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Webster

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[54] **STAINLESS STEELS**

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[21] Appl. No.: **314,686**

Related U.S. Application Data

[62] Division of Ser. No. 171,181, Aug. 12, 1971, Pat. No. 3,756,808.

[52] **U.S. Cl.**..... **148/37,** 148/125, 148/135

[51] **Int. Cl.**.... **C22c 39/10,** C22c 41/04, C21d 1/18

[58] **Field of Search**..... 148/37, 38, 125, 134, 135, 148/143

[56] **References Cited**

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Primary Examiner—C. Lovell

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[57] **ABSTRACT**

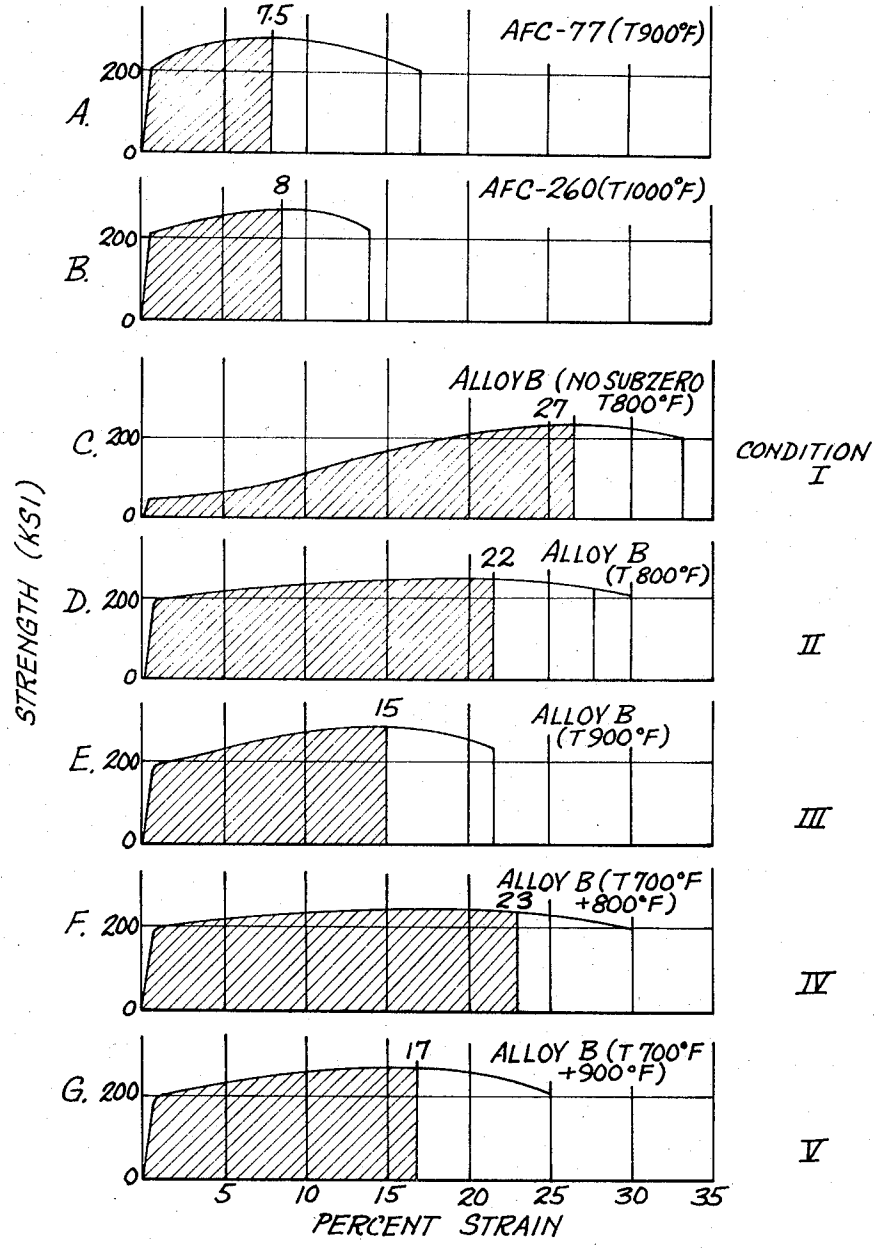
Disclosed are high-strength stainless steels of the following composition:

Element	Weight Percent
Carbon	0.12 to 0.20
Nitrogen	0 to 0.07
Chromium	12 to 16
Molybdenum	0 to 7
Vanadium	0 to 0.6
Cobalt	12 to 16
Nickel	0.5 to 1.5
Niobium	0.1 to 0.3
Iron	Balance

These steels exhibit high stength, fracture toughness, ductility and uniform elongation.

