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[54] **PRECIPITATION-HARDENABLE CHROMIUM-NICKEL STAINLESS STEEL**
15 Claims, No Drawings

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[56] **References Cited**

UNITED STATES PATENTS

2,932,568	4/1960	Kegerise	75/125
2,482,096	9/1949	Clarke	75/125
2,784,083	3/1957	Linnert	75/125
2,784,125	3/1957	Clarke	75/125
2,848,323	8/1958	Harris	75/125
2,850,380	9/1958	Clarke	75/125
3,306,736	2/1967	Rundell	75/128.5
3,401,036	9/1968	Dulis	75/125
2,797,993	7/1957	Tanczyn	75/125

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ABSTRACT: Martensitic precipitation-hardenable chromium-nickel stainless steel of high-impact strength. The steel comprises about 10 percent to 17 percent chromium, about 3.7 percent to 10 percent nickel, with or without about 2.5 percent to 5 percent copper, 0.01 percent to 0.06 percent carbon, manganese not exceeding 0.50 percent, silicon not exceeding 0.15 percent, phosphorus not exceeding 0.30 percent, sulphur not exceeding 0.020 percent, nitrogen not exceeding 0.025 percent, with or without columbium up to about 0.25 percent and with or without titanium up to about 0.15 percent, and remainder substantially all iron. Where the chromium content exceeds 13 percent and copper is present in the amount of about 2.5 percent to 5 percent, at least three of the four ingredients manganese, silicon, sulphur and nitrogen are further limited: the manganese to 0.30 percent max., silicon 0.10 percent max. and each of sulphur and nitrogen 0.010 percent max.

PRECIPITATION-HARDENABLE CHROMIUM-NICKEL STAINLESS STEEL

As a matter of introduction, my invention is concerned with the precipitation-hardenable chromium-nickel steels and with a variety of articles, products, apparatus and equipment comprising such steels.

One of the objects of my invention is the provision of a chromium-nickel stainless steel which is substantially fully martensitic and is peculiarly suited to high-temperature applications over prolonged periods of time without encountering losses of strength, ductility and toughness, and especially without undue sacrifice of impact strength.

Another object is the provision of a precipitation-hardenable chromium-nickel martensitic stainless steel which readily may be melted to desired specification, which handles well in the hot-mill and the cold-mill, which readily lends itself to a variety of forming and shaping operations and yet which may be hardened by simple treatment at rather modest temperatures to give desired hardness and strength yet with retained ductility and impact strength over prolonged periods of use.

A further object is the provision of a precipitation-hardenable martensitic chromium-nickel stainless steel of good sustained impact strength which readily lends itself to the production of bar, rod and wire, as well as to the production of plate, sheet, strip and other converted forms, in addition to the production of castings and forgings of desired size and shape.

A still further object of my invention is the provision of a precipitation-hardenable chromium-nickel stainless steel which in cast, forged or machined form is peculiarly suited to the production of jet engine compressor blades, discs, bearings, and the like and which in such form, moreover, is suited to the production of drive shafts and scram mechanisms of atomic reactors, and which in the form of sheet and strip is peculiarly suited to the production of frames and skin of supersonic aircraft.

Other objects in part will be readily apparent and in part particularly pointed to in the description which follows.

My invention, in short, resides in the combination of elements and in the relation between the same, all as more particularly described herein, the scope of the application of which is set out in the claims at the end of this specification.

BACKGROUND OF THE INVENTION

Now as an aid to a better understanding of my invention, it may be noted at this point that the precipitation-hardenable chromium-nickel stainless steels are pretty well established at this date. And they are widely accepted in the art. Much of the practical advantage enjoyed by the steels derives from the circumstance that in one condition of heat treatment (in solution-treated or annealed condition) they are comparatively soft and ductile and readily lend themselves to forming and shaping in the fabrication of a host of articles of ultimate use. And that when so formed and shaped the steel and articles are hardened and strengthened by simple precipitation-hardening treatment, that is, heating at modest temperatures.

Typical of the known and used precipitation-hardenable steels is the copper-bearing chromium-nickel stainless steel essentially consisting of about 17 percent chromium, about 4 percent nickel, about 3.5 percent copper, with carbon not exceeding about 0.10 percent, and remainder iron, this being the subject of my prior U.S. Letters Patent 2,482,096 entitled Alloy and Method. Another is the aluminum-bearing chromium-nickel stainless steel essentially consisting of about 17 percent chromium, about 7 percent nickel, about 1 percent aluminum, with a carbon content not exceeding about 0.10 percent, and remainder iron. A further aluminum-bearing steel essentially consists of about 15 percent chromium, about 7 percent nickel, about 2 percent molybdenum, about 1 percent aluminum, with a carbon content not exceeding 0.10 percent, and remainder iron. Another aluminum-bearing steel contains about 13 percent chromium, about 8 percent nickel, about 2 percent molybdenum, about 1 percent aluminum, with carbon not exceeding 0.10 percent, and remainder iron. There, too, is the known titanium-bearing chromium-nickel stainless steel essentially consisting of about 18 percent chromium, about 8 percent nickel, about 1 percent titanium, and remainder iron, and the further titanium-bearing steel essentially containing about 12 percent chromium, about 9 percent nickel, about 2.5 percent copper, about 1.2 percent titanium, and remainder iron.

The several aluminum-bearing, copper-bearing and titanium-bearing chromium-nickel stainless steels of the prior art are variously possessed of a combination of strength, ductility, workability and hardenability which peculiarly suits one steel to one application and other steels to others. Unfortunately, however, none of these steels is entirely satisfactory under all conditions of use, and particularly none is satisfactory in prolonged use at temperatures on the order of 650° F., or even temperatures on the order of 550° F. I find that under prolonged use at elevated temperatures these various steels suffer a loss of ductility and impact strength; they become brittle.

Accordingly, it is an object of my invention to provide a precipitation-hardenable chromium-nickel stainless steel which, while readily lending itself to melting and subsequent conversion into bars, rods and wire or into plate, sheet and strip, or even to the production of castings and forgings, lends itself to a variety of known and accepted forming and fabricating procedures, is substantially fully martensitic and is possessed of a combination of strength and ductility in the hardened condition and, moreover, is possessed of a ductility and resistance to impact which are retained throughout long periods of use at elevated temperatures.

SUMMARY OF THE INVENTION

Turning now to the practice of my invention, I provide a chromium-nickel martensitic stainless steel in which the chromium and nickel contents are properly correlated one to the other and which essentially requires the presence of a small but critical amount of carbon. The steel, moreover, essentially requires that the silicon found in all chromium-nickel stainless steels be maintained at a critically low value. And the best steel also contains copper in substantial amount. In my steels a best combination of properties is had where the manganese content, an ingredient also found in virtually all chromium-nickel stainless steels, is maintained at a critically low value, along with a critically low sulfur content. The phosphorus and nitrogen contents, two further ingredients commonly found in all chromium-nickel stainless steels, likewise are best maintained at critically low amount. The steel is substantially fully martensitic with any austenite ordinarily not over some 4 percent or 5 percent by volume. Even with unusually high temperatures of precipitation-hardening treatment, that is, about 1150° F., the austenite does not exceed some 10 percent or 12 percent; certainly it is less than 15 percent.

In my steels I find particular advantage in the inclusion of the ingredient columbium in small critical amounts, columbium being especially beneficial where the carbon content is at a minimum. Titanium also may be included in the composition, where desired.

More particularly, the precipitation-hardenable chromium-nickel stainless steel according to my invention in preferred broad aspect essentially consists of about 10 percent to about 17 percent chromium, about 3.7 percent to about 10 percent nickel, about 2.5 percent to about 5 percent copper, about 0.01 percent to about 0.06 percent carbon, particularly about 0.02 percent to about 0.05 percent carbon, with a silicon content not exceeding 0.40 percent and for best results not exceeding 0.15 percent or even not exceeding 0.10 percent, and remainder substantially all iron. For best results the manganese present in the steel is maintained at a value not exceeding 0.10 percent and certainly at a value not exceeding 0.40 percent or 0.50 percent. The phosphorus content is maintained at a value not exceeding 0.030 percent, preferably not exceeding 0.020 percent or even 0.010 percent, with sulfur not exceeding 0.020 percent, preferably not exceeding 0.005 percent or 0.010 percent. And in the best steel nitrogen should not exceed 0.010 percent; certainly, it should not exceed 0.025 percent. In my steel there may be present the ingredient columbium, this in amounts up to about 0.25 percent, and/or titanium, this in amounts up to about 0.15 percent. For I find, as more fully described hereinafter, that both columbium and titanium employed in small amount lend something to tensile strength without at the same time sacrificing ductility and resistance to impact.

