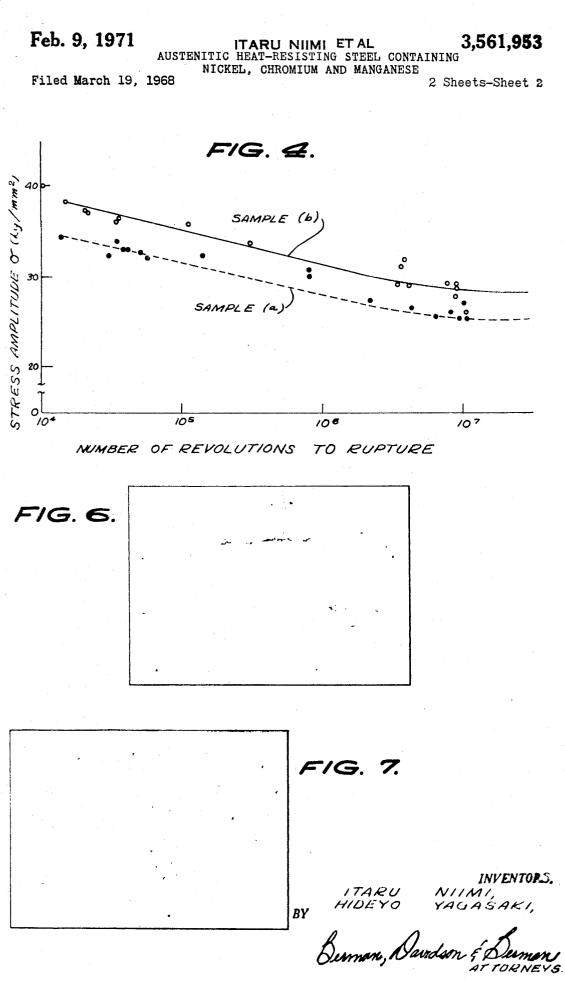


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United States Patent Office

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3,561,953 AUSTENITIC HEAT-RESISTING STEEL CONTAIN-ING NICKEL, CHROMIUM AND MANGANESE Itaru Niimi, Toyota-shi, and Hideyo Yagasaki, Sendai-shi, Japan, assignors to Toyota Jidosha Kogyo Kabushiki Kaisha, Aichi-ken, Japan Filed Mar. 19, 1968, Ser. No. 714,213 Int. Cl. C22c 39/20 2 Claims

U.S. Cl. 75-128

ABSTRACT OF THE DISCLOSURE

An austenitic heat-resisting steel, for engine valves and similar applications, capable of withstanding conditions 15 encountered in modern high performance engines requiring hardness, high temperature strength and toughness, consisting essentially of 0.1-0.6% carbon, 0.1-2.0% silicon, 3.0-15.0% manganese, 1.0-15% nickel, 15.0-28.0% chromium, 0.01-2.0% tungsten, 0.01-1.5% molybdenum, 200.01-1.5% vanadium, 0.01-1.5% columbium, 0.2-0.6% nitrogen, 0.001-0.020% calcium, less than 0.008% oxygen, and the balance of iron with incidental impurities.

25The present invention relates to austenitic heat-resisting steels containing nickel, chromium and manganese for engine valves and similar products requiring hardness, high temperature strength and toughness when used ia modern high performance engines.

30 Hitherto extensively used heat-resisting steels have been presented as for example in U.S. Pat. Nos. 2,602,738, 2,657,130, 2,671,726 and 2,698,785.

Applicants have discovered that the age-hardenability, high temperature strength and toughness of a steel such 35 as proposed in the above-named patents, and containing 21% Cr-4% Ni-9% Mn-0.4% can be improved by addition of tungsten, molybdenum, columbium and vanadium so as to produce a valve steel which can stand the heavy conditions of modern high performance engines. 40 While by mere addition of these elements, the agehardenability and high temperature strength of the steel is considerably bettered, it was also found that the steel turned poor in hot-workability and lost practical value.

