



(11) **EP 1 775 351 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
18.04.2007 Bulletin 2007/16

(51) Int Cl.:
C22C 33/00 (2006.01) C22C 38/00 (2006.01)

(21) Application number: **06255276.5**

(22) Date of filing: **13.10.2006**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**
Designated Extension States:
AL BA HR MK YU

(30) Priority: **14.10.2005 US 251308**

(71) Applicant: **Alloy Technology Solutions, Inc.
Marinette WI 54143-0198 (US)**

(72) Inventor: **Liang, Xuecheng
Green Bay, Wisconsin 54313 (US)**

(74) Representative: **Setna, Rohan P.
Boult Wade Tennant
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)**

(54) **Acid resistant austenitic alloy for valve seat insert**

(57) A high-carbon austenitic iron-base alloy for wear and corrosion resistant applications is developed for valve seat insert applications when corrosion resistance is required. The alloy comprises 1.8-2.8 wt% carbon, 0.5-3.5 wt% silicon, 12.0-22.0 wt% chromium, less than 1.5 wt% manganese, 2.0-16.0 wt% molybdenum and

tungsten combined, 0.05-4.0 wt% niobium and vanadium combined, 0-1.0 wt% titanium, 0.01-0.2 wt% aluminum, 12-25 wt% nickel, 0.05-3.0 wt% copper, and the balance being iron and a small amount of impurities.

EP 1 775 351 A1

Description**BACKGROUND OF THE INVENTION****Technical Field**

[0001] This invention relates to an acid corrosion resistant and wear resistant austenitic iron-base alloy that possesses excellent resistance to sulfuric acid and is superior to high speed steels for many applications where both sulfuric acid corrosion and wear occur simultaneously. This invention further relates to such a corrosion resistant alloy useful for making valve seat inserts used in internal combustion engines with exhaust gas recirculation (EGR) system.

Description of Related Art

[0002] Internal combustion engines equipped with EGR systems require intake valve seat insert materials with excellent corrosion resistance due to formation of sulfuric acid in the intake insert area when sulfur oxide that comes from diesel fuel after combustion meets with moisture from incoming air. Sulfur content in diesel fuel seems relatively low; however, the concentration of sulfuric acid will likely increase with engine running time as combustion deposits from exhaust gas accumulated around the inner wall area of an intake insert will absorb more sulfuric acid. Severe corrosion can occur on intake valve seat inserts made from M2 tool steel once the amount of high concentration acid is enough. Cobalt-base alloy Stellite® 3 possess excellent corrosion resistance and good wear resistance under diesel engine intake working condition and therefore this cobalt alloy is normally the choice as the intake insert material to ensure the valve train service life in EGR device equipped diesel engines. (®Registered Trademarks of Deloro Stellite Company Inc.)

[0003] Traditionally, modified M2 tool steel and Silichrome XB are two common material choices for making diesel engine intake valve seat inserts. In broad ranges, modified M2 tool steel comprises 1.2-1.5 wt% carbon, 0.3-0.5 wt% silicon, 0.3-0.6 wt% manganese, 6.0-7.0 wt% molybdenum, 3.5-4.3 wt% chromium, 5.0-6.0 wt% tungsten, up to 1.0 wt% nickel, and the balance being iron. Modified Silichrome XB contains 1.3-1.8 wt% carbon, 1.9-2.6 wt% silicon, 0.2-0.6 wt% manganese, 19.0-21.0 wt% chromium, 1.0-1.6 wt% nickel, and the balance being iron. Another common iron-base alloy for intake valve seat inserts contains 1.8-2.3 wt% carbon, 1.8-2.1 wt% silicon, 0.2-0.6 wt% manganese, 2.0-2.5 wt% molybdenum, 33.0-35.0 wt% chromium, up to 1.0 wt% nickel, and the balance being substantially iron. There are also several high chromium-type iron-base alloys available for making intake valve seat inserts.