8 Claims, 4 Drawing Figures

Fig. 1


7.5
AFC-77 (T900°F)
A.
200
0
8
AFC-260 (T1000°F)
B.
200
0
ALLOY B (NO SUBZERO
27 T800°F)
C. 200
0
CONDITION I
22 ALLOY B (T800°F)
D. 200
0
II
15
ALLOY B (T900°F)
E. 200
0
III
ALLOY B (T700°F
23 +800°F)
F. 200
0
IV
17
ALLOY B (T700°F
+900°F)
G. 200
0
V
STRENGTH (KSI)
5
10
15
20
25
30
35
PERCENT STRAIN

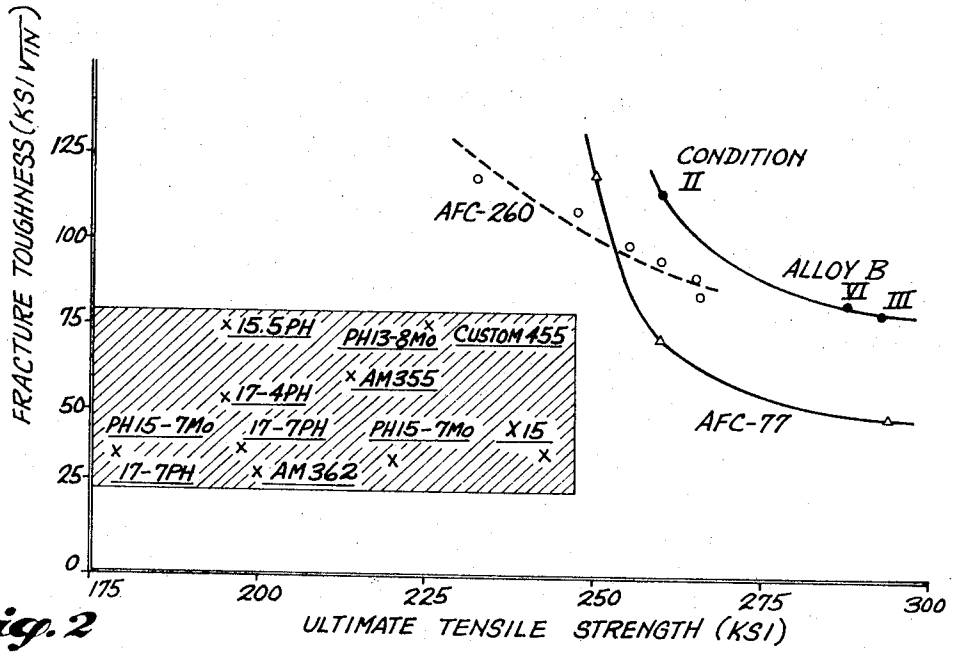

FRACTURE TOUGHNESS (KSI √IN)
125
100
75
50
25
0
175
200
225
250
275
300
ULTIMATE TENSILE STRENGTH (KSI)
AFC-260
CONDITION II
ALLOY B
VI
III
AFC-77
15.5PH
PH13-8Mo
CUSTOM 455
AM355
17-4PH
PH15-7Mo
17-7PH
PH15-7Mo
X15
17-7PH
AM 362