One method for improving hot-workability is to add boron or other elements. The present inventors, however, succeeded to improve hot-workability and some other characteristics by minimizing the oxygen content and by addition of calcium in the steel.

Chemical composition of the austenitic heat-resisting 50 steel according to the present invention is by weight as follows: carbon 0.1-0.6%; silicon 0.1-2.0%; manganese 3.0-15.0%; nickel 1.0-15.0%; chromium 15.0-28.0%; tungsten 0.01-2.0%; molybdenum 0.01-1.5%; columbium 0.01-1.5%; vanadium 0.01-1.5%; nitrogen 0.2-0.6%; 55 calcium 0.001-0.020%; oxygen less than 0.008%; balance of iron and unavoidable incidental impurities.

From the above it will be apparent that a primary object of the present invention is to provide a steel characterized by improved age-hardenability, high tempera-60 ture strength and toughness which can better withstand conditions encountered in modern high performance engines.

Another important object of the invention is to provide an improved steel composition by inclusion of tung-65 sten, molybdenum, columbium and vanadium.

Still another important object of the invention is to provide an improved steel composition, having the above described characteristics, wherein hot-workability is also improved, a preferred treatment including the minimizing of oxygen content and addition of calcium to the steel.

The novel features that are considered characteristic

of the invention are set forth with particularity in the appended claims. The invention, itself, however, both as to its organization and its method of operation, together with additional objects and advantages thereof, will best be understood from the following description of specific embodiments when read in connection with the accompanying drawings, wherein like reference characters indicate like parts throughout the several figures and in which:

FIG. 1 is a diagram showing the relationship between testing temperature and elongation of test specimens of steels of the present invention and conventional steels obtained by tensile tests in the hot-working temperature range:

FIG. 2 is a diagram showing hardness change in aging after solution treatment of the steels of the present invention and that of the conventional steels;

FIG. 3 is a diagram showing machinability of the steels of the present invention compared to that of conventional steels:

FIG. 4 is a diagram showing fatigue strength of the steels of the present invention compared with that of conventional steels obtained by fatigue tests at elevated temperature:

FIG. 5 is an elevation of a test specimen partially broken away to reveal sections before tensile test at elevated temperature;

FIGS. 5a and 5b illustrate the appearance of similar test specimens of conventional steel and steel according to the present invention, respectively, after tensile test;

FIG. 6 is a microphotograph of non-metallic inclusions in a conventional steel; and

FIG. 7 is a microphotograph of non-metallic inclusions of the steel according to the present invention.

Referring more particularly to the drawings wherein the characteristics of improved high temperature heatresisting steels according to the invention are compared under various tests to conventional steels, it is first stated that the improved steel is made by adding to a conventional stainless steel melt appropriate quantities, as above indicated, of tungsten, molybdenum, columbium and vanadium either as pure elements or in combination with other elements. The age-hardenability and the high temperature strength are increased by precipitation of complex compounds of chromium, tungsten and molybdenum $[(Cr, W, Mo)_{23}(C, N)_6]$ and complex compounds of columbium and vanadium [(Cb, V)(C, N)].

The refining practice of the improved steel is generally carried out in the following way. The material is refined in a basic furnace either by use of lime rich white slag of basicity more than 2, or, at the last stage of the same basic process, by electrolyzing the white slag by applying direct current to reduce oxygen content to less than 0.008% and sulfur to less than 0.01%.

Concerning deoxidation by slag-electrolyzing, U.S. Pat. No. 3,203,883 shows that deoxidation and desulfurization of 13% chromium stainless steel, for instance, may be carried out electrochemically by applying direct current at the last stage of refining using lime rich slag, and oxygen and sulfur content in the steel is reduced to 0.0045 to 0.0029% and 0.004% respectively. This patented method for deoxidation and desulfurization may be followed to make the present steel easily and with certainty. In case of refining only by the white slag, however, much skill is required because slag control is fairly difficult.

Subsequent to said refining, the steel is tapped out of the furnace, at which time 0.1-0.25% calcium is added by using the rare earth calcium silicon alloy or the ferrosilicon calcium alloy for reducing oxygen to less than 0.008% and leaving 0.001 to 0.020% of calcium in the steel.