[0004] U.S. Patent No. 6,916,444 discloses an iron-base alloy containing a large amount of residual austenite for intake valve seat insert material. This alloy contains 2.0-4.0% carbon, 3.0-9.0% chromium, 0.0-4.0% manganese, 5.0-15.0% molybdenum, 0.0-6.0% tungsten, 0.0-6.0% vanadium, 0.0-4.0% niobium, 7.0-15.0% nickel, 0.0-6.0% cobalt, and the balance being iron with impurities. U.S. Patent No. 6,436,338 discloses a corrosion resistant iron-base alloy for diesel engine valve seat insert applications. The alloy is composed of carbon 1.1-1.4%, chromium 11-14.5%, molybdenum 4.75-6.25%, tungsten 3.5-4.5%, cobalt 0-3%, niobium 1.5-2.5%, vanadium 1-1.75%, copper 0-2.5%, silicon 0-1%, nickel 0-0.8%, iron being the balance with impurities. U.S. Patent No. 6,866,816 discloses an austenitic type iron-base alloy with good corrosion resistance. The chemical composition of the alloy is 0.7-2.4% carbon, 1.5-4.0% silicon, 5.0-9.0% chromium, less than 6.0% manganese, 5.0-20.0% molybdenum and tungsten, the total of vanadium and niobium 0-4.0%, titanium 0-1.5%, aluminum 0.01-0.5%, nickel 12.0-25.0%, copper 0-3.0%, and at least 45.0% iron. However, more severe corrosion conditions in some engines with high sulfur fuel and high humidity demands materials with corrosion resistance much better than the above iron-base alloys.

[0005] High carbon and high chromium type nickel-base alloys normally do not exhibit good wear resistance under intake valve seat insert working conditions due to lack of combustion deposits and insufficient amount of metal oxides to protect the valve seat insert from direct metal-to-metal wear. Eatonite 2 is one example of the nickel-base alloys used for making exhaust valve seat inserts, which contains 2.0-2.8 wt% carbon, up to 1.0 wt% silicon, 27.0-31.0 wt% chromium, 14.0-16.0 wt% tungsten, up to 8.0 wt% iron, and the balance being essentially nickel. Eatonite is a trademark of Eaton Corporation. Several similar nickel-base alloys with added iron and/or cobalt are also available for exhaust valve seat inserts. U.S. Patent No. 6,200,688 discloses high silicon and high iron-type nickel-base alloy used as material for valve seat inserts. These nickel-base alloys may possibly be used in EGR engines only when the wear rate of intake insert is moderate.

[0006] Wear resistant cobalt-base alloys are another type of materials used in the industry, and the most commonly used ones are Stellite® 3 and Tribaloy® T-400 for more demanding applications. As disclosed in U.S. Patent Nos. 3,257,178 and 3,410,732, Tribaloy® T400 contains 2.0-2.6 wt% silicon, 7.5-8.5 wt% chromium, 26.5-29.5 wt% molybdenum, up to 0.08 wt% carbon, up to 1.50 wt% nickel, up to 1.5 wt% iron, and the balance being essentially cobalt. Stellite® 3 contains 2.3-2.7 wt% carbon, 11.0-14.0 wt% tungsten, 29.0-32.0 wt% chromium, up to 3.0 wt% nickel, up to 3.0 wt% iron, and the balance being cobalt. The above cobalt-base alloys possess both excellent corrosion and wear resistance. However, the cost of these cobalt-base alloys only allows these alloys to be used in limited applications.

(®Registered Trademarks of Deloro Stellite Company Inc.) Austenitic iron-base valve alloys or valve facing alloys may also be classified-into the same group of materials. U.S. Patent No. 4,122,817 discloses an austenitic iron-base alloy with good wear resistance, PbO corrosion and oxidation resistance. The alloy contains 1.4-2.0 wt% carbon, 4.0-6.0 wt% molybdenum, 0.1 to 1.0 wt% silicon, 8.0-13.0 wt% nickel, 20.0-26.0 wt% chromium, 0-3.0 wt% manganese, with the balance being iron. U.S. Patent No. 4,929,419 discloses a heat, corrosion and wear resistant austenitic steel for internal combustion exhaust valves, which contains 0.35-1.5 wt% carbon, 3.0-10.0 wt% manganese, 18.0-28.0 wt% chromium, 3.0-10.0 wt% nickel, up to 2.0 wt% silicon, up to 0.1 wt% phosphorus, up to 0.05 wt% sulfur, up to 10.0 wt% molybdenum, up to 4.0 wt% vanadium, up to 8.0 wt% tungsten, up to 1.0 wt% niobium, up to 0.03 wt% boron, and the balance being essentially iron.

