81**
10V-12	2100	0.49	11.22	0.82	1.69	-	-	-	0.003	**13.97**
S90V	2100	0.54	12.33	0.75	1.71	-	-	-	0.002	**14.84**
Elmax	2100	0.57	12.7	0.92	1.17	-	-	-	0.021	**16.08**
S30V	2000	0.46	10.92	1.71	1.03	-	-	-	0.005	**16.65**
X235	2100	0.52	13.97	0.91	1.15	-	0.01	-	0.013	**17.17**
M390	2100	0.52	13.79	0.93	1.31	0.55	-	-	0.025	**18.16**
MPL-1	2100	0.54	12.64	2.37	1.67	-	-	-	0.004	**20.52**
S110V	2100	0.48	13.66	2.53	1.31	-	0.01	2.47	0.005	**22.09**

[0040]

Table 7. Pitting potentials (E_{pit}) in 1 %NaCl aqueous solution.

Alloy	PRE	E_{pit} [mV] vs. SCE			
		500°F	750°F	975°F	1025°F
440C	12.81	-140	-249	-355	-321
Anval 10V-12	13.97	9	38	-180	-138
CPM S90V	14.84	59	-17	-176	-183
Elmax	16.08	213	243	-211	-216
CPM S30V	16.65	79	-2	-240	-236
X235	17.17	97	138	-164	-282
M390	18.16	160	-121	-170	-179
MPL-1	20.52	-72	15	-94	-100
04-099	22.09	403	272	-17	-71

Microstructure

[0041] Figure 3 shows the microstructure of an alloy of the invention (alloy number 04-099). The alloy was hardened from 2150°F in oil and tempered at 975°F for 2h+2h+2h. After etching with Vilella's reagent for 90 seconds, the total volume of primary carbides was measured to be 21.7 percent, the standard deviation being 0.7 percent.

[0042] During the designing stage, the thermodynamics calculations performed on the Fe-2.8C-14Cr-3.5Mo-9V-3.5Nb-0.13N alloy indicated the presence of ferrite (α) when the alloy is austenitized at a temperature that is below 2156°F (see Figure 1). The γ+MC+M_7C_3 field needed to be expanded, or, in other words, the line that divides the γ+MC+M_7C_3 field and the α+γ+ MC+M_7C_3 field needed to be shifted toward the left-hand side of the diagram in order to prevent the presence of ferrite in the heat-treated microstructure.

[0043] Additional thermodynamic calculations indicated that the addition of about 2 wt % of cobalt would sufficiently extend the γ+ MC+M_7C_3 field, eliminating the possibility of the ferrite presence in the hardened condition (see Figure 2).

[0044] The first set of compositions examined experimentally was centered around the Fe-C-17Cr-2.5Mo-2.5W-3.5Nb-5Co-0.2N system (alloys 02-354 through 02-359; see Table 1). The problem with this alloying system was retained austenite that was difficult to transform into martensite even after sub-zero treatments.

[0045] The second set of compositions examined experimentally was centered around the Fe-C-14Cr-3Mo-8V-3Nb-2Co-N system (alloys 03-192 through 03-195 and 03-199 through 03-201). The levels of carbon balance tested ranged from -0.20 to +0.20, and were calculated using the following formula:

$$C_{bal} = \%C - [0.4 + 0.099\times(\%Cr - 11) + 0.063\times\%Mo + 0.177\times\%V + 0.13\times\%Nb - 0.85\times\%N]$$

[0046] It is a well established fact that the amount of carbon present in the steel has the most profound effect on the properties of any corrosion and wear resistant tool steel grade. The amount of carbon has a direct effect on the hardness, the wear resistance, and the corrosion resistance of wear and corrosion resistant tool steel. For a given chemical composition of the steel, the carbon balances were targeted to be close to zero (±0.2%).

[0047] The alloys that are based on the Fe-C-14Cr-3Mo-8V-3Nb-2CoN system exhibited better hardness response, better corrosion resistance, and marginally better wear characteristics when compared to other corrosion and wear resistant martensitic tool steels.

