

Dec. 17, 1963

G. STEVEN ETAL

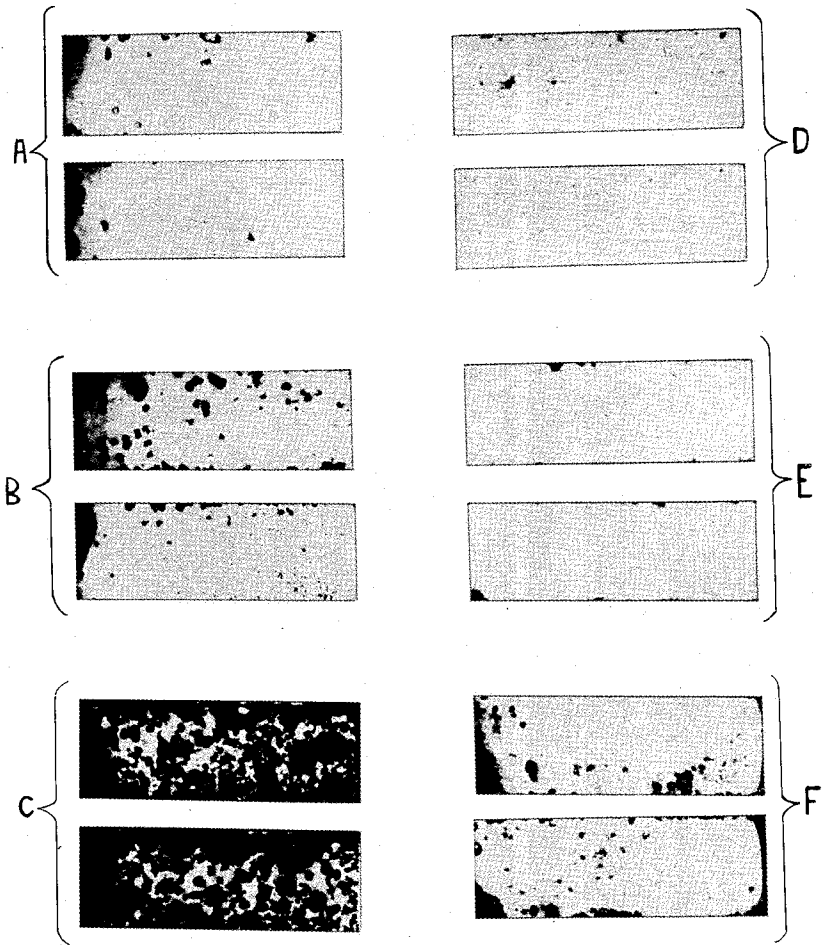
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HIGH TEMPERATURE CORROSION-RESISTANT STEEL

Filed Aug. 1, 1960

4 Sheets-Sheet 1

FIG. 1.



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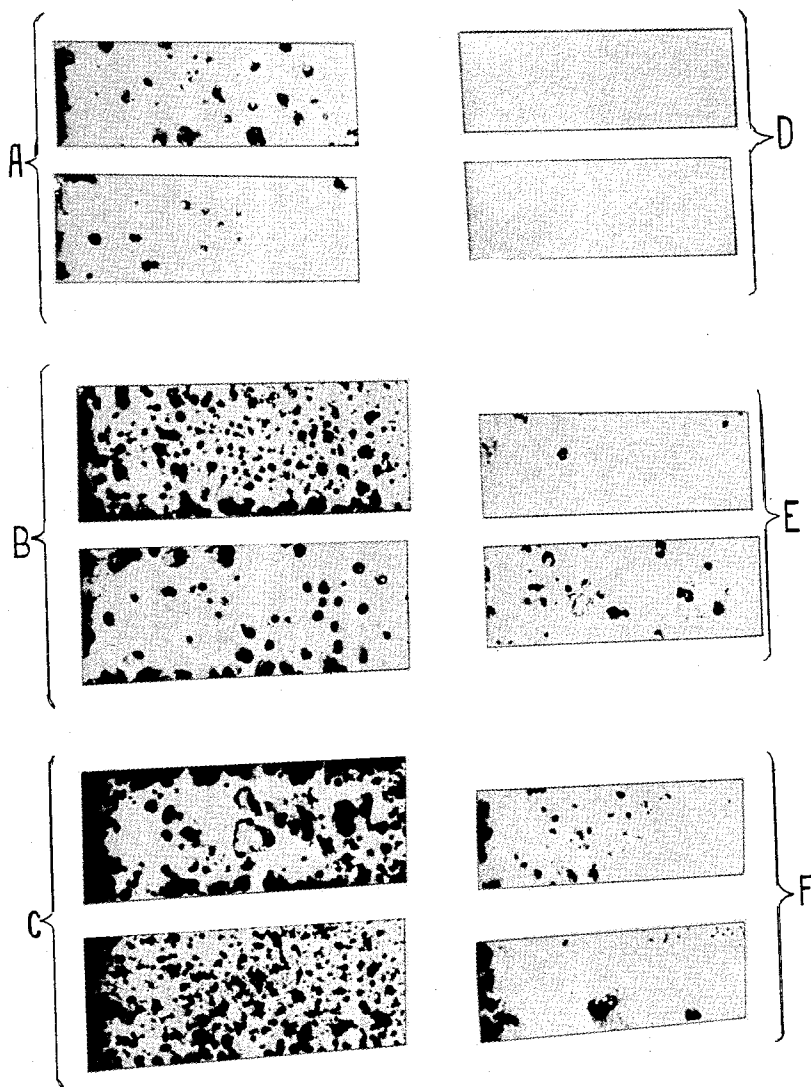
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HIGH TEMPERATURE CORROSION-RESISTANT STEEL

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4 Sheets-Sheet 2

FIG. 2



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FIG.3.

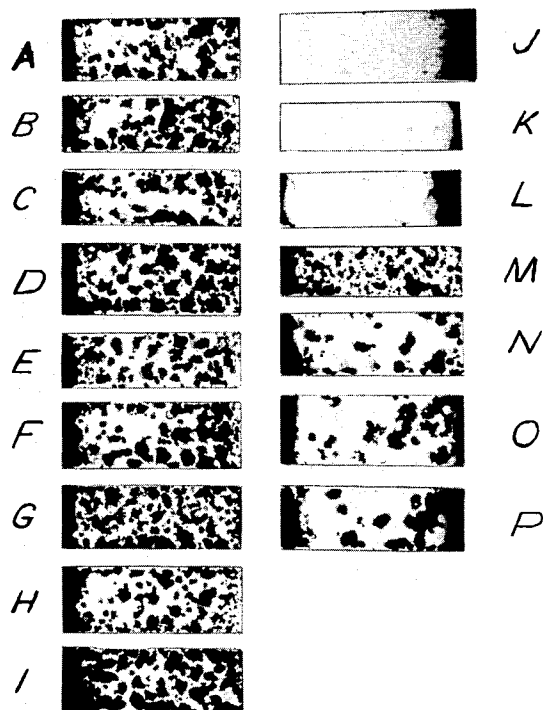


FIG.4.