For certain applications I omit copper as a necessary and essential ingredient of my steel, this being accompanied by some sacrifice in strength for a given heat treatment. The copper-free precipitation-hardenable chromium-nickel stainless steel, while of approximately the same chromium and nickel contents, actually contemplates about 10 percent to about 12 percent or 15 percent chromium, about 4.5 percent to about 9.5 percent nickel, with a carbon content of 0.01 percent to 0.05 percent, manganese not exceeding 0.30 percent, silicon not exceeding 0.15 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.015 percent, and remainder substantially all iron.

In my steel the ingredients chromium, nickel, carbon, silicon, sulfur and nitrogen are highly critical, for I find that when the amount of any one of these is significantly departed from, the desired combination of properties is not had. Where the chromium content falls below 10 percent, the corrosion-resisting properties of the steel immediately suffer. And where it rises above about 15 percent, and certainly where it rises above about 17 percent, delta-ferrite is introduced and the hot workability of the metal directly suffers. Moreover, the steel becomes brittle, with loss of impact strength following prolonged use at elevated temperature, this as more fully pointed to hereinafter; the best steels having a chromium content not exceeding about 13 percent. Similarly, I recognize sharp criticality in the silicon content of my steel, for I find that where silicon exceeds 0.40 percent it becomes objectionably brittle. And even where silicon exceeds 0.15 percent of even 0.10 percent, there is an inclination toward embrittlement following long, sustained use at elevated temperature. In general, the same may be said with respect to sulfur. The sulfur content of my steel should not exceed 0.020 percent, and for best results, should not exceed 0.005 percent, for with a sulfur content exceeding 0.005 percent and certainly with a sulfur content exceeding 0.010 percent, the metal is inclined to become brittle under sustained elevated-temperature use.

While the manganese content of my steel is not as sensitive as the silicon content, yet I find that manganese should not exceed 0.50 percent, and for best results should not exceed 0.10 percent, for otherwise there is a loss of ductility and gain in brittleness following sustained elevated-temperature duty. In general, the same may be said with respect to the nitrogen content of my steel, for where nitrogen exceeds 0.015 percent, or even where it exceeds 0.010 percent, brittleness is detected and impact values suffer.

The carbon content of my steel must not exceed 0.06 percent, and for best results is maintained at a value not exceeding 0.05 percent, for otherwise the steel becomes too stable. In order to assure desired transformation and precipitation-hardening effect the 0.06 percent figure and preferably the 0.05 percent figure must not be exceeded. Moreover, with an excess of carbon there is noted a brittleness following prolonged use at high temperatures. A small critical amount of carbon, however, is essential to the steel of my invention, for with a carbon content less than 0.01 percent, and even less than about 0.03 percent, I note the presence of delta-ferrite and a loss of strength as well as a loss of impact resistance.

While neither columbium nor titanium is essential to the steel of my invention, for a best combination of properties I include one or both of columbium in amounts up to about 0.25 percent and titanium in amounts up to about 0.15 percent. These, too, are critical because where the columbium is in excess of about 0.25 percent and/or the titanium is in excess of about 0.15 percent brittleness seems to appear with prolonged elevated-temperature use.

In my steel the ingredient copper, while important to certain applications of the steel where maximum strength in the precipitation-hardened condition is required, seems to have little or no effect on brittleness. Copper, where employed, however, should not be less than about 2.5 percent, for otherwise its effect is of little notice, and should not exceed about 5 percent, for otherwise the steel suffers in the hot-mill.

In the steel of my invention nickel of course is a necessary and essential ingredient, as pointed to above. In the copper-bearing steel the nickel content should not be less than about 3.7 percent, for with a lesser nickel content delta-ferrite appears and the hot-working properties suffer. As well, the cold-workability and formability suffer as a result of a loss of ductility. In this steel the nickel content should not exceed about 10 percent, for with an excess of nickel the metal becomes fully austenitic and not subject to precipitation-hardening treatment. In the copper-free chromium-nickel steel of my invention a somewhat higher nickel content is employed, the nickel there ranging from about 4.5 percent to about 9.5 percent, with chromium ranging from about 10 percent to about 12 percent or even to about 15 percent. A nickel content less than about 4.25 percent results in a sacrifice of the working and forming characteristics as noted, and a nickel content exceeding about 9.5 percent results in a steel not subject to precipitation hardening.

The ingredient nitrogen, as noted above, should not exceed 0.025 percent and preferably should not exceed 0.010 percent. For with an excess of nitrogen the structural balance is upset; the metal is inclined to retain too much austenite, the hot-working characteristics are adversely affected, and the metal becomes brittle and the impact strength immediately suffers.

Where the chromium content of the steel exceeds 13 percent, I find that it becomes necessary to further restrict at least three of the four ingredients manganese, silicon, sulfur and nitrogen in order to achieve the desired retained impact strength. The further limiting figure for the manganese content is 0.30 percent max., that for silicon is 0.10 percent max., and that for each of sulfur and nitrogen is 0.010 percent max., all as more particularly pointed to hereinafter.

The steel of my invention conveniently is melted in the vacuum furnace, although, where desired, it may be melted in the electric arc furnace. I find, however, that where I melt the steel in the electric arc furnace considerable care is required in the selection of raw materials in order to enjoy the required low contents of silicon, manganese, nitrogen, sulfur and even carbon. As a practical matter, the steel is best melted in the vacuum furnace or in the electric arc furnace with subsequent remelt in the vacuum furnace. In any event, the steel is suitably produced in the form of ingots, billets or slabs which are readily converted in the mill through appropriate hot- and cold-working operations into plate, sheet and strip, or into bars, rods and wire of desired specification. Of course, the steel lends itself to forging from suitable forging stock. Or it may be cast into articles of desired size and configuration.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

One steel according to my invention essentially consists of about 11 percent to about 16 percent chromium, about 4 percent to about 8 percent nickel, about 3 percent to about 4 percent copper, 0.02 percent to 0.05 percent carbon, with manganese not exceeding 0.30 percent, silicon not exceeding 0.15 percent, and remainder substantially all iron. In this steel phosphorus is in an amount not exceeding 0.020 percent and sulfur and nitrogen each is of a value not exceeding 0.010 percent. Where desired, there may be included columbium in amounts up to about 0.25 percent and/or titanium up to about 0.15 percent. A somewhat better steel, that is, a steel enjoying a better combination of properties, essentially consists of about 11 percent to about 15 percent chromium, about 4.5

percent to about 7.5 percent nickel, about 2.5 percent to about 5 percent copper, with 0.03 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur and nitrogen each not exceeding 0.010 percent, up to about 0.25 percent columbium, and remainder substantially all iron. This steel enjoys a good combination of tensile strength and impact strength, with minimum embrittlement over prolonged periods of use at elevated temperatures.

A further preferred steel essentially consists of about 12 percent to about 16 percent chromium, about 4 percent to about 7 percent nickel, about 3 percent to about 4 percent copper, 0.03 percent to 0.04 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.15 percent, phosphorous not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.010 percent, and remainder substantially all iron. Such a steel suffers very little embrittlement with prolonged use at high temperatures, as more fully appears hereinafter.

The steel which perhaps enjoys the best combination of tensile strength and ductility, which properties are retained through prolonged use at elevated temperatures, essentially consists of about 11 percent to about 13 percent chromium, about 5 percent to about 7 percent or about 8 percent nickel, about 2.5 percent to about 5 percent copper, 0.02 percent to 0.05 percent and preferably 0.01 percent to 0.035 percent carbon, with manganese and silicon each not exceeding 0.10 percent, and preferably sulfur not exceeding 0.010 percent, with remainder substantially all iron. In a more preferred form of this steel columbium is present, this in the amount of about 0.10 percent to about 0.25 percent. In somewhat more specific composition such a steel essentially consists of chromium about 10.5 percent to about 11.5 percent or about 11.5 percent to about 12.5 percent, with nickel about 5.75 percent to about 8.5 percent for the one and about 5.75 percent to about 6.25 percent for the other, about 3 percent to about 4 percent copper, 0.03 percent to 0.05 percent carbon, manganese and silicon each not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent and preferably not exceeding 0.005 percent, nitrogen not exceeding 0.010 percent, and remainder substantially all iron. In this steel columbium preferably is included, this in the amount of about 0.05 percent to about 0.25 percent, for I find that with this addition the tensile strength is noticeably improved, as more particularly noted below.