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The amount of non-metallic inclusions in the steel of the present invention is extremely small and particularly their appearances rarely involve silicates and sulphides elongated along the fiber flow as seen in conventional steels, but only involve inclusions dispersed in fine particles. Appearances of these non-metallic inclusions are shown in FIGS. 6 and 7.

FIG. 6 shows the non-metallic inclusions in the conventional steel products. As seen in the figure, the amount of non-metallic inclusions in the conventional steel is rather large and they appear as elongations along the fiber flow. FIG. 7 shows the non-metallic inclusions in the steel of the present invention. By contrast, the amount of non-metallic inclusions is extremely small and they appear as a dispersion of fine particles. By presence of 15 plitude (σ , kg./mm.²). calcium under oxygen minimization, the non-metallic inclusions were reduced and the appearance of them was improved. Grain refining of the matrix by a carbonitride of columbium and vanadium, and calcium improved hot toughness, hot-workability and machinability.

In the present invention, these excellent characteristics can be attained only when deoxidation and desulfurization refining are made as above described and thereafter said calcium alloy has been additionally applied.

Characteristic features of the steel of the present invention are illustrated below referring to some test examples. Table 2 shows chemical analyses of specimens in the test. In the table, the specimen (a) is a typical heatresisting steel containing 21% Cr-4% Ni-9% Mn-0.4% N obtained by conventional process. Specimens (b) and 30 (c) are steels according to the present invention.

TABLE 2 .- CHEMICAL ANALYSES (by WEIGHT PERCENT)

	Specimen		
	(a)	(b)	(c)
	Conven- tional steel	Present steel	Present steel
C	0.48	0, 43	0.41
Si	0.23	0.28	0.35
Mn	8.55	7.95	8, 50
P	0,022	0.021	0,023
S	0.015	0.004	0.003
Ni	4.15	3, 98	4.08
Cr	20.86	20.08	22,06
W		0.35	0.30
Mo		0, 12	0.22
Cb		0.152	0.315
V		0.31	0.45
Ca		0.0098	0.0065
N	0.36	0.47	0,43
0	0.0099	0.0058	0.0042

Varied characteristic features of these specimens are 50 shown by comparison in Table 3 and in FIGS. 1 to 5b.

TABLE 3.-MECHANICAL PROPERTIES AT THE ELEVATED TEMPERATURE (TESTED AT 700° C.)

The results shown in Table 3 indicate that the steel of the present invention is fairly high in tensile strength and creep rupture strength so that the steel excels conventional steels in high temperature strength, and from its high elongation, reduction of area, and Charpy impact value, its excellent toughness is clearly shown.

Also the results of fatigue tests at elevated temperature show that the steel of the invention is higher in hot fatigue strength than conventional steels, and that the former is practically valuable for engine valves. FIG. 4 shows 10 results of fatigue tests of specimens (a) and (b). They were tested at the temperature of 700° C. under revolution of 3600 r.p.m. The abcissa shows number of revolution to rupture (N) and the ordinate shows stress am-

The relationship of testing temperature and elongation of the specimens of the present steels and conventional one, obtained by tensile tests in hot-working temperature range, is shown in FIG. 1.

In FIG. 1, the testing temperature (° C.) was taken 20as an abcissa and the elongation (percent) as an ordinate. As seen in FIG. 1, the elongation of the steels of the present invention as compared with conventional steel at 1100° C. is apparently very high showing excellent hot workability. The typical appearance of the specimens after 25 the test is shown in FIGS. 5a and 5b in comparison with that of before the test, shown in FIG. 5. The elongation in the course of heating of the specimen (b) was much larger than the specimen (a) which shows large hot ductility and excellent hot workability of the present steel.

Comparison of steels by other methods also indicated that the steel of the present invention is higher in the hot workability than the conventional steels.