[0048] In order to examine whether the wear and corrosion resistance of the second set of compositions could be further improved, an additional set of compositions centered around the Fe-2.8C-14Cr-3.5Mo-9V-3.5Nb-2Co-0.13N system was manufactured and experimentally examined (alloys 04-098 through 04-100). The tests showed that the alloys of the third set exhibited better heat treat response (see Table 4) and better wear characteristics (see Table 5) compared to CPM S90V. The alloy of the invention also has better corrosion resistance (see Table 6) compared to other widely used corrosion and wear resistant tool steels (see Table 6).

Influence of Cobalt on the Microstructure

[0049] An alloy (04-100) was prepared specifically to demonstrate the influence of cobalt and the necessity to use it in the alloy of the invention. Both thermodynamic calculations and experimental results clearly indicated that the Fe-2.8C-14Cr-3.5Mo-9V-3.5Nb-0.13N system has to contain at least 1.5 wt. pct. Co, if ferrite is to be eliminated from the heat treated microstructure. The major alloying elements in the alloy of the invention (chromium, molybdenum, vanadium, and niobium) are all ferrite forming elements. The presence of ferrite, as well as a poor heat treat response, was indeed observed in the alloy that contained no cobalt (04-100).

[0050] As predicted by thermodynamic calculations, the matrix of the heat treated alloy that contains no cobalt (alloy number 04-100) has some ferrite present (see Figure 4), which resulted in poor heat-treat response for the alloy (less than 54 HRC). The other two alloys of the third set that contain about 2 wt. pct. of cobalt (04-098 and 04-099) developed desired heat-treated responses (62.5 HRC and 63.5 HRC, respectively) as well as microstructures that consist of V-Nb-rich MC and Cr-rich M_7C_3 primary carbides in the matrix of tempered martensite.

Corrosion Resistance

[0051] **Pitting Resistance Equivalent Number:** The pitting resistance equivalent number (PRE) is useful for evaluating the resistance of an austenitic stainless steels to pitting and crevice corrosion. The PRE is calculated using the following equation:

$$Cr + 3.3(Mo + 0.5W) + 16N$$

[0052] Generally, the PRE is calculated using the bulk chemical composition. However, the alloys disclosed herein contain high amounts of primary carbides that deplete the matrix of some of the necessary elements needed for corrosion resistance. Therefore, the PRE of these alloys was calculated using an estimated matrix composition as determined by Thermo-Calc software (see Table 6). The alloys are listed by increasing PRE values.

[0053] Based on the matrix composition, the invention alloy (04-099) has the highest PRE even though it does not have the highest matrix chromium content. The PRE of this alloy (04-099) is even higher than those alloys with higher bulk chromium contents such as MPL-1, X235, M390 and Elmax. Since the matrix chromium content of these alloys is similar, the high PRE of the invention alloy is due to its high contents of chromium and molybdenum in the matrix. This is because 30-47.5% of the chromium in the high chromium alloys is used in the formation of the primary carbides in these materials. Only about 2.5% of the chromium in the invention alloy is used in the formation of the primary carbides thereby keeping most of the chromium in the matrix to aide in corrosion resistance. More chromium is present in the matrix in the invention alloy due to the presence of niobium and vanadium which preferentially form more stable MC type carbides compared to the M_7C_3 type (chromium rich) carbides.

[0054] **Corrosion Tests:** Potentiodynamic tests were used to evaluate the pitting resistance of the invention alloy and of commercially available wear and corrosion resistant alloys. The tests were conducted in an aqueous solution containing 1% NaCl. The tests were conducted by varying the potential from -0.8V vs. SCE (saturated calomel reference electrode) to at most 0.5V at a scan rate of 0.2mV/sec. Two graphite rods were used as the counter electrodes. The test solution was purged with nitrogen gas for at least 20 minutes before testing each specimen. The pitting resistance of the alloys is defined by the pitting potential (E_{pit}) obtained from a potentiodynamic curve. The more positive the pitting potential, the more resistant the alloy is to pitting. Prior to each test, the specimen was ground down by 600 grit paper. The specimen was then washed and dried with alcohol.