BRIEF SUMMARY OF THE INVENTION

[0007] A new austenitic iron-base alloy has been invented that possess corrosion resistance close to Stellite 3 under diluted hot sulfuric acid condition. The cost of the alloy is significantly lower than cobalt-base alloys, such as Stellite® and Tribaloy®. In one aspect, the present invention is an alloy with the following composition:

Element	wt. %
Carbon	1.8-2.8
Silicon	0.5-3.5
Chromium	12.0-22.0
Molybdenum and tungsten combined	2.0-16.0
Nickel	12.0-25.0
Niobium and vanadium combined	0.05-4.0
Titanium	0-1.0
Aluminum	0.01-0.2
Copper	0.05-3.0
Iron and impurities	Balance

[0008] In another aspect of the invention, metal components are either made of the alloy, such as by casting, or by the powder metallurgy method by forming from a powder and sintering. Furthermore, the alloy can be used to hardface the components as the protective coating.

[0009] It is the object of this invention to develop an austenitic iron-base alloy with excellent corrosion resistance to meet the specific demand from more severe corrosion conditions in diesel engines with EGR systems.

[0010] It is another object of this invention to develop a corrosion resistant iron-base alloy with good wear resistance.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Numerous experiments have been accomplished in order to achieve the above objectives. Alloys with excellent corrosion resistance under static immersion type test may perform poorly under cyclic heating corrosion because of different corrosion behaviors at high temperature and the possible influence of oxidation to the corrosion process. The high temperature cyclic corrosion tester provides a tool to study corrosion behavior with the influence of oxidation under high temperature condition. According to our studies, a number of alloy elements can affect corrosion and hardness of the alloy, where it is preferred to have a minimum hardness of 34.0 HRC in order to achieve good wear resistance in the inventive austenitic alloy. However, the austenitic alloy can become too brittle when the hardness of the alloy exceeds 54.0 HRC due to formation of intermetallic compounds like sigma phase from excessive amount of alloy elements. It is relatively easier to achieve enough corrosion resistance with higher chromium and nickel contents under low carbon content. In stainless steels, like AISI 300 series, carbon content is controlled to a minimum level in order to reduce both chromium content tied with carbon and carbide/matrix boundaries for better corrosion resistance. Unfortunately valve seat insert alloys almost always have much higher carbon content than corrosion resistant stainless steels because a large volume fraction of alloy carbides is mandatory for higher hardness and better wear resistance in wear resistant alloys using alloy carbides as primary hard phases, which is contrary to the high corrosion resistance requirement. U.S. Patent No. 6,866,816 discloses an austenitic alloy using low to medium chromium content and high molybdenum with about 1.6 wt% carbon to achieve good corrosion resistance and wear resistance. To obtain an even higher corrosion resistance, much higher chromium content is used in the present inventive alloy with a higher carbon content to form more alloy carbides in order to compensate for the reduction of hardness and wear resistance due to higher chromium content. Unlike U.S. Patent No. 6,866,816, in which high contents of refractory alloy elements, like molybdenum and

tungsten, are used for higher corrosion resistance and higher hardness, high refractory alloy element contents can cause brittleness problem in the present inventive alloys when these refractory alloy elements combine with chromium, silicon and other alloy elements to form harmful intermetallic phases. Other different approaches need to be tested in order to increase the hardness of the current high chromium type inventive alloy. Through many experimental tests it has been found that the hardness of the current inventive alloy can reach to the hardness of the alloy disclosed in U.S. Patent No. 6,866,816 when carbon is between 2.3-2.7 wt%, chromium 16.0-20.0 wt%, silicon 0.5-3.0 wt%, a combination of tungsten and molybdenum 3.0-7.0 wt% (preferably all tungsten), nickel 14.0-18.0 wt%, copper 1.0-2.0 wt%, vanadium 0.02-3.0 wt%, niobium 0.02-3.0 wt% (with the combination of vanadium and niobium being 0.05-4.0 wt%), aluminum 0.03-0.06 wt%, and the balance being iron with other inevitable impurities. Preferably the iron content will be at least 50 wt%.