A steel enjoying a combination of tensile strength and impact strength adequate for many applications essentially consists of about 10 percent to about 12.5 percent or 13 percent chromium, about 4 percent or 5 percent to about 9 percent nickel, about 2.5 percent to about 5 percent copper, 0.02 percent or 0.03 percent up to 0.05 percent carbon, manganese not exceeding 0.50 percent and preferably not exceeding 0.10 percent, silicon not exceeding 0.40 percent and preferably not exceeding 0.10 percent, phosphorus not exceeding 0.030 percent, sulfur not exceeding 0.020 percent, nitrogen not exceeding 0.015 percent, and remainder substantially all iron. Such a steel may be melted in the electric arc furnace.

While the several preferred steels of my invention described above enjoy a best combination of tensile and impact strengths, with substantial freedom from embrittlement over sustained periods of use at elevated temperatures. I find that for certain applications a lesser strength is adequate. A preferred precipitation hardening chromium-nickel stainless steel which enjoys a combination of good tensile strength and good impact strength with little or no embrittlement under prolonged use at elevated temperatures is free of the ingredient copper, that is, in such a steel I make no purposeful addition of copper. This steel in broad view essentially consists of about 10 percent or 11 percent to about 15 percent chromium, about 4.5 percent to about 9.5 percent nickel, more particularly about 5 percent to about 6 percent nickel, 0.01 percent or even 0.02 percent to 0.05 percent carbon, manganese not exceeding 0.30 percent, particularly not exceeding 0.10 percent, silicon not exceeding 0.15 percent, especially not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent or 0.030 percent, sulfur not exceeding 0.010 percent, preferably not exceeding 0.005 percent, with nitrogen not exceeding 0.015 percent and preferably not exceeding 0.010 percent, and remainder substantially all iron. In this steel columbium may be present, this in amounts up to about 0.25 percent. A best preferred steel of good tensile strength and good sustained impact strength essentially consists of about 10 percent to about 12 percent chromium, about 4.5 percent to about 9.5 percent nickel, 0.02 percent to 0.05 percent carbon, manganese and silicon each not exceeding 0.20 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.005 percent, nitrogen not exceeding 0.010 percent, and remainder substantially all iron.

As particularly illustrative of the steels of my invention and the critical character of the chemical composition as that composition relates to the tensile strength and resistance to embrittlement under conditions of prolonged use at elevated temperatures, I give below a series of chromium-nickel-copper stainless steels of closely related chemical compositions. Some of these steels answer to the requirements of my invention while others of rather similar composition differ therefrom. This difference is reflected in a critical difference in properties.

A series of chromium-nickel-copper stainless steels with chromium ranging from about 11 percent to about 17 percent, nickel from about 4 percent to about 8 percent, and copper about 3 percent, is given below in table I(*a*); and their tensile properties and resistance to embrittlement as determined by the accelerated test of resistance to impact at room temperature following exposure for 500 hours at 800° F. are set forth in table I(*b*).

TABLE I(A).—CHEMICAL COMPOSITION OF NINE CHROMIUM-NICKEL-COPPER STAINLESS STEELS

	C	Mn	P	S	Si	Cr	Ni	Cb	Cu	N
Heat No.:										
344 [1]	.040	.01	.007	.008	<.10	11.24	7.37	.04	2.21	.007
347 [2]	.037	<.02	.009	.005	.04	15.09	4.69	.04	3.20	.005
348 [2]	.044	.35	.009	.009	<.10	16.17	4.24	.05	3.19	.007
349 [2]	.042	<.01	.008	.008	<.10	14.10	6.17	.04	3.29	.007
350	.040	.02	.009	.005	.63	16.28	4.38	.04	3.19	.010
351 [1]	.038	<.01	.008	.006	<.10	12.64	7.54	.19	3.24	.007
353 [2]	.040	<.10	.008	.007	<.10	14.03	5.93	.20	3.29	.005
354 [2]	.041	<.10	.008	.007	<.10	13.95	6.00	.15	3.30	.006
355 [2]	.052	.02	.009	.006	.04	16.02	4.38	.04	3.23	.006

[1] Steels according to the invention enjoying a best combination of properties.
[2] Steels according to the invention.

The mechanical properties of the steels of table I(*a*) in the precipitation-hardened condition, that is, solution-treated at 1900° F., oil quenched, hardened by reheating at 1100° F. and cooling, both prior to exposure to elevated-temperature test and following exposure for 500 hours at a temperature of 800° F., are given below in table I(*b*). In addition to ultimate tensile strength in kilopounds per square inch, 0.2 percent yield strength in kilopounds per square inch, percent reduction in area, and percent elongation in 2 inch, there are given Charpy V-notch impact strength in ft.-lbs. as well as Rockwell hardness on the C-scale, both prior to exposure and following exposure at 800° F. for 500 hours. In some instances the impact strength following exposure at 800° F. for 1,000 hours is given.

TABLE I(b).—TENSILE PROPERTIES AND IMPACT STRENGTHS OF THE STEELS OF TABLE I(a)

	Comparative tensile prop.		Impact strength		
	No exp.	500-hr. exp.	No exp.	500-hr. exp.	1,000-hr. exp.
Heat No.:					
344: [1]					
Ult., k.s.i.	139	141	125/123	125/121	118/107
Yld., k.s.i.	106	124			
Percent R.A.	64.6	64.0			
Percent elong.	20.0	21.0			
Hard.	C30	C31			

TABLE I(b).— Continued

TENSILE PROPERTIES AND IMPACT STRENGTHS OF THE STEELS OF TABLE I(a)

	Comparative tensile prop.		Impact strength		
	No exp.	500-hr. exp.	No exp.	500-hr. exp.	1,000-hr. exp.
347: [2]					
Ult., k.s.i.	134	152			
Yld., k.s.i.	122	146			
Percent R.A.	68.0	58.0	172/162	112/112	----------
Percent elong.	21.0	18.0			
Hard.	C28	C32			
348: [2]					
Ult., k.s.i.	135	161			
Yld., k.s.i.	119	154			
Percent R.A.	69.0	57.7	182/173	113/97	----------
Percent elong.	20.0	18.5			
Hard.	C28	C34			
349: [2]					
Ult., k.s.i.	138	147			
Yld., k.s.i.	105	133			
Percent R.A.	67.5	62.0	177/176	119/119	106/101
Percent elong.	20.0	21.5			
Hard.	028	C32			
350:					
Ult., k.s.i.	140	162			
Yld., k.s.i.	123	155			
Percent R.A.	63.7	54.0	171/151	58/59	----------
Percent elong.	18.5	17.0			
Hard.	C29	C35			
351: [1]					
Ult., k.s.i.	146	140			
Yld., k.s.i.	125	123			
Percent R.A.	64.0	67.2	146/137	122/127	109/108
Percent elong.	20.0	23.0			
Hard.	C30	C32			
353: [2]					
Ult., k.s.i.	143	151			
Yld., k.s.i.	114	138			
Percent R.A.	69.5	63.0	169/169	121/122	87/90
Percent elong.	21.0	21.0			
Hard.	C29	C33			
354: [2]					
Ult., k.s.i.	141	152			
Yld., k.s.i.	115	138			
Percent R.A.	68.0	62.0	150/144	120/118	95/89
Percent elong.	21.0	20.0			
Hard.	C30	C34			
355: [2]					
Ult., k.s.i.	140	162			
Yld., k.s.i.	118	153			
Percent R.A.	62.6	52.0	143/151	78/89	----------
Percent elong.	18.5	16.5			
Hard.	C30	C34			

[1] Steels according to the invention enjoying a best combination of properties.

[2] Steels according to the invention.

In reviewing the test data presented above in table I(b), particularly the impact strength results, it will be seen that the 11 percent chromium steel of Heat No. 344 (11.24 percent chromium, 7.37 percent nickel, 3.21 percent copper, 0.040 percent carbon, 0.01 percent manganese, 0.007 percent phosphorus, 0.008 percent sulfur, silicon less than 0.10 percent, 0.007 percent nitrogen, and balance iron) suffers no loss in tensile properties as a result of the accelerated embrittlement test of 500 hrs. at 800° F. Moreover, the steel suffers no loss in impact strength. The test results show that the impact strength of 125/123 ft.-lbs. Charpy V-notch prior to exposure at elevated temperatures remains virtually the same, namely 125/121 ft.-lbs. following the 500-hr. exposure at 800° F. Upon exposure for an additional 500-hr. period, giving a total exposure of 1,000 hrs., the impact strength drops somewhat, namely, to 118/107 ft.-lbs.