[0055] Depending on the application, the wear and corrosion resistant alloys are given different heat treatments. If corrosion resistance is of utmost concern, the alloy is typically tempered at or below 750°F, which allows more of the chromium to stay in the matrix by minimizing the precipitation of secondary carbides. If hardness and wear resistance is the primary concern, then the alloys are typically tempered at 950°F and above to allow for secondary hardening effects to take place. Therefore, each alloy was tempered at 500°F, 750°F, 975°F and 1025°F.

[0056] **Corrosion Resistance Results:** The pitting potential (E_{pit}) for each alloy at each tempering temperature is given in Table 7. The results show that the invention alloy (04-099) with the highest PRE also has the highest resistance to pitting at aii tempering temperatures. The E_{pit} for the invention alloy is almost 50% higher that that of the next closest alloy, Elmax, at a tempering temperature of 500°F. In general, the alloys with 18-20% bulk chromium content, i.e., Elmax, M390 and X235, have mediocre pitting resistance compared to the invention alloy at all tempering temperatures. The alloy with the highest bulk chromium content actually has one of the lowest pitting potentials at the low tempering temperatures. These results indicate that the total chromium content is not an indicator of how resistant the material is to corrosion.

[0057] The matrix compositions of X235 and the alloy of the invention are similar. However, the pitting resistance of these two alloys is significantly different. This difference in pitting resistance is attributed to the higher molybdenum content of the invention alloy. The cobalt in the invention alloy is not expected to significantly affect the pitting resistance of the alloy of the invention.

Heat Treatment Response

[0058] When compared with CPM S90V, the alloys of the invention (04-098 and 04-099) offer better heat-treatment response—approximately 1.5-2.0 HRC higher for the same heat treatment. The heat-treatment responses of the alloys of the invention and CPM S90V are given in Table 4.

Abrasive Wear Resistance

[0059] All the pin-abrasion wear resistance test specimens were austenitized at 2150°F for 10 minutes, quenched in oil, and then tempered at either 500°F (for maximum corrosion resistance) or 975°F (for maximum secondary-hardening response) for 2h+2h+2h. The results are given in Table 5. The pin-abrasion wear resistance of other corrosion and wear resistant martensitic tool steels is included as well for comparison purposes.

[0060] All element amounts are reported in weight percent.

Claims

1. A corrosion and wear resistant tool steel article produced by hot isostatic compaction of nitrogen gas atomized prealloyed powder particles consisting essentially of, in weight percent:

    C: 2.0 - 3.5;
    Si: 1.0 max.;
    Mn: 1.0 max.;
    Cr: 12.0-16.0;
    Mo: 2.0-5.0;
    V: 6.0-11.0;
    Nb: 2.0-6.0;
    Co: 1.5-5.0;
    N: 0.05-0.30;

    and the balance is essentially iron and incidental impurities.

2. A corrosion and wear resistant tool steel article produced by hot isostatic compaction of nitrogen gas atomized

prealloyed powder particles consisting essentially of, in weight percent:

C: 2.7 - 3.0;
Si: 0.50 max.;
Mn: 0.50 max.;
Cr: 13.5-14.5;
Mo: 3.0-4.0;
V: 8.5-9.5;
Nb: 3.0-4.0;
Co: 2.0-3.0;
N: 0.10-0.20;
and the balance is essentially iron and incidental impurities.