Fig. 2

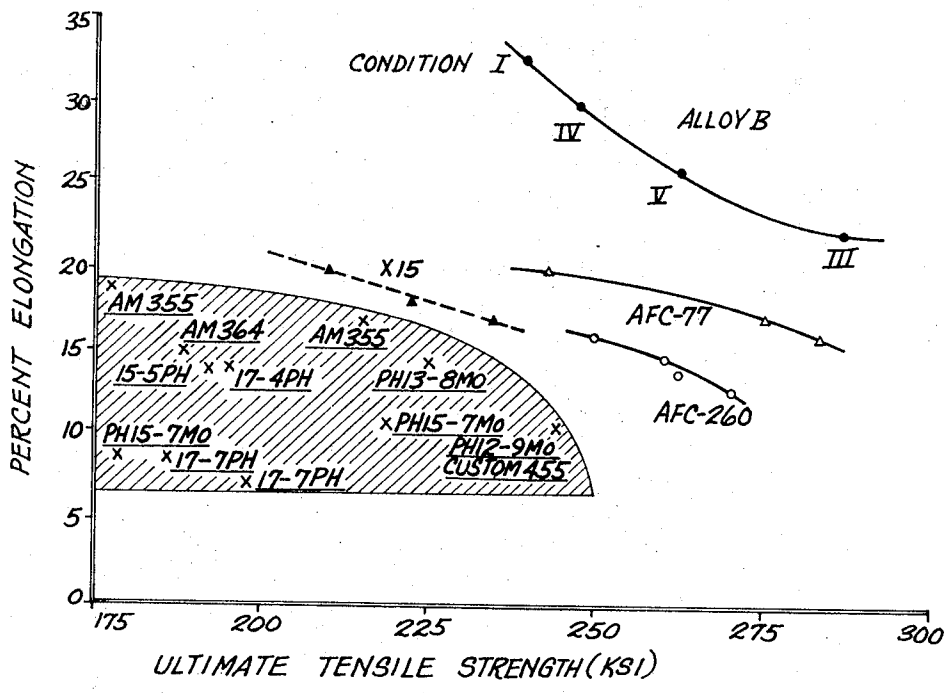

PERCENT ELONGATION
35
30
25
20
15
10
5
0
175
200
225
250
275
300
ULTIMATE TENSILE STRENGTH (KSI)
CONDITION I
IV
ALLOY B
V
III
X15
AFC-77
AFC-260
AM 355
AM 364
AM 355
15-5PH
17-4PH
PH13-8MO
PH15-7MO
PH15-7MO
17-7PH
PH12-9MO
CUSTOM 455
17-7PH