It is particularly noted that the yield of end product 35 in processing of the steel of the present invention which is oxygen-minimized and calcium-restricted greatly increased as compared with the conventional steel of 21% Cr-4% Ni-9% Mn-0.4% N. The comparison of the yield

40 of both steels in the processing from 200 kg. ingots to 9.3 mm. round bars was carried out in the following way. In the test, both steels containing the same materials were refined in a basic Heroult arc furnace of 1.5 ton in capacity. The tests were made on two heats of 21% Cr-4%

45 Ni-9% Mn-0.4% N steel and five heats of the steel of the present invention. Seven pieces of 200 kg. ingots were cast from each heat. Refining of the steel of this invention was carried carefully with consideration of deoxidation and desulfurization.

The processing diagram is as follows:

	- III 100	0.0			
· · · · · · · · · · · · · · · · · · ·		Specimens			heat to 1150° C.
Properties	(a) Conven- tional steel	(b) Present steel	(c) Present stee	55	200 kg. ingot \longrightarrow 110 mm. x 110 mm. rough forging $\xrightarrow{\text{heat to } 1225^{\circ} \text{ C.}}$ 40 mm. x 40 mm. rough rolling $\xrightarrow{\text{heat to } 1200^{\circ} \text{ C.}}$
Tensile strength, kg./mm. ² Elongation, percent Reduction of area, percent Charpy impact value, kg. m./cm Creep rupture strength hours (700° C., 27 kg./mm. ²) Fatigue strength, kg./mm. ²	47.8 15.2 13.6 2.1 14 25.8	51.8 28.9 35.6 3.7 138 28.8.	52, 5 26, 7 34, 5 3, 8 156	60	9.3 mm. round bar final rolling The yield in the above process is shown in Table 4.

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NOTE: Heat treatment; 1,200° C.×1 hr. W.C. and 850° C.×5 hrs. A.C.

TABLE 4.-YIELDS OF CONVENTIONAL 21% Cr-4% Ni-9% Mn-0.4% N STEEL

AND PRESENT STEEL				
	200 kg. ingots	110 mm. x 110 mm. billets	40 mm. x 40 mm. billets	9.3 mm : round bars
Conventional steel: Weight (kg.) Yield from ingot (porcent) Present steel:	2, 704. 8	1, 306. 4 48. 3	1, 154. 9 42. 7	1, 098. 1 40. 6
Weight (kg.) Yield from ingot (percent)	6, 786. 5	5, 626. 0 82. 9	5, 347. 8 78. 8	5, 157. 7 76. 0

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In the conventional steel, cracks often occurred in the course of rough forging from ingots to billets. These cracks appeared also in the course of rough rolling of billets. The yield of the conventional steel from the ingots to 9.3 mm. round bars was 40.6%, as shown in Table 4. In contrast, no crack appeared in the present invention steel through the whole processing and the yield was 76.0%

A good yield was also obtained in manufacturing engine valves from the steel of the present invention.

FIG. 2 shows the hardness change when all specimens were heated at 1150° C. and 1200° C. for one hour, water cooled and aged at 700° C. and 750° C., respectively. In FIG. 2, the aging time (hr.) was taken as an abscissa and the Rockwell C-scale Hardness (H_RC) as an ordinate. As shown in the figure, the hardness of the steel of the present invention, specimens (b) and (c), after 100 hours aging was H_RC 39-41, while that of the conventional steel, specimen (a), was H_RC 32-34, whereby it is evident that the age-hardenability of the steel of the present invention is much improved over that of the conventional steel.

FIG. 3 shows the results of machining test of each specimen. In the tests, round bars of 35 mm. in diameter were employed. The hardness of specimen (a) was H_RC 27.7-28.9; that of specimen (b) was H_BC 28.4–29.6 and that of specimen (c) was H_RC 29.2–31.0. The cutting tools were a straight tool manufactured from high speed steel with chemical composition of 0.8% C-4% Cr-18% W-1% V, and hardened to H_RC 64.3-64.9. The cutting conditions 30 were fixed as follows; the depth of cut was 1.0 mm.; feed 0.15 mm./rev.; and cutting speed was varied between 24-112 m./min. Cutting length causing a definite wear in the tool edge was determined at each cutting speed.