3. The article of claim 1 or claim 2, wherein carbon is balanced with chromium, molybdenum, vanadium, and nitrogen in accordance with:

$$C_{min} = 0.4 + 0.099\times(\%Cr - 11) + 0.063\times\%Mo + 0.177\times\%V + 0.13\times\%Nb - 0.85\times\%N$$

$$C_{max} = 0.6 + 0.099\times(\%Cr - 11) + 0.063\times\%Mo + 0.177\times\%V + 0.13\times\%Nb - 0.85\times\%N.$$

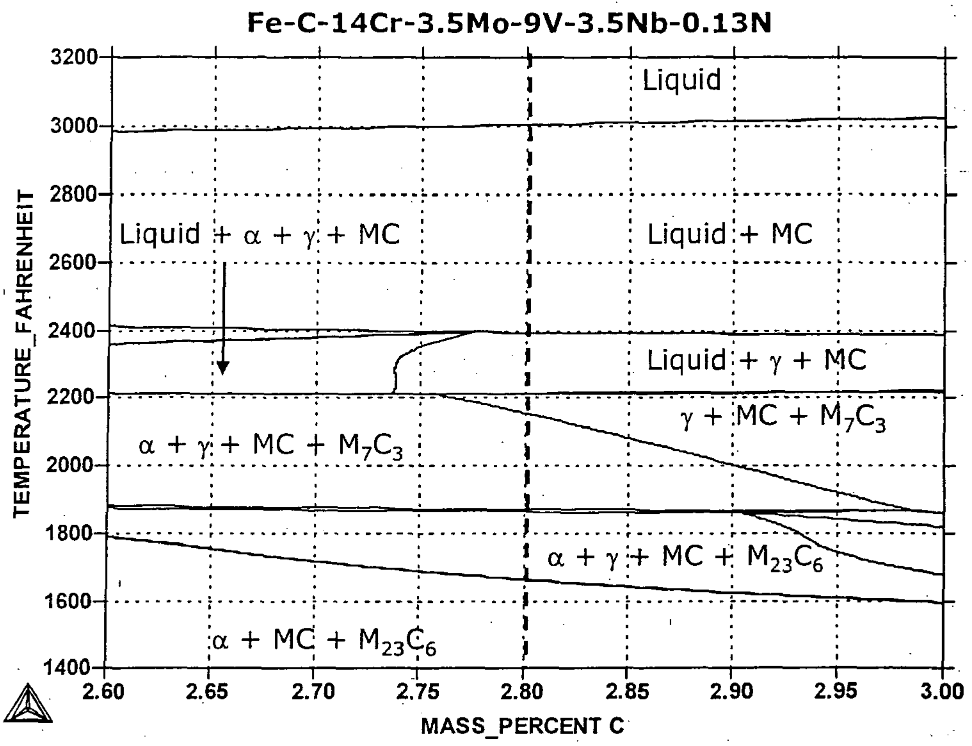

Figure 1. Vertical section of the Fe-C-Cr-Mo-V-Nb-N system at 14 wt % Cr, 3.5 wt % Mo, 9 wt % V, 3.5 wt % Nb, and 0.13 wt % N.