Fig. 3

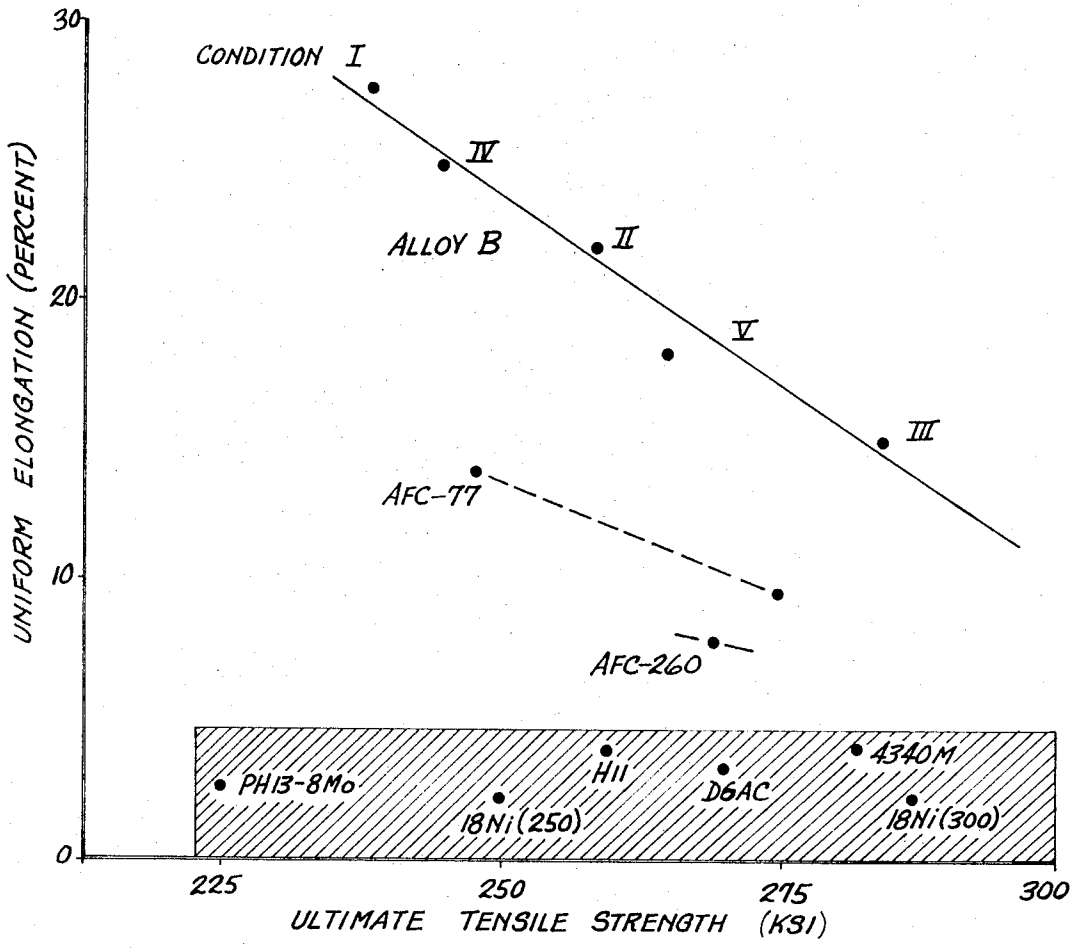

30
20
10
0
UNIFORM ELONGATION (PERCENT)
CONDITION I
IV
ALLOY B
II
V
III
AFC-77
AFC-260
PH13-8Mo
18Ni(250)
H11
D6AC
4340M
18Ni(300)
225
250
275
300
ULTIMATE TENSILE STRENGTH (KSI)

Fig. 4

STAINLESS STEELS

This is a division, of application Ser. No. 171,181, filed Aug. 12, 1971 now U.S. Pat. No. 3,756,808.

BACKGROUND OF THE INVENTION

This invention relates to stainless steels and more particularly to hardenable stainless steels which exhibit combinations of high strength, toughness, ductility and uniform elongation not heretofore obtainable.

Two recently introduced stainless steels, AFC–77 and AFC–260 (both developed by Crucible Steel Company of America — see U.S. Pat. No. Re. 26,225), possess combinations of strength and elongation which are superior to previous stainless steels. The compositions of these two steels are shown in Table I. AFC–77 is martensitic in character, while AFC–260 is semiaustenitic.

The compositions of both are balanced such that heat treatment will substantially eliminate retained austenite. AFC–77 can be heat-treated to strengths of up to about 290 ksi by tempering at from 900° to 1,100° F. However, its fracture toughness and ductility are limited by the small amounts of austenite retained at such tempering temperatures. In its austenitic condition, AFC–260 is characterized by low yield strength and reasonable ductility. With thermal treatment of AFC–260 to effect austenite-to-martensite transformation, tensile strengths of about 265 ksi can be obtained. Up to its maximum tensile strength, AFC–260 does exhibit good toughness.

It is an object of this invention to provide high strength stainless steels exhibiting combinations of strength, toughness, ductility and uniform elongation which are superior to those of AFC–77, AFC–260 and other prior art steels. It is a further object of this invention to provide high strength stainless steels of the type described which also exhibit improved stress corrosion resistance and decreased fatigue crack growth rate. It is another object of this invention to provide heat treatment procedures by which the mechanical properties of the steels of this invention can be optimized.

SUMMARY OF THE INVENTION

The steels of this invention consist essentially of the following:

TABLE I

Element	AFC-77 (wt. %) Normal Range			Aim	AFC-260 (wt. %) Normal Range			Aim
Carbon	0.13	to	0.17	0.15	0.05	to	0.09	0.07
Silicon	0	to	0.30	—	0.20	to	0.35	0.25
Manganese	0	to	0.25	—	0.15	to	0.30	0.25
Sulfur	0	to	0.010	—	0	to	0.015	—
Phosphorus	0	to	0.010	—	0	to	0.015	—
Nickel	0	to	0.25	—	1.7	to	2.0	1.85
Chromium	14.0	to	14.7	14.5	15.2	to	15.8	15.5
Molybdenum	4.7	to	5.1	5.0	4.25	to	4.75	4.5
Vanadium	0.3	to	0.4	0.5	None			—
Cobalt	13.0	to	14.0	13.5	12.6	to	13.6	13.0
Niobium	None			—	0.10	to	0.25	0.15
Nitrogen	0.03	to	0.06	0.05	0.01	to	0.05	0.03
Iron	Balance			Balance	Balance			Balance