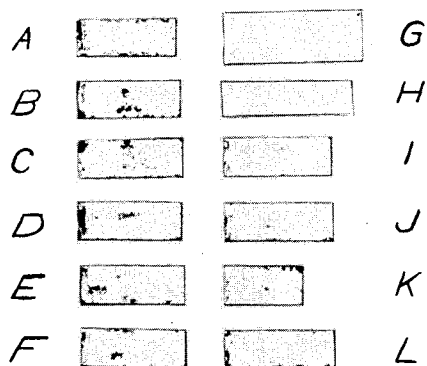
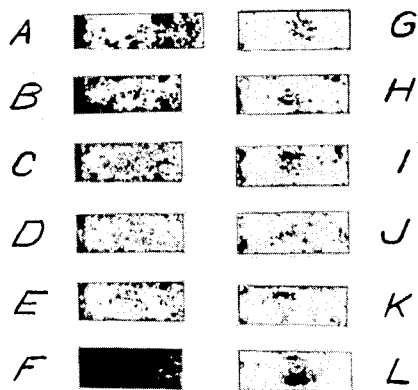


FIG.5.



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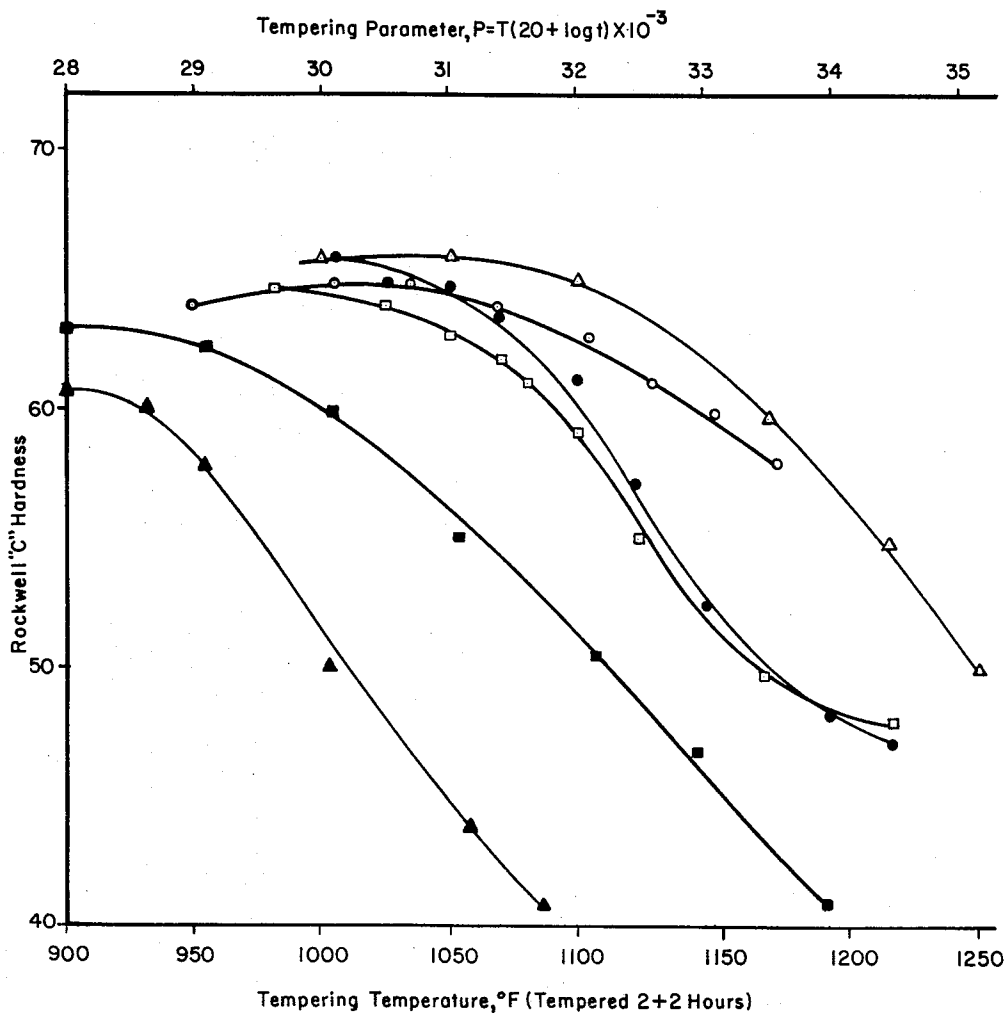
HIGH TEMPERATURE CORROSION-RESISTANT STEEL

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4 Sheets-Sheet 4

Fig.6

- △ AISI M-2
- AISI M-50
- Experimental Steel #65
- Experimental Steel #66
- AISI 440C+Mo
- ▲ AISI 440C



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HIGH TEMPERATURE CORROSION-RESISTANT STEEL

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10 Claims. (Cl. 75-126)

This invention pertains to improved alloy steel compositions, and more particularly to high temperature, corrosion resistant steels, especially suitable for the construction of bearings and like articles intended for elevated temperature service.

Recent years have witnessed an increasing demand for materials of construction having the characteristics of prolonged life, high strength and hardness, and corrosion resistance upon prolonged exposure to elevated temperatures, e.g., in the neighborhood of 1000° F. In particular, there is a present and increasing need for materials for construction of bearings subjected to such environments. Many prior art materials have been utilized for such purposes, such as various stainless steels, for example, AISI 440-C, AISI 440-C+Mo, etc., and various tool steels, such as, AISI M-2 and AISI M-50. However, such prior art materials have many disadvantages. Thus, the stainless steels, while highly corrosion-resistant, have a low order of hardness retention at the elevated temperatures contemplated, and the tool steels, although retaining a high degree of hardness at elevated temperatures, are quite susceptible to corrosive attack, for example, by atmospheric oxygen and water vapor, salts, etc.

Materials of construction for dies for hot forming of materials such as glass and the like have need of the same or similar properties as bearing materials.

Accordingly, it is an object of this invention to provide a family of steels capable of retaining a high degree of hardness at elevated temperatures, in the neighborhood of 1000° F.

It is a further object of the invention to provide high temperature steels which exhibit a high degree of resistance to corrosion.