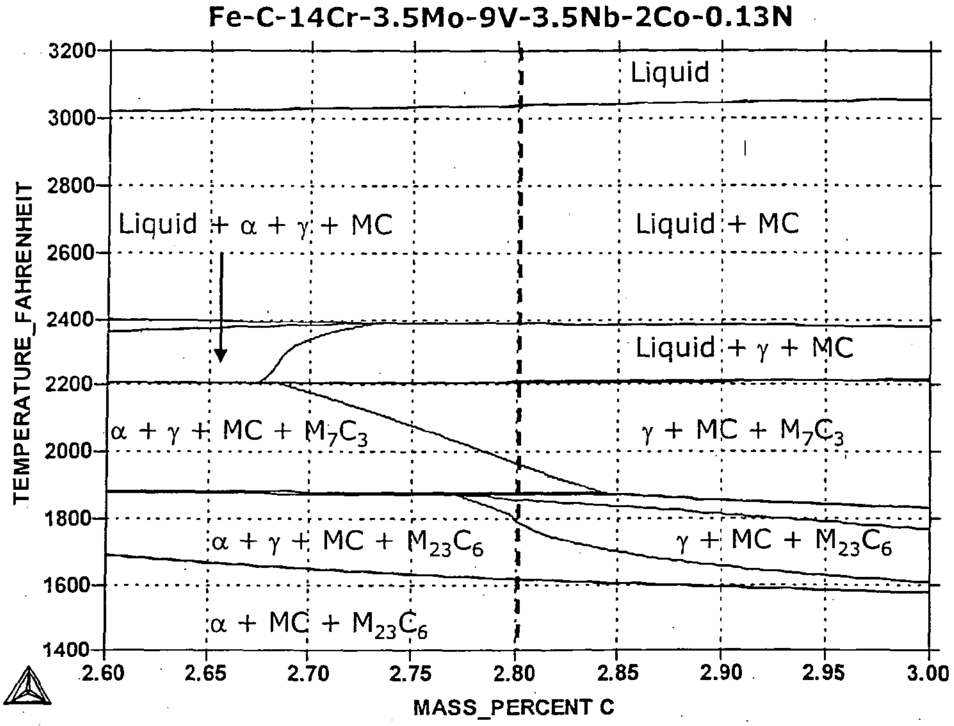

Figure 2. Vertical section of the Fe-C-Cr-Mo-V-Nb-N system at 14 wt % Cr, 3.5 wt % Mo, 9 wt % V, 3.5 wt % Nb, 2 wt Co, and 0.13 wt % N.