A steel of good retained impact strength but in which some loss nevertheless is observed is the 15 percent chromium steel of Heat No. 347 (15.09 percent chromium, 4.69 percent nickel, 3.20 percent copper, 0.037 percent carbon, less than 0.02 percent manganese, 0.009 percent phosphorus, 0.005 percent sulfur 0.04 percent silicon, 0.005 percent nitrogen, and remainder iron). That steel, having an impact strength of 172/162 ft.-lbs. prior to exposure, retains a strength of 112/112 ft.-lbs. following the 500-hour exposure. The same may be said for the 16 percent chromium steel of Heat No. 348, suffering a loss of impact strength from 182/173 ft.-lbs. at no exposure to 113/97 ft.-lbs. following exposure, and also for the 16 percent chromium steel of Heat No. 355. That steel is seen to have an impact strength of 143/151 ft.-lbs. with no exposure, a value which falls to 78/89 ft.-lbs. with 500-hour exposure at 800° F.

It is my view that the lowering of impact strength of the steels of Heat Nos. 347, 348 and 355 following prolonged treatment at elevated temperature may be attributed to the somewhat higher chromium content, this as compared with the steel of Heat No. 344. It is my view that chromium in a measure works against the bond existing between the molecules of chromium and iron making up the steel, for electron-micro examination of the steel at some 20,000× reveals something in the steel which is subject to embrittlement which does not appear in the steel which is free of embrittlement.

None of the steels of table I(a) as reflected by their impact strengths as given in table I(b) seems to be particularly sensitive with regard to the ingredient nickel. Any difference, however, seems to be in favor of the steels of the higher nickel contents, the 6 percent nickel steel of Heat No. 349 (14.10 percent chromium, 6.17 percent nickel, 3.29 percent copper, 0.042 percent carbon, less than 0.01 percent manganese, 0.008 percent phosphorus, 0.008 percent sulfur, less than 0.10 percent silicon, 0.007 percent nitrogen and remainder iron) revealing a retained impact strength of 119/119 ft.-lbs. after 500 hours (initial impact strength 177/176 ft.-lbs.) as compared to the lower retained impact strength after 500 hours, namely, 113/97 ft.-lbs. of the 4 percent nickel steel of Heat No. 348 (initial impact strength 182/173 ft.-lbs.).

I find that silicon is a potent factor working toward embrittlement with elevated-temperature use. The 0.60 percent silicon steel of Heat No. 350 (16.28 percent chromium, 4.38 percent nickel, 3.19 percent copper, 0.040 percent carbon, 0.02 percent manganese, 0.009 percent phosphorus, 0.005 percent sulfur, 0.63 percent silicon, 0.010 percent nitrogen, and remainder iron), having an impact strength of 171/151 ft.-lbs. prior to exposure, retains only a strength of 58/59 **ft.-lbs. following** 500-hour exposure at 800° F. A comparison between the 0.60 percent silicon steel of Heat No. 350 with the 0.10 percent silicon steel of Heat No. 348 of substantially the same chemical composition except for silicon contents, immediately suggests that the great loss in retained impact strength of the high-silicon steel derives from the high silicon content. And although the tensile properties differ little between the two steels either before or following the 500-hour treatment at elevated temperature, the loss in impact strength makes the high-silicon steel of Heat No. 350 unsuited to elevated-temperature applications. It is not a steel according to my invention.

In my steel the presence of a small amount of columbium seems desirable. Compare, for example, the 14 percent chromium, 6 percent nickel steels of Heat Nos. 353 and 354, with a columbium content of 0.20 percent for the one and 0.15 percent for the other, with the 14 percent chromium, 6 percent nickel steel of Heat No. 349, with residual columbium of 0.04 percent. While all enjoy fairly good retained impact strengths following prolonged treatment at elevated temperatures, it is the steels of the purposeful columbium additions (Heat Nos. 353 and 354) which have somewhat better retained tensile strengths (about 151 K s.i. ultimate strengths and 138 K s.i. yield strengths as compared to 147 K s.i. ultimate strength and 133 K s.i. yield strength). And, here again, it is the steel of the somewhat lower chromium content, Heat No. 351, with chromium 12.64 percent, as compared to the steel of Heat No. 353, with a chromium content of 14.03 percent, which has the somewhat better retained impact strength after prolonged treatment at elevated temperature, notably 109/108 ft.-lbs. following a 1,000-hour treatment at 800° F. as compared to 87/90 ft.-lbs. At the same time it may be noted that the low-chromium, high-nickel steel of Heat No. 351, with purposeful columbium addition, differs little from the low-chromium low-nickel steel with residual columbium of Heat No. 344. The initial tensile strength and the initial impact strength are in favor of the columbium-bearing steel, although following prolonged high-temperature treatment little difference between the two appears either in matters of tensile properties or impact properties. It is the steels of the lower chromium and higher nickel balance (11 percent chromium, 7 percent nickel of Heat No. 344 and 15 percent chromium, 5 percent nickel of Heat No. 347), and especially the 13 percent chromium, 8 percent nickel steel of Heat No. 351 with a 0.2 percent columbium content, that enjoys the best combination of tensile strength and retained impact strength.

The effect of the columbium addition in my steel is perhaps better revealed by a comparative study of the several steels presented below, these having a chromium content of about 12 percent, a copper content of about 3.5 percent, with nickel contents of about 6 percent, 6.5 percent and 7 percent, and carbon contents of about 0.03 percent, 0.04 percent and 0.05 percent. In general, it appears that in all of these steels the columbium addition improves the tensile properties. In the steels of the lower carbon contents, the columbium addition has little effect on the tendency toward embrittlement with prolonged use at elevated temperatures. In the steels of the higher carbon contents the columbium has no adverse effect on impact strength, as noted hereinafter.

A series of eight chromium-nickel-copper stainless steels according to my invention, four groups of two each, one of each having a columbium addition of about 0.20 percent and the other with a residual columbium content of 0.01 percent or less, are set out below in table II(*a*). The tensile properties and the impact strengths of these steels prior to elevated-temperature treatment and following treatment at 800° F. for 500 hours, and also following treatment at 800° F. for 1,000 hours, are set out below in table II(*b*). All steels are in precipitation-hardened condition, that is, solution-treated at 1900° F. and oil quenched followed by reheating at 1100° F. and air cooling.

In the table II(*b*) below the tensile properties of ultimate tensile strength in kilopounds per square inch, 0.2 percent yield strength in kilopounds per square inch, percent reduction in area, percent elongation in 2 inches and Rockwell hardness on the C-scale are given for each of the steels in the three conditions of prior-to-elevated-temperature treatment, subsequent-to-elevated-temperature treatment for 500 hours and for 1,000 hours at 800° F. Additionally, there are given in table II(*b*) for all steels the impact strength prior to elevated-temperature treatment and following the treatments at 800° F. for 500 hours and for 1,000 hours, this in terms of ft.-lbs. for the two samples of each steel.

TABLE II(a).—CHEMICAL COMPOSITION OF EIGHT CHROMIUM-NICKEL-COPPER STAINLESS STEELS

	C	Mn	P	S	Si	Cr	Ni	Cb	Cu	N
Heat No.										
VR 74 [1]	.033	<.05	.007	.005	<.05	12.00	6.90	.01	3.48	.004
VR 75 [1]	.035	<.05	.006	.005	<.05	11.98	6.90	.20	3.41	.003
VR 76 [1]	.037	<.05	.006	.005	<.05	11.96	5.85	<.01	3.35	.004
VR 77 [1]	.043	<.05	.005	.005	<.05	11.78	5.89	.19	3.40	.004
VR 78 [1]	.038	<.05	.006	.005	<.05	11.11	6.88	.01	3.42	.004
VR 79 [1]	.042	<.05	.006	.005	<.05	11.17	6.88	.20	3.56	.003
VR 81 [1]	.049	<.05	.006	.005	<.05	11.88	6.47	<.01	3.40	.004
VR 82 [1]	.051	<.05	.007	.005	<.05	11.88	6.50	.20	3.39	.003

[1] Steels according to the invention.