It is still another object of the invention to provide bearings, and hot-forming dies and like articles capable of extended periods of operation at elevated temperatures, and highly resistant to mechanical erosive attack and chemical corrosion.

In accordance with the foregoing objects, the present invention provides alloy steels having the following broad compositions, expressed in weight percentages: from about 1.0 percent to about 1.3 percent carbon, from about 12 percent to about 17 percent chromium, from about 1.5 percent to about 4.5 percent vanadium, from about 1.5 percent to about 7.0 percent tungsten, from about 2.5 percent to about 7.0 percent molybdenum, from about 3 percent to about 15 percent cobalt, and the balance iron, together with the usual steelmaking elements, silicon and manganese in amounts up to about 2 percent each. A more limited, preferred class of steels of the invention comprise from about 1.0 to 1.2 percent carbon, 13 to 16 percent chromium, 2 to 4 percent vanadium, 2 to 3 percent tungsten, 3.5 to 4.5 percent molybdenum, 4 to 9 percent cobalt, balance iron, with silicon and manganese as aforesaid. An especially preferred composition range for our steels comprises about 1.05 to 1.15 percent carbon, 14.0 to 16.0 percent chromium, 2.2 to 2.8 percent

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vanadium, 2.0 to 2.5 percent tungsten, 3.75 to 4.25 percent molybdenum, 5.0 to 5.5 percent cobalt, and the balance iron plus silicon and manganese as aforesaid.

The foregoing and other objects of the invention will be more fully understood by reference to the following specification and drawings wherein:

FIGS. 1-5 are photographic representations of the results of water vapor corrosion tests upon test specimens of prior art stainless and tool steels and of a number of experimental steels and illustrate the relative resistance of these compositions to corrosive attack upon prolonged exposure to water vapor at elevated temperatures, and

FIG. 6 is a graphical representation illustrating the comparative hardness retentivities of the steels of the invention and prior art stainless steels, as well as certain tool steels commonly used for bearing fabrication.

The compositions of a number of the experimental steels are given in Table I.

TABLE I

Experimental Steel Compositions

Experimental Steel Designation	Alloying Elements, Percent						Annealed Hardness (Rc)
	C	Cr	V	W	Mo	Co	
17	1.11	16.8	1.7	4.7	2.6		
21	1.04	13.9			3.6		21
24	1.05	13.8	0.9		3.8		19
25	1.05	15.8			3.6		19
26	1.06	15.6	0.9		2.7		19
27	1.08	15.5	0.9		3.7		20
28	1.07	15.6	1.0	2.2	3.8		20
29	1.17	15.4	0.9	2.3	3.8		22
30	1.17	15.6	0.9	2.3	5.1		22
32	1.17	14.0	1.8		3.9		24
33	1.06	13.9	1.9		3.9		23
36	1.09	13.9	2.0	2.2	3.9		25
38	1.15	15.8	1.4		4.3		25
39	1.19	15.7	1.4	2.2	4.4		26
41	1.20	15.9	1.5		5.3		23
42	1.19	15.8	1.5	2.2	5.3		27
43	1.27	16.0	1.5	2.3	5.4		25
44	1.35	15.8	1.5	2.2	6.3		27
46	1.14	14.0	1.6	2.2	3.9		18
48	1.15	14.1	2.8	2.2	3.9	3.2	20
49	1.13	14.2	2.8	2.2	3.7	5.0	22
50	1.12	14.1	3.8	2.2	3.7	5.0	22
51	1.14	14.1	3.8	2.2	3.7	7.3	24
52	1.10	13.7	1.5	2.3	3.8		23
53	1.08	15.9	1.6	2.1	3.7		15
54	1.04	15.8	1.6	3.1	3.7	3.1	21
55	1.08	16.0	2.1	3.2	3.8	6.3	24
56	1.10	16.2	2.9	2.2	3.9	5.1	22
57	1.11	16.1	3.7	2.2	3.9	5.1	21
58	1.10	16.3	3.7	2.2	3.8	7.3	23
59	1.10	16.1	1.5	2.3	3.8	5.0	29
60	1.15	16.0	2.7	2.3	3.9		36
61	1.15	16.0	1.6	2.2	3.8		41
62	1.11	14.1	2.7	2.2	3.7	8.7	28
63	1.12	14.2	3.7	2.2	3.9	8.7	28
64	1.10	14.2	3.7	2.2	3.9	10.9	31
65	1.12	13.8	2.5	2.3	4.0	5.2	28
66	1.12	15.7	2.6	2.4	4.0	6.1	27
67	1.15	12.0	2.2	2.4	4.0	3.7	22
68	1.15	12.0	2.2	2.3	4.0	5.5	25
69	1.15	12.0	2.9	2.3	4.0	5.5	27
70	1.15	12.0	2.9	2.4	4.0	5.5	25

After melting, the experimental steels of Table I were cast into ingots and forged into ¾ inch square bars. The bars were then annealed by heating to 1650° F. for two hours, furnace cooled at a rate of 25° F. per hour to 1300° F. and then air cooled to room temperature. As will be noted from the last column of Table I, the experimental steels, almost without exception, showed acceptable as-annealed hardness and, hence, are suitable for fabrication in the as-annealed condition.

Following forging and determination of annealed hard-

ness, 5/8 inch thick specimens were cut from the annealed bars and subjected to an austenitizing and tempering treatment to determine (1) the highest solution temperature which would not cause an excessive grain coarsening or incipient grain boundary melting but which would produce maximum hardening in the hardened and tempered steels, and (2) the approximate phase boundaries of the alloys at temperatures between 2000° and 2250° F. A knowledge of the latter characteristic was required in order to determine under what conditions alloy modifications might be necessary to counteract the undesirable formation of delta-ferrite due, in part, to the high chromium contents and relatively large amounts of the delta-ferrite promoters vanadium, tungsten, and molybdenum, which we have determined to be necessary in our steels to suit them for the intended purposes. Delta-ferrite is an undesirable constituent of our steels in that the two-phase structures resulting from the presence of even relatively small amounts of delta-ferrite do not achieve full hardness. Moreover, the presence in our martensitic steels of substantial amounts of retained austenite after quenching and tempering, is also undesirable for a similar reason, and for the further reason that retained austenite imparts dimensional instability.

Ideal steels for the applications contemplated herein would contain no retained austenite, but, practically, for most applications, some retained austenite can be tolerated. Such steels should not, however, contain in excess of about twenty percent retained austenite, as quenched, and, as a class, our steels contain less than that amount. Moreover, our steels are substantially free of delta-ferrite.