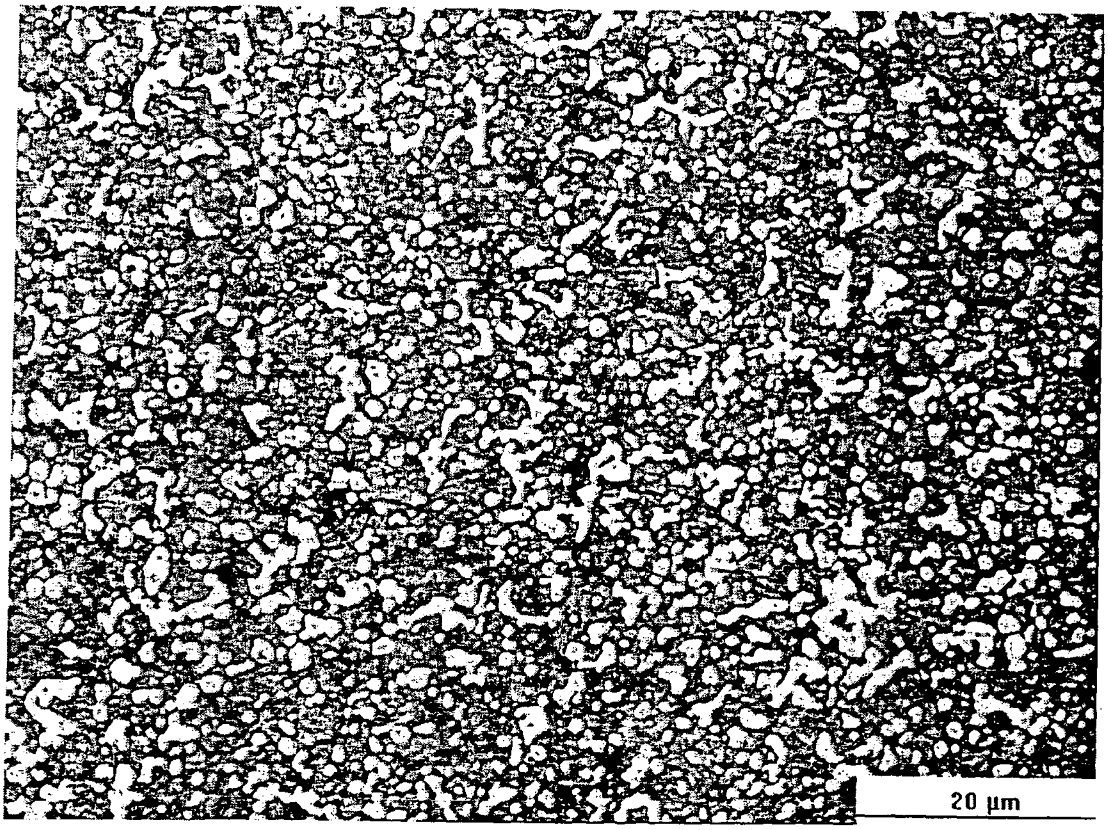

Figure 3. Microstructure of the alloy of the invention (04-099) hardened from 2150°F in oil and tempered at 975°F for 2h+2h+2h. Etched with Vilella's reagent for 90 seconds.

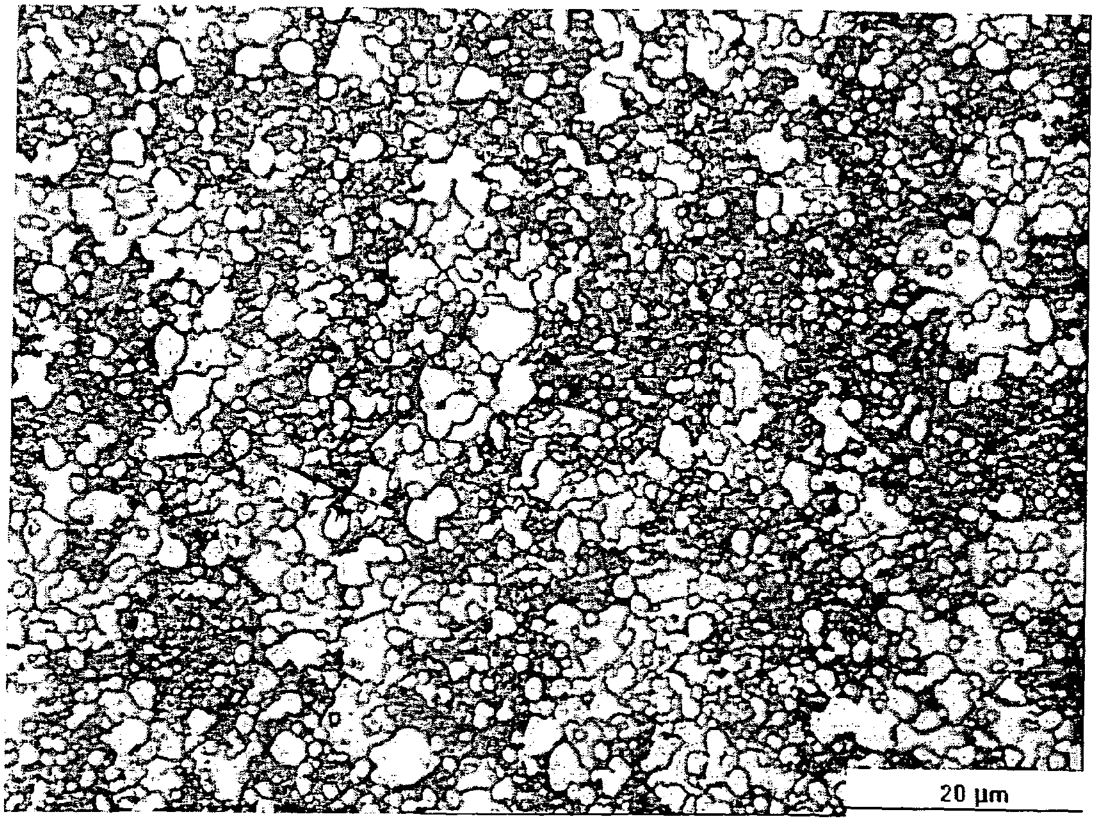

Figure 4. Microstructure of the alloy of the invention with no cobalt present (04-100). The alloy was hardened from 2150°F in oil and tempered at 975°F for 2h+2h+2h. Etched with Vilella's reagent for 90 seconds. Note the presence of ferrite in the matrix.