TABLE II(B).—TENSILE PROPERTIES AND IMPACT STRENGTHS OF THE STEELS OF TABLE II(A)

	Comparative tensile Properties			Impact strength		
	No exp.	500-hr. exp.	1,000 hr. exp.	No exp.	500-hr. exp.	1,000 hr. exp.
Heat No.:						
VR 74:[1]						
Ult., k.s.i	137	132	132			
Yld., k.s.i	105	115	117			
Percent R.A	66	66	66	127/139	109/121	111/116
Percent elong	19	21	21			
Hard	C26	C30–28	C29–29			
VR 75:[1]						
Ult., k.s.i	140	137	139			
Yld., k.s.i	118	123	127			
Percent R.A	67	66	69	151/128	120/138	114/116
Percent elong	20	21	22			
Hard	C29	C30–30	C32–32			
VR 76:[1]						
Ult., k.s.i	125	125	127			
Yld., k.s.i	107	112	114			
Percent R.A	70	70	70	170/180	174/163	158/148
Percent elong	21	22	23			
Hard	C24	C27–28	C28–29			
VR 77:[1]						
Ult., k.s.i	137	137	140			
Yld., k.s.i	118	128	133			
Percent R.A	69	69	67	156/166	147/120	116/117
Percent elong	20	21	20			
Hard	C28	C31–31	C31–32			
VR 78:[1]						
Ult., k.s.i	129	129	129			
Yld., k.s.i	101	114	116			
Percent R.A	68	68	68	120/159	187/155	145/150
Percent elong	20	21	22			
Hard	C26	C28–28	C28–27			
VR 79:[1]						
Ult., k.s.i	139	136	138			
Yld., k.s.i	117	124	127			
Percent R.A	66	68	68	140/142	121/131	118/124
Percent elong	21	22	22			
Hard	C29	C31–30	C31–32			
VR 81:[1]						
Ult., k.s.i	132	132	133			
Yld., k.s.i	101	116	116			
Percent R.A	65	65	66	142/150	141/141	129/137
Percent elong	20	21	22			
Hard	C27	C29–28	C30–30			
VR 82:[1]						
Ult., k.s.i	141	138	140			
Yld., k.s.i	118	124	129			
Percent R.A	65	67	66	116/124	135/126	118/127
Percent elong	20	22	22			
Hard	C28	C31–31	C31–31			

[1] Steels according to the invention.

In reviewing the tensile properties and the impact values set out above, it will be seen that the steels of purposeful columbium addition are directly benefited. This is particularly felt in the low-carbon steels, for example, the 0.035 percent carbon steel of Heat No. VR 75, with 0.20 percent columbium and having an initial impact strength of 151/128 ft.-lbs. as compared to the 0.01 percent columbium steel of Heat No. VR 74 having an initial impact strength of 127/139 ft.-lbs. And the benefit in initial impact strength is substantially retained following prolonged exposure at elevated temperatures, notably 1,000 hours at 800° F., with retained values of about 111/116 ft.-lbs. The tensile properties are much the same, any difference being in favor of the columbium-bearing steel, both initially and following prolonged treatment at elevated temperature.

In the steels of the higher carbon contents, that is, about 0.04 percent (Heat Nos. VR 76 and VR 77 for one pair and VR 78 and VR 79 for another) and about 0.05 percent (Heat Nos. VR 81 and VR 82), it rather clearly appears that while the tensile properties are benefited by the columbium addition, both initially and following prolonged elevated-temperature treatment, the impact values are inclined to suffer a bit. Thus, the columbium-bearing steel of Heat No. VR 77, having a tensile strength of 137 K s.i. prior to elevated-temperature treatment and 140 K s.i. following that treatment for 1,000 hours, is recognizably better than the 125 K s.i. tensile figure for the steel of Heat VR 76 prior to treatment and 127 K s.i. following prolonged treatment.

As distinguished from the recognizable improvement in tensile properties with the columbium addition, there is some sacrifice in impact resistance, both initially and with prolonged treatment at elevated temperatures. In the columbium-bearing steel of Heat No. VR 77, the initial impact strength of 156/166 ft.-lbs. prior to treatment falls to 116/117 ft.-lbs. following heating at 800° F. for 1,000 hours, this as distinguished from the columbium-free steel of Heat No. VR 76, where the higher initial impact strength of 170/180 ft.-lbs. falls only to 158/148 ft.-lbs. following the 1,000-hour treatment. Similar results are had for the comparative steels of Heat No. VR 79 containing columbium and Heat No. VR 78 free of columbium, where a higher nickel content is had, namely, about 7 percent. Particular comment on these steels seems unnecessary to remark that the columbium addition seems less beneficial with the increased nickel content.

In general, a like improvement in tensile properties, but some further loss in impact strength, is had in the columbium-bearing steels of even higher carbon content, that is, about 0.05 percent. It will be seen that the steel of Heat No. VR 82, containing about 0.20 percent columbium, while possessed of somewhat better tensile properties than the steel of Heat No. VR 81, which is substantially free of columbium, is of somewhat lower initial impact strength and at the same time is possessed of somewhat lower impact strength following prolonged heating at elevated temperature. Surprisingly enough, however, the difference between the initial impact strength and the impact strength following prolonged heating at elevated temperatures is less for the columbium-bearing steel than it is for the other. It is thought that in a way this result may be attributed to the somewhat higher carbon and lower nickel contents of the Heat Nos. VR 81 and VR 82 (0.05 percent carbon and 6.5 percent nickel) as compared to the Heat Nos. VR 78 and VR 79 (0.04 percent carbon and 7 percent nickel) wherein there is had a loss in impact strength after prolonged duty at elevated temperatures.

A series of six chromium-nickel-copper stainless steels of differing silicon contents, of differing nitrogen contents and of differing chromium and nickel contents is given below in table III(*a*). Of these steels it will be seen that only one, the steel of low silicon and nitrogen contents, as well as low manganese and sulfur, is characterized by a high retained impact strength following prolonged exposure to elevated temperatures, although one of the low-silicon steels, the steel of the lower chromium content and higher nickel content, is possessed of good retained impact strength.

TABLE III(a).—CHEMICAL COMPOSITION OF SIX CHROMIUM-NICKEL-COPPER PRECIPITATION-HARDENABLE STAINLESS STEELS.

	C	Mn	P	S	Si	Cr	Ni	N	Cu	Cb
Heat No.:										
4734	.045	.33	.017	.020	.16	15.35	4.22	.030	.3.05	.24
4735	.050	.34	.011	.006	.14	15.72	4.10	.018	2.94	<.05
4736[1]	.051	.21	.010	.002	<.10	12.14	5.86	.023	2.95	<.05
4737	.045	.36	.018	.924	.85	16.14	4.20	.029	3.14	.21
4738	.040	.35	.017	.019	.56	16.12	4.21	.05	3.16	.24
V-179[2]	.046	.09	.011	.008	.12	16.04	4.17	.008	3.30	.06

[1] Steel according to the invention.
[2] Steel according to the invention enjoying a best combination of properties.

The Charpy V-notch impact values in ft.-lbs. for the six steels of table III(*a*) are given below in table III(*b*). Values are given for two samples of each of the steels prior to exposure to elevated temperatures and subsequent to exposure at a temperature of 800° F. for 25 hours, for 125 hours and for 400 hours, this with the exception of the steel of Heat No. V179 which is subjected to an exposure of 316 hours at 800° F. followed by an exposure of 12 hours at 900° F. All steels are in the precipitation-hardened condition (solution-treated at 1900° F. and oil quenched followed by reheating at 1,100° F. and air cooled.)

TABLE III(b).—IMPACT STRENGTH OF THE SIX CHROMIUM-NICKEL-COPPER STEELS OF TABLE III(a)

	Impact strength			
	No exp	25-hr. exp.	125-hr. exp.	400-hr. exp.
Heat No.:				
4734	37/40	26/33	17/20	13/12
4735	79/81	75	48/49	44/40
4736[1]	79/80	74/77	58/59	54/55
4737	45/46	27/30	13/13	4/5
4738	39/45	35/36	15/16	7/10
V179[2]	>120/>120	>120/123	111/116	[3] 102/119

[1] Steel according to the invention.
[2] Steel according to the invention enjoying a best combination of properties.
[3] 316 hrs. at 800° F. plus 12 hrs. at 900° F.

In studying the test data presented in table III(*b*) above for the several steels of chemical composition given in table III(*a*), it will be immediately seen that the steel of Heat No. 4737 of high silicon content (silicon 0.85 percent) has the poorest impact strength following prolonged exposure to elevated temperatures. The steel quickly becomes brittle with elevated-temperature use, falling from an initial impact strength of 45/46 ft.-lbs. prior to exposure, to some 13/13 ft.-lbs. after exposure for 125 hours, and 4/5 ft.-lbs. after exposure for 400 hours. The same may be said for the steel of Heat No. 4738 of the somewhat less high silicon content of 0.56 percent but of the high nitrogen content of 0.05 percent.