The excellent high temperature hardness retention of the steels of the invention will be more readily apparent by reference to Tables II and III wherein are set forth the results of tests in which a number of experimental steels, including the steels of this invention, were subjected to tempering treatments at various elevated temperatures. Experimental low chromium steels (e.g., about 12 to 14.5 percent chromium) are set out in Table II whereas the results set out in Table III pertain to steels of relatively higher chromium contents within our broad chromium range. In each of Tables II and III, the results of elevated temperature hardness tests on both cobalt-free experimental steels and the cobalt-containing steels of the invention are set out.

TABLE II

Hardness of Lower Chromium Experimental Steels After Austenitizing and Tempering for 2+2 Hours

Experimental Steel No.	Austenitizing Treatment		Rockwell "C" Hardness			
	Temp. (° F.)	Time (Min.)	As Quenched and Refrigerated (to -105° F.)	Tempering Temperature, ° F.		
				1,000	1,040	1,090
21 ¹	2,100	15	58	62	61	54
24 ¹	2,100	15	63	65	59	53
32 ¹	2,150	12	60	66	62	53
33 ¹	2,150	12	61	66	61	53
36 ¹	2,150	12	62	66	63	56
46 ¹	2,150	10	62	66	-----	57
52 ¹	2,100	15	62	66	65	56
48	2,200	10	61	65	64	60
49	2,200	10	61	65	65	60
50	2,250	7	59	64	62	60
51	2,200	10	60	64	63	60
62	2,200	10	57	64	-----	58
63	2,200	10	58	63	63	60
64	2,150	12	59	63	62	60
65	2,200	10	59	66	65	61
67	2,250	10	59	² 66	-----	-----
68	2,250	10	58	² 66	-----	-----
69	2,250	10	59	² 66	-----	-----

¹ Cobalt free steels.

² Tempered (1+refrigeration)+(1+refrigeration)+2 hours.

TABLE III

Hardness of Higher Chromium Experimental Steels After Austenitizing and Tempering for 2+2 Hours

Experimental Steel No.	Austenitizing Treatment		Rockwell "C" Hardness			
	Temp. (° F.)	Time (Min.)	As Quenched and Refrigerated (to -105° F.)	Tempering Temperature, ° F.		
				1,000	1,040	1,090
25 ¹	2,100	15	58	63	57	53
26 ¹	2,100	15	61	64	58	53
27	2,100	15	62	64	58	54
28 ¹	2,100	15	62	65	61	55
29 ¹	2,100	15	63	65	61	56
30 ¹	2,100	15	62	65	62	57
33 ¹	2,100	15	62	64	61	55
39 ¹	2,100	15	60	65	64	53
41 ¹	2,100	15	61	65	63	56
42 ¹	2,100	15	62	65	64	58
43 ¹	2,100	15	61	65	64	53
44 ¹	2,100	15	62	65	64	53
53 ¹	2,200	10	62	65	63	54
60 ¹	2,100	15	59	62	60	55
54	2,200	10	60	65	65	57
55	2,200	10	58	64	65	-----
56	2,200	10	59	64	63	58
59	2,100	15	54	62	62	59
66	2,200	10	59	65	63	59

¹ Cobalt free steels.

The high hardness retention of the steels of the invention is evident from the data of Tables II and III. The superiority, in this regard, of our steels over similar steels containing no cobalt is also apparent. Moreover, the superior hardness retention of our preferred steels, as compared with that of other steels within our broad range, will also be noted from the results in Table II.

FIG. 6, wherein Rockwell "C" hardness of representative steels of the invention and of several prior art steels commonly used in bearing construction is plotted against tempering temperature for 2+2 hours, graphically illustrates the high degree of utility of our steels for the intended purposes. Also plotted, as abscissa, is the tempering parameter

$$P = T(20 + \log t) \times 10^{-3}$$

where

T = temperature, ° R

t = time, hours

which thus combines the effect, upon the experimental steels, of temperature and time at the tempering temperature and is thus, when plotted against hardness, a good measure of the hardness retention capacity of the steels, i.e., their resistance to softening upon tempering.¹

It will be seen, by reference to FIG. 6, that the representative steel Nos. 65 and 66 have initial hardnesses which are equal to the high hardness tool steels AISI M-2 and M-50 and which are appreciably greater than the hardnesses of the prior art corrosion resistant stainless steels AISI 440C and 440C+Mo, the latter being commonly utilized in bearing construction. Moreover, our steels retain their high hardnesses even when tempered at greatly elevated temperatures. From FIG. 6, it is apparent that our steels are highly superior, in respect to hardness retention, to AISI 440C and 440C+Mo at all tempering temperatures and are substantially equal or only slightly inferior, in this respect, to AISI M-2 and M-50 up to temperatures of about 1100° F. Further, even above the 1100° F. tempering range our steels retain excellent hardnesses. This ability of our steels to retain exceptionally high hardnesses upon high temperature tempering makes them admirably suited for the contemplated applications, as bearing and hot-forming die construction, where minimum life expectancy of the part frequently must be at least 500 hours at temperatures of about 900° F.

¹ Hollomon, J. H., and Jaffe, L.C., Trans. AIME, 162, 75 223-249 (1945).

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Steels suitable for applications as bearings and the like must possess not only a high degree of resistance to loss of hardness upon prolonged exposure to elevated temperatures, but they must also possess good resistance to corrosion in order to give long service life under corrosive environmental conditions. In accordance with the objects of the invention, our steels provide excellent corrosion resistance, as well as high initial hardnesses and a high degree of hardness retention. This combination of properties has heretofore been unknown in the art.

The corrosion resistant properties of our steels are made apparent as the result of severe corrosion testing. For this purpose, a water vapor corrosion bath was utilized wherein one extremity of each of a number of flat strip specimens, measuring about 1/2 inch in width by about 1 1/2 inches in length, was cemented to a glass rod support, and the specimens were then positioned at an angle of 30° from the vertical, 8 inches from the top of a large plastic cylindrical container open at the lower end, the lower end of which was placed in a tray of water. The specimens were spaced from the water level a distance of about 12 inches. The water was heated by electrical resistors and the heating was continued for eight hours, during which time the specimens were surrounded by water vapor. At the end of the eight-hour testing period, the current to the resistors was turned off and the specimens allowed to remain in place for an additional sixteen hours. This cycle of eight hours wet and sixteen hours dry was repeated until visually observed corrosion was noted.

The specimens comprised a number of experimental steels, including those contemplated by the invention, as well as certain prior art stainless and tool steels.

FIG. 1 illustrates the results of a representative comparative test of certain experimental steels of the invention with certain of these prior art steels, the steels characterized therein by the letters A-F being identified, as to composition and heat treatment, in Table IV.