EXAMPLES

[0012] Chemical compositions of all samples are given in Table 1. These alloy samples were prepared in a 60 pounds industry frequency induction furnace by conventional atmosphere melting process, and the corrosion and hardness samples were cast into shell molds. The comparative alloy samples have compositions outside the scope of this invention. There are also two commercial alloys Stellite 3 and M2 listed in the table as comparative alloys.

[0013] Ring samples with 45 mm outer diameter, 32 mm inner diameter and 5 mm thickness were used as hardness samples and the hardness values of all samples were obtained using a Rockwell C hardness tester.

[0014] A high temperature cyclic corrosion tester was built to simulate sulfuric acid corrosion at high temperature. The new corrosion tester provides a better corrosion measurement method than the traditional static immersion corrosion test, as both oxidation and high temperature are also important factors contributing to the corrosion process in the intake insert working environment.

[0015] The high temperature cyclic corrosion test rig is composed of a heating coil, an air cylinder, a sample with its holder, a control unit, and an acid solution container. First, the air cylinder lifts the sample up into the heating coil to heat the specimen. The sample is held inside the coil for about 22 seconds so that the specimen temperature reaches about 300 °F. Then the air cylinder moves the heated sample down into the sulfuric acid solution container, and the cycle continues to repeat. All acid solution left on the sample is vaporized when the sample is heated inside the heating coil. Therefore both corrosion and oxidation occur in this process, which is closer to the actual insert corrosion in EGR equipped engines than the static acid immersion test. Corrosion also occurs when the heated specimen is pushed into the sulfuric acid solution container. The testing time is one hour. The sample dimensions are 6.35 mm in diameter and 31.75 mm in length. About 12.7 mm length of the sample is immersed into the solution. 0.25 vol. %, 0.50 vol. %, and 1.0 vol. % sulfuric acid solutions are used for each sample. A precision balance is used to measure the weight of each sample before and after the test. The precision of the balance is 0.0001 gram. The corrosion weight loss is the weight difference of a sample before and after the corrosion test. The lower the corrosion weight loss the higher the corrosion resistance of an alloy sample. From actual engine with EGR corrosion tests, the composition of the invention alloy is such as to produce a corrosion weight loss preferably less than 5.0 mg, 10.0 mg, and 18 mg in 0.25, 0.5, and 1.0 vol. % sulfuric acid solutions in the high temperature cyclic corrosion tester, respectively.

Table 1 Alloy Hardness and Chemical Composition (wt%)

Sample No.	Alloy Name	C	Si	Cr	W	Mo	Fe	V	Nb	Ni	Al	Cu	Hardness (HRC)
1	Comparative	1.2	1.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	29.0
2	Comparative	1.4	1.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	30.4
3		1.8	1.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	34.7
4		2.0	1.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	36.9
5		2.2	1.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	39.9
6		2.5	1.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	41.1
7		2.7	1.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	41.5
8	Comparative	2.5	1.0	10.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	45.3
9		2.5	1.0	12.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	45.3
10		2.5	1.0	13.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	45.6
11		2.5	1.0	15.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	44.8
12		2.5	1.0	17.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	43.0
13		2.5	1.0	20.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	38.3
14		2.5	1.0	22.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	38.1
15	Comparative	2.5	1.0	25.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	39.0
16		2.5	1.0	18.0	2.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	41.6
17		2.5	1.0	18.0	4.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	41.0
18		2.5	1.5	18.0	7.0	7.0	Bal.	1.0	1.0	25.0	0.04	1.5	40.2
19		2.5	1.0	18.0	-	5.0	Bal.	1.0	1.0	16.0	0.04	1.5	41.1
20		2.5	2.0	18.0	-	15.0	Bal.	2.0	1.0	16.0	0.04	1.5	51.0
21		2.5	1.0	18.0	7.0	-	Bal.	1.0	1.0	12.0	0.04	1.5	41.8
22		2.5	1.0	18.0	7.0	-	Bal.	1.0	1.0	20.0	0.04	1.5	38.9
23		2.5	1.0	18.0	7.0	-	Bal.	1.0	1.0	25.0	0.04	1.5	38.6
24		2.2	1.0	18.0	7.0	-	Bal.	3.0	1.0	16.0	0.04	1.5	38.5
25		2.5	3.0	18.0	7.0	-	Bal.	1.0	1.0	16.0	0.04	1.5	36.1
									Co:				
26	Stellite 3	2.4	-	30.0	12.8		2.0	-	50.8	2.0	-	-	55.0
27	M2	1.6	1.3	4.0	5.5	6.5	Bal.	1.5	-	-	-	-	42.0
	Tribaloy								Co:				
28	T400	0.08	2.6	8.5	-	28.5	-	-	60.4	-	-	-	54.2
29	US6866816	1.6	2.0	9.0	-	15.0	Bal.	-	2.0	16.0	0.30	1.0	43.2
30	US6916444	2.4	1.5	6.0	-	15.0	Bal.	2.5	1.5	10.0	-	-	46.6