It is the steel of Heat No. V179, characterized by the further limitations on three of the four ingredients manganese, silicon, sulfur and nitrogen, which is possessed of superior impact strength following prolonged heating at elevated temperatures. This steel, answering to the requirements of manganese 0.30 percent max., sulfur 0.010 percent max. and nitrogen 0.010 percent max. (although not answering to silicon 0.10 percent max.) with initial impact strength of something in excess of 120 ft.-lbs., is seen to have an impact strength of 102/119 ft.-lbs. following exposure.

The steel of Heat No. 4734, where all four of the ingredients manganese, silicon, sulfur and nitrogen fail to meet the further restriction in composition, is characterized by poor retained impact strength. Although not quite so poor, the steel of Heat No. 4735, where three of the ingredients (manganese, silicon and nitrogen) fail to meet the further restriction, also has an unsatisfactory impact strength following prolonged heating.

The steel of Heat No. 4736, having a chromium content under 13 percent as against the steels of Heat Nos. 4734, 4735, 4737, 4738 and V179, all with chromium contents well over 13 percent, is seen to have good retained impact strength, the initial impact strength of 79/80 ft.-lbs. falling only to 54/55 ft.-lbs. with the prolonged high-temperature treatment. But even the steel of Heat No. 4736 falls short of the retained impact strength had with the steel of Heat No. V179 as seen from the figures given above. The difference in favor of the latter steel I attribute to the higher chromium content and the lower manganese and nitrogen contents.

I feel, as noted above, that my chromium-nickel-copper stainless steel, wherein the chromium content exceeds 13 percent, requires that at least three of the four ingredients manganese, silicon, sulfur and nitrogen be further limited to achieve good sustained impact values. This is exemplified, as pointed to above, by the Heat No. V179 of Table III(*a*) with the further restrictions on manganese, sulfur and nitrogen, and the Heat No. 348 of table I(*a*), with the further limitations on silicon, sulfur and nitrogen.

While, as pointed to above, a best combination of formability, tensile strength, impact strength and freedom from embrittlement is achieved with the chromium-nickel-copper stainless steel of low carbon and critically low amounts of silicon, manganese, phosphorus, sulfur and nitrogen, with or without the further ingredient columbium, I find that many of these properties are enjoyed in a steel without a necessary copper addition. In this connection attention is called to the table IV(*a*) below in which I give the chemical composition of some eleven chromium-nickel stainless steels. Five of the 11 steels are characterized by good tensile properties and substantial freedom from embrittlement under prolonged conditions of elevated-temperature operation as gauged by accelerated test, namely, the impact strengths had before and after sustained heating at a temperature of 800° F. for 500 hours. The remaining six steels are either deficient in tensile strength or in impact strength following prolonged heating, or both. These deficiencies I attribute to either an excessive carbon content, an unduly high chromium content, an insufficient nickel content, or even an absence of the ingredient columbium, as appears more fully hereinafter; the manganese, phosphorus, sulfur, silicon and nitrogen contents all are preserved at critically low value.

TABLE IV(A).—CHEMICAL COMPOSITION OF ELEVEN CHROMIUM-NICKEL STAINLESS STEELS

	C	Mn	P	S	Si	Cr	Ni	N	Cb
Heat No.:									
VR130 [1]	.023	.05	.003	.003	.05	11.01	5.85	.007	.12
VR131 [1]	.041	.05	.003	.002	.05	11.93	5.88	.006	.12
VR132 [2]	.037	.04	.005	.004	.04	13.13	5.96	.003	.12
VR133 [2]	.035	.05	.003	.003	.05	14.13	5.17	.005	.13
VR134 [2]	.035	.05	.005	.004	.04	15.09	4.86	.005	.12
VR135	.035	.05	.004	.003	.04	16.07	4.43	.008	.12
VR136	.027	.04	.005	.005	.05	17.01	.21	.005	<.005
VR137	.103	.04	.005	.005	.05	17.06	.20	.004	<.005
VR138	.029	.05	.005	.002	.04	16.76	2.10	.008	<.005
VR139	.033	.05	.007	.002	.04	16.78	3.98	.008	<.005
4233	.040	.25	.001	.015	.37	15.64	4.09	>.025	.17

[1] Steels according to the invention enjoying a best combination of properties.
[2] Steels according to the invention.

The tensile properties of duplicate samples of the 11 steels of table IV(*a*), these in precipitation-hardened condition (solution-treatment at 1,900° F. and oil quench followed by reheating at 1,100° F. for 4 hours and air cooling) as well as the impact values and Rockwell hardnesses in precipitation-hardened condition prior to exposure to elevated temperatures and also in the condition following exposure at 800° F. for 125 hrs. and for 500 hrs., are given below in table IV(*b*). The tensile properties reported are: ultimate tensile strength in kilopounds per square inch, 0.2 percent yield strength in kilopounds per square inch, percent reduction in area, and percent elongation in 2 inches. The impact values of course are reported in ft.-lbs.

TABLE IV(b).—TENSILE PROPERTIES, IMPACT STRENGTH AND ROCKWELL HARDNESS OF THE ELEVEN STEELS OF TABLE IV(a)

	Comparative tensile properties	Impact strength and Rockwell hardness		
		No exp.	125-hr. exp.	500-hr. exp.
Heat No.:				
VR130: [1]				
Ult., k.s.i	126.3/126.6			
Yld., k.s.i	111.8/108.8	98/100	119/113	108/111
Percent R. A	68.6/66.7	C27/C27	C27/C27	C30/29.5C
Percent elong	19.5/20.0			
VR131: [1]				
Ult., k.s.i	126.6/125.8			
Yld., k.s.i	110.4/106.7	120/126	126/117	117/99
Percent R. A	68.2/68.1	C26/C27	C28/C28	C31/C30
Percent elong	19.5/19.5			
VR132: [2]				
Ult., k.s.i	128.1/125.8			
Yld., k.s.i	110.5/105.7	140/137	111/119	95/104
Percent R. A	69.1/70.1	C26/C27	C29/C29	C32/C32
Percent elong	20.0/20.0			
VR133: [2]				
Ult., k.s.i	127.3/126.3			
Yld., k.s.i	113.3/110.3	132/128	119/119	89/99
Percent R. A	70.0/69.8	C27/C27	C29/C29	C32.5/C32.5
Percent elong	20.0/20.5			
VR134: [2]				
Ult., k.s.i	127.8/127.1			
Yld., k.s.i	115.3/114.1	143/146	128/109	78/103
Percent R. A	70.9/71.6	C27/C26	C30/C30	C34/C32
Percent elong	20.0/20.0			
VR135:				
Ult., k.s.i	128.3/128.8			
Yld., k.s.i	118.3/119.3	159/151	99/106	65/50
Percent R. A	71.5/73.0	C27/C27	C31/C31	C33/C33
Percent elong	20.0/20.5			
VR136:				
Ult., k.s.i	56.0/56.7			
Yld., k.s.i	—/31.0	84/120	87/108	40/13
Percent R. A	71.3/72.3	B70/B72	B74/B74	B76/B77
Percent elong	41.5/40.5			
VR137:				
Ult., k.s.i	79.6/79.9			
Yld., k.s.i	49.3/49.6	20/20	5/12	8/6
Percent R.A	60.5/62.5	B86/B85	B87/B87	B90/B89
Percent elong	28.5/27.0			
VR138:				
Ult., k.s.i	88.2/87.4			
Yld., k.s.i	70.3/69.9	240/240	219/219	187/126
Percent R.A	79.3/79.2	B91/B91	B95/B95	B95/B98
Percent elong	28.5/30.0			
VR139:				
Ult., k.s.i	104.0/104.0			
Yld., k.s.i	85.9/85.5	205/207	164/155	155/130
Percent R. A	75.3/74.6	B98/B99	C23/C23	C25.5/C26.5
Percent elong	26.0/26.0			
4233		42.5/37.0	[3] 18.0/24.0	9.0/7.0

[1] Steels according to the invention enjoying a best combination of properties.
[2] Steels according to the invention.
[3] 100-hour exposure at 800° F.