TABLE IV

Fig. No.	Steel Designation	Heat Treatment	Hardness After Heat Treatment
1-A-----	64-----	Austenitized at 2200° F., refrigerated and tempered (1+refrigeration) + 2 hours at 1000° F.	R _c 66
1-B-----	64-----	Austenitized at 2200° F., refrigerated and tempered (1+refrigeration) + 2 hours at 1100° F.	R _c 60
1-C-----	REX 49 ¹ -----	Austenitized at 2225° F., tempered 2+2 hours at 1050° F.	R _c 68
1-D-----	AISI 430 Stainless Steel	Annealed-----	R _b 84
1-E-----	65-----	Austenitized at 2200° F., refrigerated and tempered (1+refrigeration) + 2 hours at 1000° F.	R _c 64
1-F-----	65-----	Austenitized at 2200° F., refrigerated and tempered (1+refrigeration) + 2 hours at 1100° F.	R _c 59

¹ High Hardness, high speed steel containing about 1 percent carbon, 4 percent chromium, 2 percent vanadium, 6.5 percent tungsten, 3.5 percent molybdenum, 5.5 percent cobalt, balance iron. "REX" is the registered trademark of Crucible Steel Company of America.

From FIG. 1, it will be seen that our steels, represented by experimental steel Nos. 64 and 65, are substantially equal to AISI 430 stainless steel in respect to their resistance to corrosion by water vapor, and that they are markedly superior, in this respect, to the prior art low alloy, high temperature steel of FIG. 1-C.

FIG. 2 illustrates the results of another such water vapor corrosion test wherein the corrosion resistance of experimental steels, Nos. 65 and 66, is compared with that of AISI 430, an extremely corrosion resistant stainless steel, and with AISI 440 C + Mo, commonly used in the construction of bearings. The steels of FIG. 2 (A-

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F) are identified, as to composition and heat treatment, as set out in Table V.

TABLE V

Fig. No.	Steel Designation	Heat Treatment	Hardness After Heat Treatment
2-A-----	Experimental Steel No. 65	Austenitized at 2200° F., refrigerated and tempered (1+refrigeration) + (1+refrigeration) + 2 hours at 1000° F.	R _c 66
2-B-----	AISI 440 C+Mo	Austenitized at 2050° F., refrigerated and tempered (1+refrigeration) + (1+refrigeration) + 2 hours at 1000° F.	R _c 61
2-C-----	AISI 440 C+Mo	Austenitized at 1950° F., refrigerated and tempered (1+refrigeration) + (1+refrigeration) + 2 hours at 1000° F.	R _c 61
2-D-----	AISI 430-----	Annealed at 1500° F.	R _b 84
2-E-----	Experimental Steel No. 66	Same as 2-A-----	R _c 64
2-F-----	Experimental Steel No. 65	Same as 2-A-----	R _c 66

From FIG. 2, it will be noted that AISI 430 stainless steel is the most resistant of the tested steels to corrosive attack in the water vapor corrosion test, but that experimental steels, Nos. 65 and 66, are superior, in their corrosion resistance, to AISI 440 C + Mo. The duplicate 440 C + Mo test specimens of FIG. 2-B were subjected to substantially the same heat treatment as the test specimens of the experimental steels, whereas the heat treatment accorded the 440 C + Mo specimens of FIG. 2-C is one currently utilized in industry in the manufacture of bearings.

FIGS. 3-5 illustrate the results of further water vapor corrosion tests upon sample specimens of a number of experimental steels, prior art stainless, tool and bearing steels, the compositions and hardnesses of the tested steels being set out in Table VI.

TABLE VI

Fig. No.	Steel Designation	Austenitizing Temperature (° F.)
3-A-----	Experimental No. 38-----	2,100
3-B-----	Experimental No. 33-----	2,150
3-C-----	Experimental No. 36-----	2,150
3-D-----	Experimental No. 42-----	2,100
3-E-----	Experimental No. 41-----	2,100
3-F-----	Experimental No. 44-----	2,100
3-G-----	Experimental No. 39-----	2,100
3-H-----	Experimental No. 30-----	2,100
3-I-----	Experimental No. 43-----	2,100
3-J-----	AISI 430-----	Annealed
3-K-----	AISI 440C ¹ -----	1,900
3-L-----	Experimental No. 17+3 Co-----	2,150
3-M-----	AISI 440C ² -----	1,900
3-N-----	Experimental No. 27-----	2,100
3-O-----	Experimental No. 28-----	2,100
3-P-----	Experimental No. 29-----	2,100
4-A-----	Experimental No. 17+3 Co-----	2,150
4-B-----	Experimental No. 48-----	2,150
4-C-----	Experimental No. 54-----	2,150
4-D-----	Experimental No. 54-----	2,200
4-E-----	Experimental No. 49-----	2,150
4-F-----	Experimental No. 50-----	2,150
4-G-----	AISI 430 ³ -----	Annealed
4-H-----	AISI 440C ⁴ -----	1,900
4-I-----	Experimental No. 63-----	2,150
4-J-----	Experimental No. 63-----	2,200
4-K-----	Experimental No. 55-----	2,200
4-L-----	Experimental No. 49-----	2,200
5-A-----	AISI 440C ⁵ -----	1,900
5-B-----	Experimental No. 46-----	2,150
5-C-----	Experimental No. 52-----	2,100
5-D-----	Experimental No. 59-----	2,200
5-E-----	Experimental No. 60-----	2,100
5-F-----	REX 49 ⁶ -----	2,225
5-G-----	Experimental No. 56-----	2,200
5-H-----	Experimental No. 48-----	2,200
5-I-----	Experimental No. 62-----	2,150
5-J-----	Experimental No. 64-----	2,150
5-K-----	Experimental No. 53-----	2,200
5-L-----	Experimental No. 51-----	2,200

¹ Tempered for 1 hour at 400° F.

² Tempered for 1 hour at 900° F.

³ Air cooled.

⁴ Oil quenched and tempered for two hours at 400° F.

⁵ Tempered for two hours at 1100° F.

⁶ Composition same as for footnote ¹ of Table IV. Tempered for 2+2 hours at 1050° F.

Except as otherwise noted, the steel specimens of FIGS. 3-5 were oil quenched, refrigerated (-105° F.) and tempered for 2+2 hours at 1000° F.