(continued)

Sample No.	Alloy Name	C	Si	Cr	W	Mo	Fe	V	Nb	Ni	Al	Cu	Hardness (HRC)
31	US6436338	1.3	0.6	13.2	4.0	5.8	Bal.	1.3	2.1	0.6	-	Co:2.1	45.0
32	US4122817	1.7	0.5	24.0	Mn:1.4	3.9	Bal.	-	-	9.2	-	-	38.2

5

10

15

20

25

30

35

40

45

50

55

[0016] Samples 1-7 contain carbon contents from 1.2 to 2.7 wt% with silicon 1.0 wt%, chromium 18.0 wt%, tungsten 7.0 wt%, nickel 16 wt%, vanadium 1.0 wt%, niobium 1.0 wt%, aluminum 0.04 wt%, copper 1.5 wt%, and the balance is iron with other impurities associated with casting raw materials. Hardness increases rapidly with carbon content increasing from 1.2 to 2.2 wt% and then slowly increases with further carbon content. Carbon content in the inventive alloy needs to be at least 1.8 or higher in order to achieve required hardness because the hardness of sample alloys with 1.2 and 1.4 wt% carbon is only 29.0 and 30.4 HRC. On the other hand, if the carbon content of the alloy is more than 2.8 wt%, shrinkage will become a major problem for insert-type ring shaped castings. Therefore, the carbon content is defined to be within the range of from 1.8 to 2.8 wt% for good hardness and casting properties, and preferably in the range of 2.3-2.7 wt%.

[0017] Samples 8-15 contain chromium from 10.0 to 25.0 wt% with carbon 2.5 wt%, silicon 1.0 wt%, tungsten 7.0 wt%, nickel 16 wt%, vanadium 1.0 wt%, niobium 1.0 wt%, aluminum 0.04 wt%, copper 1.5 wt%, and the balance is iron with other impurities associated with casting raw materials. These different chromium contents containing samples illustrate the effects of chromium on hardness and corrosion resistance. Lower chromium containing alloy gives lower corrosion resistance while alloys with higher chromium contents have lower hardness. Therefore chromium content in the inventive alloy is defined to be within 12.0 to 22.0 wt%, preferably 16.0 to 20.0 wt%, for the balance of good corrosion resistance and adequate hardness. While sample 15 has adequate hardness, it is expected that it will have too high of a wear rate.