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 468 (C-1244), 31 August 1994 (1994-08-31) -& JP 06 145901 A (KAWASAKI STEEL CORP), 27 May 1994 (1994-05-27) * abstract * -----	1,3 2	INV. C22C38/36 C22C38/22 C22C38/24 C22C38/26 C22C38/30 C22C33/02
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 12, 3 January 2001 (2001-01-03) -& JP 2000 239779 A (KAWASAKI STEEL CORP), 5 September 2000 (2000-09-05) * abstract * -----	1-3	
Y	US 2004/094239 A1 (SANDBERG ODD ET AL) 20 May 2004 (2004-05-20) * claims 1-23 * * paragraph [0001] - paragraph [0020] * -----	1-3	
A	EP 0 559 899 A (KAWASAKI STEEL CORPORATION) 15 September 1993 (1993-09-15) * claims 1-6 * * tables 1,7 * * page 4, line 34 - page 6, line 29 * -----	1-3	TECHNICAL FIELDS SEARCHED (IPC) C22C
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 420 (C-1093), 5 August 1993 (1993-08-05) -& JP 05 086435 A (HITACHI METALS LTD), 6 April 1993 (1993-04-06) * abstract * ----- -/--	1-3	

The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
The Hague	24 July 2006	Vlassi, E

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Application Number
EP 06 25 2443

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 05, 31 May 1996 (1996-05-31) -& JP 08 027543 A (HONDA MOTOR CO LTD), 30 January 1996 (1996-01-30) * abstract * -----	1-3	
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 523 (C-657), 21 November 1989 (1989-11-21) -& JP 01 212737 A (SUMITOMO ELECTRIC IND LTD), 25 August 1989 (1989-08-25) * abstract * -----	1-3	
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 232 (C-437), 29 July 1987 (1987-07-29) -& JP 62 047451 A (HITACHI LTD), 2 March 1987 (1987-03-02) * abstract * -----	1-3	TECHNICAL FIELDS SEARCHED (IPC)
A	US 6 506 227 B1 (TORNBERG CLAES) 14 January 2003 (2003-01-14) * claims 1-26 * * column 1, line 5 - column 3, line 9 * -----	1-3	
A	DE 199 24 515 A1 (EDELSTAHL WITTEN-KREFELD GMBH) 30 November 2000 (2000-11-30) * claims 1-11 * * table 1 * -----	1-3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	24 July 2006	Vlassi, E

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24-07-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 06145901 A	27-05-1994	JP 2974226 B2	10-11-1999
JP 2000239779 A	05-09-2000	NONE	
US 2004094239 A1	20-05-2004	BR 0207667 A	27-04-2004
		CA 2436423 A1	12-09-2002
		CN 1492939 A	28-04-2004
		EP 1366204 A1	03-12-2003
		JP 2004523656 T	05-08-2004
		SE 518678 C2	05-11-2002
		SE 0100737 A	07-09-2002
		WO 02070769 A1	12-09-2002
EP 0559899 A	15-09-1993	DE 69227504 D1	10-12-1998
		DE 69227504 T2	08-04-1999
		EP 0562114 A1	29-09-1993
		ES 2124728 T3	16-02-1999
		WO 9305192 A1	18-03-1993
		WO 9305193 A1	18-03-1993
		KR 9605598 B1	26-04-1996
		US 5316596 A	31-05-1994
JP 05086435 A	06-04-1993	NONE	
JP 08027543 A	30-01-1996	NONE	
JP 01212737 A	25-08-1989	NONE	
JP 62047451 A	02-03-1987	NONE	
US 6506227 B1	14-01-2003	AT 411580 B	25-03-2004
		AT 5852001 A	15-08-2003
		EP 1249510 A2	16-10-2002
DE 19924515 A1	30-11-2000	WO 0073527 A1	07-12-2000
		EP 1185719 A1	13-03-2002

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