Reference to FIGS. 3-5 will show the striking difference in corrosion resistance between the cobalt-free experimental steels and the cobalt-containing steels of the invention. Thus none of the cobalt-free experimental steels of FIG. 3 exhibited a corrosion resistance approaching that of AISI 430 or of AISI 440 C, whereas experimental steel number 17, with the addition of 3 percent cobalt, was only slightly inferior to these prior art corrosion resistant, steels. Each of the cobalt-containing steels illustrated in FIG. 4 is seen to be substantially equally as corrosion-resistant as AISI 430 and AISI 440 C. Moreover, from FIG. 5, it will be seen that, in the tests therein illustrated, our cobalt-containing steels proved to be generally superior, in respect to corrosion resistance, to AISI 440 C and markedly superior in that respect to the prior art, low alloy high hardness, elevated temperature steel of FIG. 5-F. The unexpected ability of cobalt to enhance the corrosion resistance of the experimental steels is strikingly illustrated by a comparison of the corrosion resistance exhibited by similar experimental steels with and without cobalt. For example, experimental steel number 36, containing 1.09 percent carbon, 13.9 percent chromium, 2.0 percent vanadium, 2.2 percent tungsten, 3.9 percent molybdenum, balance iron, is seen, in FIG. 3-C to be greatly inferior to AISI 430 and to AISI 440 C (400° F. temper) in respect to corrosion resistance. Experimental steel number 49, on the other hand, comprising 1.13 percent carbon, 14.2 percent chromium, 2.8 percent vanadium, 2.2 percent tungsten, 3.7 percent molybdenum, and containing, in addition, 5.0 percent cobalt, is seen, in FIG. 4-E, to possess a corrosion resistance only very slightly less than that of AISI 430 and AISI 440 C.

Corrosion resistance to various salts and chemicals is also a desirable attribute of metals for bearings, hot dies, and similar applications. The utility of our steels in this regard is illustrated by the results of copper chloride, copper sulfate and sodium chloride corrosion tests, as set out in Table VII.

manner with a test solution consisting of 4 grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 10 ml. concentrated H_2SO_4 in 90 ml. distilled water. The presence of copper deposits upon certain of the test specimens was indicative of dissolution of the specimen surface by electrochemical action, the dissolved iron passing into solution.

The salt spray tests reported in Table VII were conducted in accordance with the Salt Spray (Fog) Test No. B117-57T, described in American Society for Testing Materials Standards, 1958, Part III, except that room temperature was utilized. Strip specimens were used, as in the water vapor tests, and the tests were continued, in each case, for a period of two hours.

From Table VII, it is apparent that the steels of the invention are superior to AISI 440 C and superior or equal to AISI 440 C + Mo in their resistance to corrosive attack by copper chloride. Our higher chromium steels are to be preferred vis-a-vis their resistance to attack by corrosive chemical agents of the nature of copper chloride.

Table VII also shows that our steels are equal or superior to 440 C + Mo, but inferior to AISI 430 and 440 C in their ability to resist the corrosive attack of copper sulfate solutions. It will also be seen that our steels are equal or superior to the tested prior art steels, except AISI 430, in respect to resistance to corrosive attack by sodium chloride solutions.

The applications intended for the steels of the invention require that the steels possess a high room temperature hardness together with a high degree of hardness retention, at, e.g., about 900° to 1000° F. In this regard, we have found that increasing the carbon content of our steels, the other alloying elements remaining constant, increases the hardness retention somewhat. However, an increase of carbon content also results in an increase in the amount of retained austenite and, in general, decreases the forgeability of our steels. Consequently, we hold the carbon content of our steels between about 1 percent and about 1.3 percent, and preferably between about 1.05 or 1.10 percent and about 1.15 percent.

We have found that a minimum chromium content of

TABLE VII

Steel Designation	Surface Condition After Exposure		
	Copper Chloride (No. of pits under 1 drop)	Copper Sulfate	Sodium Chloride
AISI 430.....	1.....	Surface clean and clear.....	Surface clean and clear.
AISI 440C.....	60+.....	do.....	Superficial corrosion.
AISI 440C + Mo ¹	30+.....	Heavy copper deposit.....	Pitting corrosion.
Experimental steel No. 65 ²	16.....	Light copper deposit.....	Superficial corrosion.
Experimental Steel No. 66 ²	Several very small pits.....	do.....	Do.
Experimental Steel No. 67 ²	15-30+.....	Clear—heavy copper deposit.	

(¹) Heat treated as for commercial bearing application: Heated to 1950° F. For 45 minutes, oil quenched, refrigerated and tempered at 900° F. for 2+2 hours.

(²) Heated to 2200° F. for 10 minutes, oil quenched, refrigerated and tempered at 1000° F. for (1+refrigerated)+2 hours.

In the case of the copper chloride tests, one drop of the test solution, consisting of an aqueous solution containing 0.5 percent by weight of CuCl_2 , was placed upon the surface of each of the polished test specimens where it was left for a period of 30 minutes, after which the test solution was removed, the specimen washed and visually observed for incidence of pitting.

The copper sulfate tests were conducted in a similar

about 12 percent is required in our steels in order to confer a useful minimum degree of corrosion resistance. Thus, in Table VIII, are set out the visually observed results of a number of water vapor corrosion tests, as heretofore described, comparing the corrosion resistance of prior art steels with that of certain of both our higher chromium (Nos. 65 and 66) and our lower (Nos. 67-70) chromium steels.

TABLE VIII

Water Vapor Corrosion Tests

Steel Designation	Heat ¹ Treatment	Hardness	Water Vapor Corrosion	
			Surface Appearance	Spot Count ²
430 Stainless-----	A	R _h 84	Essentially unattacked.	2
440C -----	B	R _c 60	General attack over entire surface.	70
440C+Mo-----	C	R _c 61	Severe general surface attack.	-----
65-----	D	R _c 66	Slight attack around edges.	9
66-----	D	R _c 64	Essentially unattacked.	4
67-----	D	R _c 65/66	Moderate general surface attack.	-----
68-----	D	R _c 65/66	do-----	-----
69-----	D	R _c 65/66	do-----	-----
70-----	D	R _c 65/66	do-----	-----
REX 49 ³	E	R _c 68	Entire surface covered with large rust spots.	-----

¹ The heat treatments were as follows:

- A. Anneal.
 B. 1900° F., oil quench, and temper at 900° F. for 1 hour.
 C. 1950° F. for 45 minutes, oil quench, refrigerate to -105° F., tempered at 900° F. for 2+2 hours (present commercial practice).
 D. 2200° F., oil quench, immediately refrigerate to -105° F., and temper at 1000° F. for (1+refrigerate)+(1+refrigerate)+2 hours.
 E. 2225° F., oil quench and temper at 1050° F. for 2+2 hours.

² Number of pitted corrosion spots per square inch of exposed surface area, as averaged from two specimens.

³ Composition given in Table IV.