The cutting length of each specimen at the cutting speed of 62 m./min., for example, was 2000-4000 mm. for the specimen (a); 33,000-36,000 mm. for the specimen (b), and 21,000-26,000 mm. for the specimen (c) as shown in FIG. 3. The machinability of the steel of the present invention is much improved compared with conventional steels.

FIG. 4 shows results of fatigue tests of specimens (a) and (b). They were tested at the temperature of 7000° C. under revolution of 3600 r.p.m. The abcissa shows number of revolutions to rupture (N) and the ordinate ${}_{45}$ shows stress amplitude (σ , kg./mm.²)

Detailed description of the chemical analyses of steel according to the present invention to obtain improved characteristics is given below.

The lowest limit of carbon content was determined to 50 be 0.1% which is essential to form, with nitrogen, the complex compounds of chromium, tungsten, molybdenum, columbium and vanadium, and for age-hardenability and strengthening of matrix in relation to the 55 amount of other elements. The upper limit was set at 0.6% considering decrease of hot-workability and machinability.

The amount of silicon is better to be low in order to improve the corrosion resistance, but, as it is a deoxidiz- 60 ing element, its limit was set at 0.1-2.0%. The upper limit of 2.0% in this case is due to the fact that it is a maximum amount to secure hot toughness as well as corrosion resistance.

The minimum amount of manganese was set at 3.0% 65 for maintaining the steel of the present invention to austenitic structure. Manganese in excess of 15.0% lowers the oxidation resistance of the steel. The range of content was thus determined to be 3.0-15.0%.

70The minimum amount of nickel required is 1.0% in order to stabilize the austenitic structure and to improve its corrosion resistance. With increase of nickel content, these characteristics are improved but the content in ex6

economic. The range of nickel content was set at 1.0-15.0%.

Content of manganese and nickel together were, for retaining proper characteristic of the steel of the present invention, 8.0-30.0% in sum of twice the content of manganese and the content of nickel. At below 8.0%, there precipitates a free ferric which is harmful for toughness, and excess of 30.0% is uneconomic, or sometimes is accompanied by poor oxidation resistance.

Chromium is an indispensable element for providing 10 heat resistance and is also an important carbide former. The amount of this element should be 15.0% at minimum for the purpose of dissolving a large quantity of nitrogen characterizing the present steel. When the steel contains 15 more than 28.0% of chromium, the heat resistance is rarely improved and the steel becomes brittle because of delta phase and, further, sigma phase produced. Thus the range of chromium content was fixed at 15.0-28.0%, but it is more desirable to utilize between 18.0 and 23.0% for im-20 proving various characteristics of the present steel.

Tungsten and molybdenum are effective for improving age-hardenability and high temperature strength and the effect is more apparent when both elements are present. The ranges of contents of these elements were determined to be 0.01-2.0% and 0.01-1.5%, respectively, because hot workability decreases with the increase of the content. More desirable ranges of contents of tungsten and molybdenum are 0.03-1.0% and 0.02-0.5% respectively, for improving various characteristics of the steel.

Vanadium is effective for improving age-hardenability, high temperature strength, and toughness, but corresponding to its content, it tends to harm the hot workability so that the range of contents was limited to 0.01-1.5%. A more desirable range for exhibiting the characteristic 35 features of the improved steel is 0.02-0.5%.

Columbium is effective for improving hot workability and hot toughness, while the columbium compound prevents the grain growth of matrix. These effects of columbium are particularly noted in the steel of the present 40 invention which is oxygen-minimized and calcium restricted. Containing more than 0.01% of columbium, these effects are remarkable, but excess of 1.5% decreases the hot workability, and sometimes it makes austenitic matrix unstable and brittle. The range of content was, therefore, fixed at 0.01-1.5%. A more desirable range of columbium content is 0.02-0.5% for exhibiting the characteristic features of the present steel.

The described contents of tungsten, molybdenum and vanadium are required 0.2-3.5% in total, to retain characteristics of the present steel. A more desirable range of contents is 0.5-2.0% in order to exhibit the most proper characteristics.