Element	Broad Range (Weight %)			Preferred Range (Weight %)		
Carbon	0.12	to	0.20	0.13	to	0.18
Nitrogen	0	to	0.07	0.02	to	0.05
Chromium	12	to	16	13.5	to	14.5
Molybdenum	0	to	7	4.7	to	5.1
Vanadium	0	to	0.6	0.1	to	0.4
Cobalt	12	to	16	13.2	to	14.2
Nickel	0.5	to	1.5	0.85	to	1.25
Niobium	0.1	to	0.3	0.17	to	0.25
Iron	Balance			Balance		

Preferably, the elements are individually maintained within the preferred ranges indicated. Impurities such as silicon, manganese, sulfur and phosphorus can be present in the steels of this invention. Silicon and manganese contents should generally be maintained below 0.35 and 0.25 weight percent, respectively. Sulfur and phosphorus contents should each be maintained below about 0.025 weight percent, and preferably are maintained below about 0.010 weight percent.

Typical of the new steels of this invention is a steel referred to herein as "Alloy B" which has the following composition:

Element	Weight %
Carbon	0.16
Nitrogen	0.032
Chromium	13.94
Molybdenum	5.22
Vanadium	0.09
Cobalt	13.67
Nickel	1.03
Niobium	0.22
Silicon	0.06
Manganese	0.20
Sulphur	0.017
Phosphorus	0.018
Iron	Balance

This invention is also directed to a novel heat-treatment process by which the superior mechanical properties of the steels of this invention can be optimized.

BRIEF DESCRIPTION OF THE DRAWINGS

Various mechanical properties of the steels of this invention and comparisons thereof with prior art steels are graphically depicted by the accompanying drawings, wherein:

FIG. 1 shows tensile stress-strain curves for AFC–77 and AFC–260 and tensile stress-strain curves for Alloy B showing the effect of various heat treatments on strain to fracture values:

FIG. 2 shows a comparison of the toughness and tensile strength of Alloy B with existing stainless steels; and

FIG. 3 shows a comparison of elongation values of Alloy B with existing stainless steels.

FIG. 4 shows a comparison of the uniform elongation values of Alloy B with those of existing stainless steels.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the steels of this invention are critically balanced such that, even after complete heat treatment, they have a duplex structure consisting of a dispersion of on the order of from 10 to 20% of soft austenite in a matrix of hard martensite. The retained austenite, however, is sufficiently unstable that it transforms to martensite when stressed, the enhanced strength and ductility of these steels being attributed to the occurence of this transformation preferentially at regions of highest stress. During tensile tests of Alloy B, areas which attempt to neck raise the local stress at that portion of the gage length and cause the formation of stress-induced martensite. This hardens the local area sufficiently to obviate any further tendency to neck. This process occurring continuously along the entire gage length insures a high uniform elongation.

Composition-wise, the steels of this invention can be considered to be modifications of AFC–77, the modifications being the inclusion of 0.5 to 1.5% by weight of nickel and 0.1 to 0.3% by weight of niobium. The niobium addition effects refinement of the austenite grain size which increases strength and stress corrosion resistance and decreases fatigue crack growth rate. The nickel addition stabilizes the austenite, causing more austenite to be retained at high tempering temperatures.

AFC–260 can also be considered a modification of AFC–77 (see Table I), the most significant differences between the two being that AFC–260 contains 1.7 to 2.0% by weight nickel and 0.10 to 0.25% by weight niobium and has a reduced carbon content (0.05 to 0.09%). The lower carbon content in AFC–260 results in lower strength and tends to negate the austenite-stabilizing effect of the nickel.