It will be observed, by reference to Table VIII, that, whereas all of the tested steels of the invention showed better corrosion resistance than all prior art steels except AISI 430 stainless steel, Experimental Steel Nos. 65 and 66, containing relatively larger amounts of chromium, i.e., 13.8 and 15.7 percent, respectively, exhibited corrosion resistance superior to that of steel Nos. 67-70 which contained 12 percent chromium. We have found this advantage of higher chromium, i.e., up to 17 percent to be offset, to some extent however, in our steels by the occurrence of higher percentages of retained austenite in higher chromium steels and a tendency toward the production of discontinuous grain coarsening upon austenitization. Moreover, we have found, as illustrated hereinabove in Tables II and III, that our lower chromium steels have generally higher hardnesses than do the steels containing chromium in the higher portions of our broad range. We have further found that holding the chromium content to between about 14 and about 16 percent significantly increases the temper resistance of our steels and also produces higher peak hardnesses. We have additionally found, however, that if a chromium content on the high side of the contemplated range is accompanied by appropriate increases in the carbon and molybdenum contents and, especially if tungsten and vanadium are added to the steels, excellent hardness retention is obtained. Accordingly, we prefer to utilize chromium in our steels in the limited range of about 13.5 or 14 percent to about 16 percent, but can usefully incorporate chromium up to about 17 percent, especially in conjunction with carbon and molybdenum on the high sides of their respective ranges, together with additions of tungsten and vanadium.

The addition to our steels of the carbide and the ferrite formers, vanadium and molybdenum, with and without tungsten, was found to increase the hardness of the steels generally. Moreover, each of these three elements was found to increase the temper resistance of our steels. Thus, we have found that additions of vanadium, in amounts of about 1.5 to 4.5 percent, confer beneficial hardness increases upon our steels and that retention of such hardness increases is most effective within the limited vanadium range of about 2.2 to 2.8 percent. Toward the high end of our broad vanadium range, and thereover, we have found that vanadium tends to shift the steels into the delta ferrite field.

We have found molybdenum to confer added hardness and hardness retention upon our steels when utilized in a minimum amount of about 2.5 percent. Additions of molybdenum in amounts greater than about 5 to 7 percent have, however, been found to produce no appreciable further benefits, and we accordingly limit molybdenum to about 7 percent, in our broad range and to about 4.25 to 5 percent in our more limited range.

Despite the above-mentioned advantages of the elements molybdenum and vanadium, we have further found that addition of these elements has an effect similar to that of chromium in enlarging the alpha field and hence in increasing the formation of the undesirable delta ferrite which, in amounts over about 2 percent, prevents development of full potential hardness of our steels. We have also found, however, that the addition of certain amounts of cobalt, as will be apparent herein-after, counteracts this undesirable effect of molybdenum and vanadium.

We have found that additions of tungsten, in amounts of at least about 1.5 percent and up to about 7 percent, and preferably about 2.0 to 2.5 or 3 percent, lends higher initial hardness and greater hardness retention to our steels.

The addition of the aforesaid limited amounts of vanadium, molybdenum and tungsten to our steels raises the effective chromium content vis-a-vis corrosion resistance. This is due, we believe, to the ability of these elements to form carbides in preference to chromium, thereby leaving a greater quantity of the latter element free to exhibit its corrosion-resistant properties.

Cobalt is also an essential element in our steels in that we have found it to promote solubilization of the complex chromium carbides at the austenitizing temperature, thereby promoting a more uniform distribution of residual carbides and making more carbon available for subsequent secondary hardening of our steels. We have also discovered that, in the presence of 10 percent or more of chromium, cobalt has a definite gamma-field broadening effect, thereby reducing undesirable delta ferrite formation. We have found that, in our carbon-vanadium-tungsten-molybdenum high temperature alloys containing about 12 to 17 percent chromium, the presence of cobalt has a pronounced effect in enhancing the corrosion resistance in our steels. Accordingly, we require, in our steels, an amount of cobalt effective to produce enhancement of corrosion resistance. Different applications, of course, require varying degrees of corrosion resistance, but, for most applications, e.g., for construction of bearings and the like, we find that about 3 percent and preferably about 4.5 percent of cobalt is effective to confer the desired benefits. Amounts of cobalt up to 15 percent confer useful enhancement of corrosion resistance, but in amounts over about 8 or 9 percent, cobalt tends to promote an increase in retained austenite in our steels, so we set 9 percent as a preferred upper limit of cobalt and, for certain applications, we prefer 6.5 percent as an upper limit for cobalt.

Our steels, especially within our preferred ranges, being substantially free of retained austenite, possess a high degree of dimensional stability—a prerequisite for materials of which bearings, dies, etc. are made.

Thus, the dimensionally stable character of the steels of the invention is illustrated by the results of dimensional stability tests, for the purposes of which, specimens of a number of experimental steels were prepared, having a diameter of $\frac{3}{8}$ inch, and a length of 4.000 plus or minus 0.001 inches, with the ends of the specimens ground to a hemispherical configuration. Precision length measurements were made with a Johansson comparator, to an accuracy of plus or minus 2.5 microinches per inch, both before and after heating of the specimens. The specimens were contained, while being heated, within closed and evacuated glass tubes. The results of a number of such tests are given in Table IX.

TABLE IX
Dimensional Stability Tests of Some Experimental Steels
Under Thermal Stress

Steel designation	Initial Hardness (Rc)	Length Change, microin./in.				Final Hardness (Rc)			
		500 Hours		1000 Hours		500 Hours		1000 Hours	
		600° F.	900° F.	600° F.	900° F.	600° F.	900° F.	600° F.	900° F.
44-----	65	-7	+33	-7	+63	65	64.5	65	64
48-----	66	-5	+6	+13	+36	66	65	66	65
53-----	66	-8	+1,170	-4	-----	66	65	66	-----
63-----	64	-9	+142	+13	-----	64	64	64	-----
65 ¹ -----	65	-13	-13	-28	+4	65	65	65	64
66-----	66	0	-254	-2	-----	66	65	66	65

¹ Conventionally tempered for 2+2 hours. All others tempered for (1+refrigeration)+ (1+refrigeration)+2 hours. All tempering was at 1000° F.

From Table IX it will be noted that only the cobalt-free steel No. 53 exhibited a degree of dimensional instability unacceptable for most purposes. It will be further noted from Table IX that the tested experimental steels exhibited high hardness retention at temperatures up to 900° F. for periods up to 1000 hours.

The steels of the invention also exhibit the high compressive yield strengths necessary for the intended applications. For example, Experimental Steel No. 66 showed an 0.2 percent offset compressive yield strength of 387,000 p.s.i. at room temperature, 357,000 p.s.i. at 600° F., 335,000 p.s.i. at 750° and 308,000 p.s.i. at 900° F.