[0018] Samples 16-20 contain tungsten and/or molybdenum from 0 to 15.0 wt% with carbon 2.5 wt%, silicon 1.0-2.0 wt%, chromium 18.0 wt%, nickel 16.0-25.0 wt%, vanadium 1.0-2.0 wt%, niobium 1.0 wt%, aluminum 0.04 wt%, copper 1.5 wt%, and the balance is iron with other impurities associated with casting raw materials. Unlike the alloy disclosed in U.S. Patent No. 6,866,816, where corrosion resistance increase with the amount of molybdenum content, increasing tungsten and molybdenum have little effect in hardness and corrosion in the range tested. It is not necessary to use high molybdenum and/or tungsten content for better corrosion or higher hardness in the inventive alloy. Similar to high speed steels, addition of molybdenum or tungsten improves hot hardness of the inventive alloy, which is important from the designed application view as the intake insert working temperature can reach 700 °F. The combined molybdenum and tungsten content is defined to be within 2.0 to 16.0 wt%, preferably 3.0 to 15.0 wt%. In some alloys the tungsten will be between about 3.0 and about 7.0 wt%, and may contain no molybdenum. In other alloys the combination of molybdenum and tungsten will be between 10.0 and 16.0 wt%, with the molybdenum preferably 12.0 to 15.0 wt% and no tungsten. Excessive amount of tungsten or molybdenum causes a brittleness problem for castings made from the inventive alloy.

[0019] Samples 6, 21, and 23 contain nickel from 12.0 to 25.0 wt% with carbon 2.5 wt%, silicon 1.0 wt%, chromium 18.0 wt%, tungsten 7.0 wt%, vanadium 1.0 wt%, niobium 1.0 wt%, aluminum 0.04 wt%, copper 1.5 wt%, and the balance is iron with other impurities associated with casting raw materials. Nickel has a positive contribution to the corrosion resistance of the alloy. First, there is a minimum amount of nickel required in order to form stable austenite in the alloy. Second, higher nickel content improves corrosion resistance of the alloy in all acid concentrations tested. However the improvement is at the expense of lower hardness and therefore lower wear resistance. Therefore, the nickel content is defined to be within the range of 12.0 to 25.0 wt%, preferably 14.0 to 18.0 wt%.

[0020] Vanadium and niobium are strong MC carbide type forming alloy elements. A small addition of vanadium and niobium helps to improve corrosion resistance of the alloy. Too much vanadium or niobium decreases the hardness of the alloy. Samples 5 and 24 contain vanadium from 1.0 to 3.0 wt% with carbon 2.5 wt%, silicon 1.0 wt%, chromium 18.0 wt%, tungsten 7.0 wt%, niobium 1.0 wt%, aluminum 0.04 wt%, copper 1.5 wt%, and the balance is iron with other impurities associated with casting raw materials. From the corrosion and hardness test results, vanadium content should be in the range of 0.02 to 3.0 wt%. Similarly, niobium content is between 0.02 to 3.0 wt%. The combined vanadium and niobium content should be between 0.05 and 4.0 wt%, preferably between 1.5 and 2.5 wt%.

[0021] Samples 6 and 25 contain silicon from 1.0 to 3.0 wt% with carbon 2.5 wt%, chromium 18.0 wt%, tungsten 7.0 wt%, nickel 16 wt%, vanadium 1.0 wt%, niobium 1.0 wt%, aluminum 0.04 wt%, copper 1.5 wt%, and the balance is iron with other impurities associated with casting raw materials. Silicon has deoxidizing and desulfurizing effects during alloy melting process. Silicon also has the effect of improving fluidity. However, the main reasons for using silicon in the inventive alloy are that silicon can also improve corrosion and wear resistance of the alloys. Increasing silicon content from 1.0 to 3.0 wt% improves corrosion resistance of the inventive alloy. If the Si content is less than 0.5%, the effects on wear and corrosion are not achieved. If the Si content is more than 3.5 wt%, especially in the high-carbon austenitic alloy, excessive amount of silicon provides a too brittle alloy. Higher amount of silicon also decreases the hardness of the inventive alloy. Therefore, the silicon content is defined to be within the range of 0.5 to 3.5 wt%, preferably 0.5 to 3.0 wt%, and more preferably 0.5 and 1.5 wt%.

[0022] Addition of copper enhances the corrosion resistance of the alloy significantly. However excessive amount of copper decreases wear resistance of the alloy. Therefore, the range of copper in the alloy is defined to be within 0.05 to 3.0 wt%, preferably 1.0 to 2.0 wt%.