The preferred procedure for heat treating the steels of this invention is as follows:

In Stage 1, the steel is austenitized at from 1,600° to 1,800° F., and preferably at about 1,700° F., and then cooled to ambient temperature. This stage is designed to refine the austenite grain size of the steel by optimizing the size and dispersion of the niobium carbides. Austenitizing for only a few seconds at the indicated temperatures will effect some austenite grain refinement, but times of at least one hour are preferred. The rate of cooling to ambient temperature is not critical and can be in air or by oil quenching.

Stage 2 involves austenitizing at from 1,950° to 2,300° F. for at least about one-quarter hour, cooling directly to a lower temperature of from 1,800° to 2,000° F., and holding within the latter range for at least about one-half hour to remove delta ferrite, an undesirable brittle phase. The second temperature should be at least 50° F. lower than the first. The method and rate of cooling are not critical. Preferably this stage is carried out by austenitizing at from 2,000° to 2,200° F. for at least one hour, cooling to from 1,850° to 1,950° F. (preferably about 1,900° F.) and holding for at least about 1 hour within the latter range. Holding for one hour at about 1,900° F. is sufficient in most cases to remove all delta ferrite but holding times of as much as 100 hours can be beneficial if alloy segregation is severe enough to markedly slow the removal rate of delta ferrite. After the holding period, the steel is cooled in air or by oil quenching. The steel can be further cooled to −65° F. to −150° F. (preferably to about −100° F.) and held there for from one-half hour to 20 hours to effect further hardening by transforming austenite to martensite. The subzero cooling step can be omitted to reduce yield strength and increase elongation and toughness.

Stage 3 involves tempering the steel at temperatures of from 500° to 1,100° F. for at least one-half hour and preferably for 2 + 2 hours (2 hours at temperature followed by air cooling to ambient temperature followed by an additional 2 hours at the same temperature). A variation on this tempering treatment is to temper at two different temperatures, the first being a low one designed to render the austenite more stable at the second higher tempering temperature. A promising range for the first tempering temperature has been found to be from 650° to 750° F. (preferably about 700° F.). Some increase in elongation can be achieved for a given final tempering temperature by first tempering at 700° F. for 2 hours. However, this increased ductility is obtained with some sacrifice in strength.

The heat-treatment procedure described above has general applicability to stainless steels comprising from 0.01 to 0.25% by weight carbon, 11 to 16% by weight chromium, 10 to 20% by weight cobalt and up to 10% molybdenum.

One of the most important properties of the steels of this invention is high uniform elongation, i.e., the elongation before local necking or reductions in area occur. In FIG. 1 are shown the tensile stress-strain diagrams for AFC–77 (FIG. 1A), AFC–260 (FIG. 1B) and Alloy B in five different heat-treated conditions (FIG. 1C – 1G). The AFC–77 and AFC–260 specimens tested had been subjected to the following heat treatments (see U.S. Pat. No. 3,563,813): austenitizing at 2,100° F., cooling to and holding at 1,900° F. for 1 hour, oil quenching to ambient temperature and tempering for 2 + 2 hours at 900° F. (AFC–77) and 1,000° F. (AFC–260). The Alloy B specimens used to produce the five heat-treated conditions had been austenized at 1,700° F. for 1 hour, cooled to room temperature, austenized at 2,100° F., cooled to and held for one hour at 1,900° F. and then cooled to room temperature by oil quenching. To produce Condition I (FIG. 1C), Alloy B was tempered at 800° F. for 2 + 2 hours without having been previously cooled to subzero temperatures. In this condition Alloy B contains substantial amounts of retained austenite which produces a low yield point (~40 ksi), but its work hardening capacity is sufficient to produce an ultimate tensile strength of 238 ksi. Alloy B in this condition is particularly applicable whenever extensive plastic deformation in a fully heat-treated condition is required. In condition II (FIG. 1D), Alloy B is tempered at 800° F. for 2 + 2 hours after a subzero treatment (1 hour at −100° F.) which removes a large amount of retained austenite. This results in a substantial increase in yield strength with only a slight decrease in ductility. The effect of cold working on Alloy B in Condition II has been examined by cold rolling 0.080 inch sheet. Cold reductions up to 68% were obtained without edge-cracking. There is a signifi-

cant increase in both yield and tensile strengths as a result of cold working, and tensile strengths of up to 384 ksi have been obtained by this technique. Ageing at 800° F. after the working produces a further increment of strength. The elongation drops rapidly with cold working but ductility as measured by reduction of area remains at a high level for a material of this strength.