Surprisingly, our steels, despite their high hardness, are relatively easily machined as compared to prior art steels. For example, when heat treated to sub-maximum hardnesses, comparable to that obtainable with AISI 440-C, our steels exhibit a distinct superiority in machinability. This property of our steels may be clearly seen by reference to Table X.

The drilling, in the tests exemplified in Table X, was accomplished with ¼ inch round, high speed drills, at a constant speed of 735 r.p.m. with a constant feed rate effected by a 14.5 round weight attached, across an 8 inch diameter pulley, to the drill head mechanism. The test samples were in the form of discs, ¾ to 1 inch in thickness, cut from bars forged from the test steel compositions.

TABLE X
Machinability of Experimental and Prior Art Steels

Test No.	Steel Designation	Hardness (Brinell)	Time to Drill ¼ inch Deep Hole (Minutes)					Machinability Index (Percent) ¹
			1	2	3	4	Average	
1.-----	No. 65-----	262	0.41	0.37	0.44	0.40	0.40	107
1.-----	AISI 440C-----	269	0.38	0.42	0.49	0.43	0.43	100
2.-----	No. 65-----	248	0.34	0.30	0.27	0.33	0.31	138
2.-----	AISI 440C (Modified) ² -----	248	0.36	0.34	0.39	0.42	0.38	113
3.-----	No. 65-----	248	0.32	0.42	0.45	0.40	0.40	105
3.-----	AISI 440C-----	241	0.48	0.33	0.41	0.44	0.42	100
4.-----	No. 65-----	255	0.38	0.30	0.27	0.40	0.33	127
4.-----	AISI 440C (Modified) ² -----	248	0.44	0.43	0.40	0.41	0.42	100

¹ Reciprocal of ratio of average time/time for AISI 440C (using the 0.43 minute value as standard).

² 1.06 carbon, 0.63 manganese, 0.31 silicon, 0.33 nickel, 14.04 chromium, 0.08 tungsten, 3.95 molybdenum, 0.02 cobalt.

The high hardnesses of our steels, together with their ability to retain high hardnesses when exposed for extended periods of time to high temperatures, plus their pronounced corrosion resistance, their high compressive yield strengths and their dimensional stability, admirably suit our steels to a variety of applications, as aforesaid, making possible the accomplishment of a multitude of constructional and operational facilities and products heretofore unknown.

What is claimed is:

1. A high temperature, corrosion resistant, alloy steel

consisting essentially of from about 1.0 to 1.3 percent carbon, 12 to 17 percent chromium, 1.5 to 4.5 percent vanadium, 1.5 to 7.0 percent tungsten, 2.5 to 7.0 percent molybdenum, 3 to 15 percent cobalt, up to about 2 percent each of silicon and manganese, and the balance iron.

2. A high temperature, corrosion resistant, alloy steel consisting essentially of from about 1.0 to 1.2 percent carbon, 13 to 16 percent chromium, 2 to 4 percent vanadium, 2 to 3 percent tungsten, 3.5 to 4.5 percent molybdenum, 4 to 9 percent cobalt, up to 2 percent each of silicon and manganese, and the balance iron.

3. A high temperature, corrosion resistant alloy steel consisting essentially of from about 1.05 to 1.15 percent carbon, 14.0 to 16.0 percent chromium, 2.2 to 2.8 percent vanadium, 2.0 to 2.5 percent tungsten, 3.75 to 4.25 percent molybdenum, 5.0 to 5.5 percent cobalt, up to 2 percent each of silicon and manganese, and the balance substantially all iron.

4. A high temperature, corrosion resistant alloy steel consisting essentially of from about 1.0 to 1.3 percent carbon, 12 to 17 percent chromium, 1.5 to 4.5 percent vanadium, 1.5 to 3.0 percent tungsten, 2.5 to 5 percent molybdenum, 3 to 9 percent cobalt, up to about 2 percent each of silicon and manganese, and the balance iron.

5. A high temperature, corrosion resistant alloy steel consisting essentially of from about 1.10 to 1.15 percent carbon, 13.5 to 16.0 percent chromium, 2.2 to 2.8 percent

vanadium, 2.0 to 2.5 percent tungsten, 3.5 to 4.5 percent molybdenum, 4.5 to 6.5 percent cobalt, up to about 2 percent each of silicon and manganese, and the balance iron.

6. A high temperature, corrosion resistant alloy steel consisting essentially of from about 1.10 to 1.15 percent carbon, 13 to 16 percent chromium, 2 to 4 percent vanadium, 2.0 to 2.5 percent tungsten, 3.5 to 4.5 percent molybdenum, 4 to 8 percent cobalt, up to 2 percent each of silicon and manganese, and the balance iron.

7. An alloy steel consisting essentially of from about

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1.0 to 1.3 percent carbon, 12 to 17 percent chromium, 1.5 to 4.5 percent vanadium, 1.5 to 3.0 percent tungsten, 2.5 to 5.0 percent molybdenum, from about 3 to 9 percent cobalt, balance substantially iron, said steel being characterized by a corrosion resistance superior to the cobalt-free alloy, a minimum hardness of about Rc 62 after tempering for 4 hours at 1000° F., and the retention of at least said minimum hardness after exposure for 500 hours of a temperature of 900° F.

8. A bearing member comprising a high temperature, corrosion resistant alloy steel consisting essentially of from about 1.0 to 1.3 percent carbon, 12 to 17 percent chromium, 1.5 to 4.5 percent vanadium, 1.5 to 3 percent tungsten, 2.5 to 5.0 percent molybdenum, 3 to 9 percent cobalt, up to about 2 percent each of silicon and manganese, and the balance iron.

9. A corrosion resistant article for prolonged service at temperatures up to about 900° F., comprising an alloy steel consisting essentially of from about 1.05 to 1.15 percent carbon, 13 to 16 percent chromium, 2 to 4 percent vanadium, 3.5 to 4.5 percent molybdenum, 2.0 to 2.5

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percent tungsten, 4 to 8 percent cobalt, up to about 2 percent each of silicon and manganese, and the balance iron.

10. A corrosion resistant article for elevated temperature service comprising a substantially martensitic alloy steel consisting essentially of from about 1.0 to 1.2 percent carbon, 13 to 16 percent chromium, 2 to 4 percent vanadium, 3 to 5 percent molybdenum, 1.5 to 3 percent tungsten, 3 to 8 percent cobalt, balance substantially all iron, said article being characterized by a substantial freedom from dimensional instability with change in temperature, by being heat treatable to a minimum hardness of about Rc 64 and by retaining at least said minimum hardness after exposure to temperatures up to about 900° F. for periods up to 500 hours.

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