A review of the tensile properties and the impact values reported in table IV(*b*) above rather clearly reveals that it is the steels of Heat Nos. VR 130 and VR 131 which enjoy maximum freedom from embrittlement as gauged by a retained impact strength following prolonged heating at elevated temperatures. These are the steels having a chromium content of about 11 percent and about 12 percent, with a nickel content just short of 6 percent, a carbon content of 0.02 percent and 0.04 percent, and with manganese, phosphorus, sulfur, silicon and nitrogen in critically low value. The 11 percent chromium steel of Heat No. VR 130 actually shows somewhat improved impact strength as a result of the 500-hour treatment at 800° F., the initial impact figures of 98/100 ft.-lbs. for the steel prior to exposure rising to 108/111 ft.-lbs. following exposure. The impact strength of the 12 percent chromium steel of Heat No. VR 131 falls from 120/126 ft.-lbs. prior to exposure to the figure 117/99 ft.-lbs. following exposure. The somewhat higher initial impact strength of the steel of Heat No. VR 131 over that of the steel of Heat VR 130 I attribute to the higher carbon content, namely, 0.041 percent as compared to 0.023 percent.

With the further increases in chromium contents of the steels of Heat Nos. VR 132, VR 133 and VR 134, these respectively amounting to about 13 percent, about 14 percent and about 15 percent, all having carbon contents of about 0.03 percent, a further loss in impact strength following prolonged heating at elevated temperatures is observed. This falls from an initial impact strength of 140/137 to 95/104 ft.-lbs. for the steel of Heat No. VR 132, from 132/128 to 89/99 ft.-lbs. for the steel of Heat No. VR 133, and from 143/146 to 78/103 ft.-lbs. for the steel of Heat No. VR 134. And with the further increase in chromium to about 16 percent for the steel of Heat No. VR 135, with corresponding decrease in nickel, the impact strength drops from the initial figure 159/151 ft.-lbs. prior to prolonged heating to the figure 65/60 following the 500-hour heating at 800° F. Although the tensile values are substantially the same for all six steels, that is, Heat No. VR 130 through Heat No. VR 135, there is a marked drop in retained impact strength with the increase in chromium content as noted.

As the chromium content of the steel approaches 17 percent and the nickel content is lowered, particularly where columbium is absent, there is a loss of tensile strength, although the impact strength following prolonged treatment at elevated temperatures remains at a good level. Notably, the steels of the Heat Nos. VR 138 and VR 139, having chromium contents approaching 17 percent and respectively having nickel contents of about 2 percent and about 4 percent, both have fairly good values of retained impact strength, the one initially having an impact strength of 240/240 ft.-lbs., falling to 187/126 ft.-lbs. following heating at elevated temperatures and the other having an initial impact strength of 205/207 ft.-lbs. falling to 155/130 ft.-lbs. But it is the tensile properties of these two high-chromium low-nickel steels which are deficient, the one having an ultimate tensile strength of 88.2/87.4 K s.i. and the other 104/104 K s.i. as compared to about 127 K s.i. for the six steels of the Heat Nos. VR 130 through VR 135 of the lower chromium contents.

And where the ingredient nickel is virtually eliminated from the steel, as in the steels of Heat Nos. VR 136 and VR 137, not only is there a great sacrifice in tensile properties, but the impact strengths drastically suffer, both prior to and subsequent to heating at elevated temperature. Especially is this noted with the steel of the high carbon content (Heat No. VR 137 having a carbon content of 0.103 percent).

The known commercial steel of Heat No. 4233, containing about 16 percent chromium, 4 percent nickel, 0.04 percent carbon, with manganese 0.25 percent, silicon 0.37 percent, sulfur 0.015 percent; columbium 0.17 percent, and nitrogen exceeding 0.025 percent, is characterized by impact properties which are wholly unacceptable. Note, for example that the impact resistance only amounts to some 42.5/37.0 ft.-lbs. prior to exposure to elevated temperatures, and that this falls to some 9.0/7.0 ft.-lbs. following a 500-hour exposure at 800° F.

I attribute the superior impact properties of the steel of my invention to the somewhat lower chromium content, that is, a chromium content not exceeding about 15 percent, and the virtual absence of the ingredient nitrogen. Additionally, I feel that the superior properties of my steel in a measure derive from the virtual absence of manganese, silicon and sulfur. On this compare the 15 percent chromium steel of my invention (Heat No. VR 134) with the 16 percent chromium steels of Heat No. VR 135 and Heat No. 4233. As noted above, the 15 percent chromium, low nitrogen steel of my invention, with initial impact strength of 143/146 ft.-lbs. prior to exposure at elevated temperatures and 78/103 ft.-lbs. following exposure, is significantly superior to the 16 percent chromium low nitrogen steel of Heat No. VR 135, with initial impact strength of 159/151 ft.-lbs. prior to exposure to elevated temperatures, falling to 65/60 ft.-lbs. following exposure. And the 15 percent chromium low nitrogen steel of my invention is much superior to the 16 percent chromium high nitrogen steel of Heat No. 4,233, with initial impact strength of 42.5/37.0 ft.-lbs. prior to exposure to elevated temperatures, falling to 9.0/7.0 ft.-lbs. following exposure. The great loss in impact strength had with the steel of Heat 4,233 is additionally attributed to the large amounts of manganese, silicon and sulfur present in that steel.

I find the same beneficial effects in limiting the ingredient nitrogen in the chromium-nickel-copper steels. In order to more precisely point up the surprising improvement in impact resistance had with a decrease in the nitrogen content normally found in the chromium-nickel-copper stainless steels, I give below a series of such steels with differing nitrogen contents, and their corresponding tensile properties and impact strengths, both prior to and subsequent to prolonged heating at elevated temperatures. The compositions of the several steels are set out below in table V(*a*).

TABLE V(A).—FIVE CHROMIUM-NICKEL-COPPER STAINLESS STEELS OF DIFFERING NITROGEN CONTENTS

	C	Mn	P	S	Si	Cr	Ni	Cb	Cu	N
Heat No.:										
5713	.037	.12	.005	.005	<.15	11.44	7.55	.04	3.26	.176
5715	.043	.26	.009	.007	.35	14.47	4.80	.17	3.28	.015
5727	.033	.22	.014	.013	.37	15.87	4.42	-----	3.20	.023
344 [1]	.040	.01	.007	.008	<.10	11.24	7.37	.04	3.21	.007
347 [2]	.037	<.02	.009	.005	.04	15.09	4.69	.04	3.20	.005

[1] Steel according to the invention enjoying a best combination of properties.
[2] Steel according to the invention.

NOTE.—Heats 5713 and 5715 respectively contain titanium in amounts of .09% and .13%.

The tensile properties of the steels of table V(*a*) in the age-hardened condition (solution treatment at 1900° F. followed by ageing at 1100° F. and air cooling), both prior to exposure at 800° F. and following such exposure for 500 hours, are given below in table V(*b*). This table also presents the impact strength of the several steels, both before and after the 500-hour exposure, in terms of ft.-lbs.

TABLE V(b).—TENSILE PROPERTIES AND IMPACT STRENGTH OF THE FIVE STEELS OF TABLE V(a)

	Comparative tensile properties		Impact strength	
	No exp.	500-hr. Exp.	No. exp.	500-hr. Exp.
Heat No.:				
5713:				
Ult., k.s.i.	166	173	52/57	19/19
Yld., k.s.i.	74	121		
Percent R.A.	49.2	53.8		
Percent elong.	20.0	22.5		
Hard.	C36	C39		
5715:				
Ult., k.s.i.	146	168	92/89	31/33
Yld., k.s.i.	120	162		
Percent R.A.	65.0	55.4		
Percent elong.	26.0	17.0		
Hard.	C32	C38		
5727:				
Ult., k.s.i.	132	158	71/71	37/35
Yld., k.s.i.	121	153		
Percent R.A.	60.0	48.0		
Percent elong.	19.0	15.5		
Hard.	C26	C34		

TABLE V (b).-Continued
TENSILE PROPERTIES AND IMPACT STRENGTH OF THE FIVE STEELS OF TABLE V(a)

	Comparative tensile properties		Impact strength	
	No exp.	500-hr. Exp.	No. exp.	500-hr. Exp.
344:[1]				
Ult., k.s.i.	139	141	125/123	125/121
Yld., k.s.i.	106	124		
Percent R.A.	64.6	64.0		
Percent elong.	20.0	21.0		
Hard	C30	C31		
347:[2]				
Ult., k.s.i.	134	152	172/162	112/112
Yld., k.s.i.	122	146		
Percent R.A.	68.0	58.0		
Percent elong.	21.0	18.0		
Hard	C28	C32		

[1] Steel according to the invention enjoying a best combination of properties.
[2] Steel according to the invention.

In connection with the test data presented above in table V(*b*), it is immediately apparent that the strength of all of the steels is increased as a result of the 500-hour exposure to elevated temperatures, being somewhat greater for the steels of the higher nitrogen contents (Heats 5713, 5715 and 5727). The effect on impact strength, however, is adverse and very significant.