[0023] Manganese also has deoxidizing and desulfurizing effects to molten metals. However, manganese can dete-

EP 1 775 351 A1

riorate corrosion resistance if its content is too high. Therefore, the manganese range is defined to be less than 1.5 wt%, preferably 0.2 to 0.6 wt%.

[0024] A small amount of aluminum, and optionally titanium, is added in the inventive alloys for precipitation hardening purpose. The range for aluminum is between about 0.01 and about 0.2 wt%, preferably between about 0.03 and about 0.06 wt%. The range for titanium is between about zero and about 1 wt%, preferably between about 0.02 wt% and about 0.06 wt%. When these elements are added, and the alloys heat treated, wear resistance will be improved.

Table 2 Corrosion Test Results (Weight Loss; mg)

Sample No.	Alloy Name	0.25%	0.5%	1.0%
1	comparative	2.5	4.6	13.3
2	comparative	3.1	4.6	14.5
3		2.6	7.1	13.4
4		4.1	7.6	14.5
5		3.8	8.1	15.2
6		3.8	8.1	14.0
7		4.3	8.7	14.0
8	comparative	6.3	9.8	12.4
9		3.7	9.5	14.4
10		2.3	9.0	17.4
11		2.6	7.1	13.9
12		2.7	7.8	14.8
13		3.5	9.0	15.2
14		4.2	8.9	13.5
15	comparative	2.9	5.8	11.8
16		3.7	7.8	13.9
17		3.0	5.0	15.0
18		2.9	4.9	11.2
19		3.3	8.1	17.8
20		3.9	7.7	13.8
21		4.1	7.8	17.9
22		2.5	7.3	13.0
23		1.1	5.5	10.7
24		2.7	7.8	15.1
25		1.8	4.0	10.6
26	Stellite 3	2.6	5.8	7.5
27	M2	23.5	45.0	84.1
28	Tribaloy T400	1.2	4.7	11.9
29	US6866816	5.2	10.3	15.0
30	US6916444	15.2	18.7	20.2
31	US6436338	13.9	19.4	33.4
32	US4122817	8.7	14.4	23.6

[0025] Corrosion and hardness test results for M2 tool steel, Stellite 3, Tribaloy T400, and the alloys disclosed in U.S. Patent No. 6,866,816, U.S. Patent No. 6,916,444, U.S. Patent No. 6,436,338, U.S. Patent No. 3,257,178, and U.S. Patent No. 4,122,817, are also given in Table 1 and Table 2. It is clear that many inventive samples have much better corrosion and wear resistance than M2 tool steel. Some samples are even close to cobalt-base alloys Stellite 3 and Tribaloy T400 in terms of corrosion resistance. However, these samples are much less expensive than these cobalt-base alloys.

[0026] It should be appreciated that the alloys of the present invention are capable of being incorporated in the form of a variety of embodiments, only a few of which have been illustrated and described. The invention may be embodied in other forms without departing from its spirit or essential characteristics. It should be appreciated that the addition of some other ingredients, process steps, materials or components not specifically included will have an adverse impact

on the present invention. The best mode of the invention may, therefore, exclude ingredients, process steps, materials or components other than those listed above for inclusion or use in the invention. However, the described embodiments are considered in all respects only as illustrative and not restrictive, and the scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