Nitrogen, along with carbon, is of supreme importance for precipitation hardening by carbonitrides as described before and for stabilizing and strengthening the austenitic matrix of the steel. The required content of nitrogen was determined to be at least 0.2% and desirably more than 0.3%. The upper limit of nitrogen content of 0.6% is set to prevent occurrence of blow holes and other defects in the ingot.

Calcium greatly contributes to improvement of hot workability, toughness and machinability by grain refining, and reducing and improving the appearance of nonmetallic inclusions. Therefore, the steel of the present invention must contain 0.001-0.020% of calcium by addition of 0.1-0.25% of calcium alloy as described. In either case of calcium content being less than 0.001% or more than 0.020%, the effect of improvement of said characteristics is reduced. A more desirable range of calcium content for raising the characteristics of the present steel is 0.003-0.012%.

The oxygen content at less than 0.008% improves agehardenability, hot workability and toughness, and in addicess of 15.0% does not improve them and hence, is not 75 tion, in combination with calcium, improves the charac35

teristics of the steel produced by the addition of proper amount of tungsten, molybdenum, columbium and vanadium as described. The oxygen content in excess of 0.008% is less effective.

The impurities which are unavoidably mixed in the course of melting process of the present invention, are small amounts of copper, titanium, boron, lead, tin and arsenic. Among these elements, titanium and boron can be added positively to improve hot workability as de- 16 scribed. Addition of boron is described in U.S. Pat. No. 2,839,391. According to the present invention, these elements are not positively added but boron ordinarily comes into steel to the extent of about 0.001% at maximum from ferro-alloys or furnace linings, and titanium also enters the mix as an impurity at about 0.05% at maximum; both impurities remain in the steel. In general, the above-named impurities are desired to be substantially small in the present steel, but inclusion of small amounts in the mixture cannot be avoided.

As above described, the steel according to the present invention is an excellent and practical heat resisting steel suitable for use as engine valve material and in other high temperature applications. It is to be understood that, besides engine valves, the invention covers all types of steel products obtained by hot forging and rolling and manufactured by the described refining process and made of the described components.

Although certain specific embodiments of the invention have been shown and described, it is obvious that many modifications thereof are possible. The invention, therefore, is not to be restricted except insofar as is necessitated by the prior art and by the spirit of the appended claims.

What is claimed is:

1. An austenitic heat-resisting steel consisting essentially of:

		Percent
	Carbon (0.1-0.6
	Silicon	0.1-2.0
	Manganese	3.0-15.0
5	Nitrogen	0.2-0.6
0	Nickel	1.0-15.0
	Chromium	15.0-28.0
	Tungsten	0.01-2.0
	Molybdenum	0.01-1.5
10	Vanadium	0.01-1.5
10	Columbium	0.01-1.5
	Calcium	0.001-0.020
	Oxygen-less than 0.008% by weight, and	
	the balance of iron with incidental impur-	
15	ities.	. 1

2. An austenitic heat-resisting steel consisting essentially of:

		Percent
90	Carbon	0.1-0.6
20	Silicon	0.1-2.0
	Manganese	3.0-15.0
	Nitrogen	0.3-0.6
	Nickel	1.0-15.0
05	Chromium	18.0-23.0
25	Tungsten	0.03-1.0
	Molybdenum	0.02 - 0.5
	Vanadium	0.02 - 0.5
	Columbium	0.02-0.5
90	Calcium	0.003-0.012
30	Oxygen-less than 0.008% by weight, and	
	the balance of iron with incidental im-	

with incidental im purities.

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HYLAND BIZOT, Primary Examiner

	TES PATENT OFFICE E OF CORRECTION
Patent No. 3,561,953	Dated February 9, 19
Inventor(s)Itaru Niimi et a	1.
and that said Letters Patent are	rinted specification often 1
Signed and sealed this	17th day of August 1971.
(SEAL) Attest:	
EDWARD M.FLETCHER,JR. Attesting Officer	WILLIAM E. SCHUYLER, Commissioner of Pater