The three steels of the higher nitrogen content are characterized by an impact strength which is low and which, moreover, drastically suffers with prolonged exposure at elevated temperatures. For example, the 11 percent chromium, 8 percent nickel steel of Heat No. 5713, having a nitrogen content of 0.176 percent (well above the 0.025 percent limit for all steels according to the invention) has an initial impact strength of 52/57 ft.-lbs., which with the 500-hour exposure at 800° F. falls to 19/19 ft.-lbs. The same effect to somewhat lesser extent is had with the 16 percent chromium, 4 percent nickel steel of Heat No. 5727 (with nitrogen exceeding the 0.010 percent max., silicon exceeding the 0.10 percent max. and sulfur exceeding the 0.010 percent max. for the steels having a chromium content exceeding 13 percent). And, similarly, the 15 percent chromium, 5 percent nickel steel of Heat No. 5715 (with nitrogen exceeding the 0.010 percent max. and silicon exceeding the 0.10 percent max. for the steels having chromium contents exceeding 13 percent) has insufficient retained impact strength following prolonged high-temperature exposure.

On the other hand, the low nitrogen steels according to applicant's invention which additionally are low in manganese, silicon and sulfur (Heat Nos. 344 and 347) are characterized by high initial impact strengths, strengths which are substantially retained over prolonged exposure at elevated temperatures. Thus, the preferred steel of Heat No. 344, having a chromium content of about 11 percent and a nickel content of about 7 percent, and with an initial impact strength of 125/123 ft.-lbs., is seen to have an impact strength of 125/121 ft.-lbs. following the 500-hour exposure. The acceptable 15 percent chromium, 5 percent nickel steel of Heat No. 347 has an initial impact strength of 172/162 ft.-lbs. prior to exposure, which falls only to 112/112 ft.-lbs. upon exposure.

In conclusion, it will be seen that I provide in my invention a precipitation-hardenable chromium-nickel-copper stainless steel, and even a precipitation-hardenable chromium-nickel stainless steel, in which there are enjoyed the various objects of my invention as set out above. The chromium-nickel-copper stainless steels of controlled chromium, nickel and carbon contents and critically low manganese, silicon, sulfur, phosphorus and nitrogent contents, both with and without a small columbium and/or titanium addition, enjoy a best combination of tensile strength, ductility, formability and freedom from embrittlement under the conditions of high-temperature operation over prolonged periods of time as encountered in supersonic aircraft, atomic reactor control mechanisms and the like. Many of the desired properties are had in the chromium-nickel-copper stainless steels of critical carbon content but in which some latitude is provided in the silicon and sulfur contents, and more especially in the manganese, phosphorous and nitrogen contents. But, as noted above, these steels are deficient in one property or another and are of somewhat limited utility.

Similarly, the precipitation-hardenable chromium-nickel stainless steels free of copper, but of critically controlled chromium, nickel and carbon contents, as well as critically low manganese, silicon, phosphorus, sulfur and nitrogen contents, while deficient in one regard or another, nevertheless enjoy a combination of tensile strength and resistance to embrittlement which adapt them for use in a variety of useful applications.

Inasmuch as there are many embodiments which may be made of my invention, and inasmuch as many changes may be made in the embodiments set out above, it will be understood that all matter described herein is to be interpreted as illustrative and not by way of limitation.

I claim as my invention:

1. Alloy steel essentially consisting of about 10 percent to about 17 percent chromium, about 3.7 percent to about 10 percent nickel, up to about 5 percent copper, 0.01 percent to 0.06 percent carbon, manganese not exceeding 0.50 percent, silicon not exceeding 0.15 percent, phosphorus not exceeding 0.030 percent, sulfur not exceeding 0.020 percent, nitrogen not exceeding 0.025 percent, and remainder substantially all iron, in which steel where the chromium content exceeds 13 percent and the copper content is about 2.5 percent to 5 percent, at least three of the four ingredients manganese, silicon, sulfur and nitrogen are further limited, the manganese to 0.30 percent max., silicon 0.10 percent max., sulfur 0.010 percent max., and nitrogen 0.010 percent max.

2. Alloy steel essentially consisting of about 10 percent to about 17 percent chromium, about 3.7 percent to about 10 percent nickel, about 2.5 percent to about 5 percent copper, 0.02 percent to 0.05 percent carbon, manganese not exceeding 0.40 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.010 percent, and remainder substantially all iron.

3. Alloy steel essentially consisting of about 11 percent to about 16 percent chromium, about 4 percent to about 8 percent nickel, about 3 percent to about 4 percent copper, 0.02 percent to 0.05 percent carbon, manganese not exceeding 0.30 percent, silicon not exceeding 0.15 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.010 percent, up to about 0.25 percent columbium, up to about 0.15 percent titanium, and remainder substantially all iron.

4. Alloy steel essentially consisting of about 11 percent to about 15 percent chromium, about 4.5 percent to about 7.5 percent nickel, about 2.5 percent to about 5 percent copper, 0.03 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.010 percent, up to about 0.25 percent columbium, and remainder substantially all iron.

5. Alloy steel essentially consisting of about 10 percent to about 13 percent chromium, about 4 percent to about 9 percent nickel, about 2.5 percent to about 5 percent copper, 0.03 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.030 percent, sulfur not exceeding 0.020 percent, nitrogen not exceeding 0.025 percent, and remainder substantially all iron.

6. Alloy steel essentially consisting **0.020** about 12 percent to about 16 percent chromium, about 4 percent to about 7 percent nickel, about 3 percent to about 4 percent copper, 0.03 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.15 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.010 percent, and remainder substantially all iron.

7. Alloy steel essentially consisting of about 10 percent to about 12.5 percent chromium, about 5 percent to about 9 percent nickel, about 2.5 percent to about 5 percent copper, 0.03

percent to 0.05 percent carbon, manganese not exceeding 0.50 percent, silicon not exceeding 0.15 percent, phosphorus not exceeding 0.030 percent, sulfur not exceeding 0.020 percent, nitrogen not exceeding 0.025 percent and remainder substantially all iron.

8. Alloy steel essentially consisting of about 11 percent to about 13 percent chromium, about 5 percent to about 8 percent nickel, about 2.5 percent to about 5 percent copper, 0.02 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, nitrogen not exceeding 0.025 percent, sulfur not exceeding 0.010 percent, and remainder substantially all iron.

9. Alloy steel essentially consisting of about 11 percent to about 13 percent chromium, about 5 percent to about 7 percent nickel, about 2.5 percent to about 5 percent copper, 0.02 percent to 0.035 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, nitrogen not exceeding 0.025 percent, sulfur not exceeding 0.010 percent, about 0.10 percent to about 0.25 percent columbium, and remainder substantially all iron.

10. Alloy steel essentially consisting of about 10.5 percent to about 11.5 percent chromium, about 5.75 percent to about 8.5 percent nickel, about 3 percent to about 4 percent copper, 0.03 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.010 percent, and remainder substantially all iron.

11. Alloy steel essentially consisting of about 11.5 percent to about 12.5 percent chromium, about 5.75 percent to about 6.25 percent nickel, about 3 percent to about 4 percent copper, 0.03 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.005 percent, nitrogen not exceeding 0.010 percent, about 0.05 percent to about 0.25 percent columbium, and remainder substantially all iron.

12. Alloy essentially consisting of about 10 percent to about 15 percent chromium, about 4.5 percent to about 9.5 percent nickel, 0.01 percent to 0.05 percent carbon, manganese not exceeding 0.30 percent, silicon not exceeding 0.15 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.015 percent, and remainder substantially all iron.

13. Alloy steel essentially consisting of about 10 percent to about 15 percent chromium, about 5 percent to about 6 percent nickel, 0.02 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.010 percent, nitrogen not exceeding 0.015 percent, and remainder substantially all iron.

14. Alloy steel essentially consisting of about 11 percent to about 15 percent chromium, about 5 percent to about 6 percent nickel, 0.02 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.005 percent, nitrogen not exceeding 0.010 percent, up to about 0.25 percent columbium, and remainder substantially all iron.

15. Alloy steel essentially consisting of about 10 percent to about 12 percent chromium, about 4.5 percent to about 9.5 percent nickel, 0.02 percent to 0.05 percent carbon, manganese not exceeding 0.10 percent, silicon not exceeding 0.10 percent, phosphorus not exceeding 0.020 percent, sulfur not exceeding 0.005 percent, nitrogen not exceeding 0.010 percent, and remainder substantially all iron.

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