Claims

1. An austenitic iron-base alloy with good corrosion and wear resistance, comprising:
 - a) about 1.8 to about 2.8 wt% carbon;
 - b) about 12.0 to about 22.0 wt% chromium;
 - c) about 0.5 to 3.5 wt% silicon;
 - d) about 12.0 to about 25.0% nickel;
 - e) about 2.0 to about 16.0 wt% of tungsten and molybdenum combined;
 - f) about 0.05 to about 4 wt% niobium and vanadium combined;
 - g) about 0 to about 1.0 wt% titanium;
 - h) about 0.01 to about 0.2 wt% aluminium;
 - i) about 0.05 to about 3 wt% copper;
 - j) less than 1.5 wt% manganese;
 - g) the balance being iron and impurities.
2. The alloy of claim 1, wherein the amount of carbon is between about 2.3 and about 2.7 wt%
3. The alloy of claim 1 or claim 2, wherein the amount of chromium is between about 16.0 and about 20.0 wt%.
4. The alloy of any one of the preceding claims, wherein the amount of silicon is between about 0.5 and about 1.5 wt%.
5. The alloy of any one of the preceding claims, wherein the amount of tungsten is between about 3.0 and about 7.0 wt%.
6. The alloy of any one of the preceding claims, wherein the amount of nickel is between about 14.0 and about 18.0 wt%.
7. The alloy of any one of the preceding claims, wherein the amount of niobium and vanadium combined is between about 1.5 and about 2.5 wt%.
8. The alloy of any one of the preceding claims, wherein the amount of titanium is between about 0.02 and about 0.06 wt%.
9. The alloy of any one of the preceding claims, wherein the amount of aluminium is between about 0.03 and about 0.06 wt % .
10. The alloy of any one of the preceding claims, wherein the amount of copper is between about 1.0 and 2.0 wt%.
11. The alloy of any one of the preceding claims, wherein the amount of manganese is between about 0.2 and 0.6 wt%.
12. The alloy of any one of the preceding claims, wherein the amount of iron is greater than about 50 wt%.
13. The alloy of any one of the preceding claims, wherein the amount of molybdenum and tungsten combined is between about 10.0 and about 16.0 wt%.
14. The alloy of any one of the preceding claims, wherein the amount of molybdenum is between about 12.0 and about 15.0 wt%.
15. The alloy of any one of the preceding claims, wherein the amount of vanadium is between about 0.02 and about 3.0 wt%.
16. The alloy of any one of the preceding claims, wherein the amount of niobium is between about 0.02 and about 3.0 wt%.

EP 1 775 351 A1

17. A part for an internal combustion engine comprising the alloy of any one of the preceding claims.

18. The part of claim 17 where the part is formed by casting the alloy, or hardfacing with the alloy either in wire or powder form.

19. The part of claim 17 where the part is formed by a powder metallurgy method.

5

10

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 25 5276

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,A	EP 1 391 529 A (WINSERT TECHNOLOGIES INC [US]) 25 February 2004 (2004-02-25) * paragraphs [0011], [0012], [0016]; table 1 * * claims 11-4 *	1-19	INV. C22C33/00 C22C38/00
A	GB 2 301 116 A (WINSERT INC [US]) 27 November 1996 (1996-11-27) * page 1, line 3 - line 8 * * page 7; table 1 * * claims 1-14 *	1-19	
A	US 4 724 000 A (LARSON JAY M [US] ET AL) 9 February 1988 (1988-02-09) * column 3, line 7 * * column 4, line 45 - line 60; claims 1-14 *	1-19	
A	JP 48 102717 A (TOKUSHI SEIKO CO LTD.) 24 December 1973 (1973-12-24) * examples B,C,D,E; table 1 *		TECHNICAL FIELDS SEARCHED (IPC)
A,P	EP 1 614 762 A2 (ALLOY TECHNOLOGY SOLUTIONS INC [US]) 11 January 2006 (2006-01-11) * paragraph [0010] * * claims 1-14; table I *	1-19	C22C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 9 January 2007	Examiner Gavriliu, Alexandru
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

1
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 25 5276

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-01-2007

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1391529	A	25-02-2004	NONE	

GB 2301116	A	27-11-1996	DE 19621091 A1	28-11-1996
			US 5674449 A	07-10-1997

US 4724000	A	09-02-1988	DE 3770411 D1	04-07-1991
			EP 0266935 A1	11-05-1988
			JP 2687125 B2	08-12-1997
			JP 63114904 A	19-05-1988

JP 48102717	A	24-12-1973	JP 837324 C	15-12-1976
			JP 51008808 B	22-03-1976

EP 1614762	A2	11-01-2006	NONE	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 6916444 B [0004] [0024] [0025]
- US 6436338 B [0004] [0024] [0025]
- US 6866816 B [0004] [0011] [0011] [0011] [0018] [0024] [0025]
- US 6200688 B [0005]
- US 3257178 A [0006] [0025]
- US 3410732 A [0006]
- US 4122817 A [0006] [0024] [0025]
- US 4929419 A [0006]