In Conditions III, IV and V (FIG. 1E – 1G), Alloy B was subjected to a subzero treatment as in Condition II and then was tempered at 900° F. for 2 + 2 hours (Condition III); tempered at 700° F. for 2 hours, cooled to room temperature and tempered at 800° F. for 2 + 2 hours (Condition IV); or tempered at 700° F. for 2 hours, cooled to room temperature and tempered at 900° F. for 2 + 2 hours (Condition V). Alloy B in Condition III has a higher strength than in Condition II, at some sacrifice in toughness and elongation. As discussed previously, the 700° F. treatment in Conditions IV and V, stabilizes the austenite and prevents its transformation to martensite at the higher temperatures (800° – 900° F). This results in some increase in both total and uniform elongation, with a slight decrease in strength.

One of the objects of this invention is to provide a stainless steel possessing a combination of strength and toughness not available in commercial steels. The extent to which this object has been achieved can be seen from FIG. 2 which compares Alloy B in Conditions II, III and VI with existing stainless steels. Condition VI was produced in the same manner as Conditions II – V except that tempering was at 1,000° F. for 2 + 2 hours. The fracture toughness of Alloy B in Condition I is so high that measurement thereof was impractical because of the large size of specimen that would have been required. The steepness of the fracture toughness-strength relationship for AFC–77 is a reflection of the diminishing austenite content at the higher strength levels. In AFC–**260** the austenite is maintained at a high level up to the maximum strength of 265 ksi so that the strength-toughness line is considerably less steep than for AFC–**77.** Alloy B retains austenite up to an ultimate strength of 290 ksi and exhibits a better combination of strength and toughness than either AFC–77 or AFC–**260.**

A comparison of the tensile strength-elongation properties of Alloy B with those of currently available stainless steels are shown in FIG. **3.** The alloys plotted outside the shaded area are similar in composition and contain 13 to 20% cobalt. The austenite stability under stress, and hence the workhardening rate, decreases in the order AFC–**260,** AFC–77 and Alloy B, and is reflected in the increase in elongation values.

FIG. **4** shows a comparison of the more generally useful uniform elongation of Alloy B with competitive high strength steels. Uniform elongation is a measure of a material's formability and is also a design parameter in some bending applications.

The corrosion resistance, strength, toughness and ductility of the steels of this invention render them useful in many diverse applications. One application for the steels of this invention is the production of high-strength rivets which are tough and ductile enough to be gun driven without cracking, and which, after driving, have shear strength of over 170 ksi. The rivet must possess its high ductility in a fully hardened condition, since further heat treatment in situ is not usually practical. The properties of Alloy B in Conditions I and II are compared in Table II with a widely used stainless rivet material A 286.

TABLE II

Material	Condition	Tensile Strength (ksi)	Yield Strength (ksi)	Shear Strength Before Driving (ksi) *	Shear Strength After Driving (ksi) **	Charpy Impact (ft. lb.)
Alloy B	I	238	40	126	174	96
Alloy B	II	258	200	155	Not tested	34
A 286	1325° F. 16 hr.	157	110	95	100	65

* Measured by a double shear test on ½ inch diameter bar.
** Tested according to the requirements of Aerospace Research and Testing Committee report number ARTC-33 "Fastener Tension, Double Shear and Lap Joint Testing Procedures."

From Table II it will be observed that Alloy B offers a considerably higher tensile and shear strengths while maintaining a high level of toughness. During installation of the rivets by either gun driving or squeezing, Alloy B in Condition I work hardens rapidly due to martensite formation so that there is a marked increase in shear strength from 126 ksi to 174 ksi. Condition I material is the most suitable for gun driving, since its low yield strength will allow formation of the bucktail with less force than would normally be required for a material of this shear strength.

Another application for the steels of this invention is the manufacture of razor blades. The following is a thermomechanical technique which has been successfully used to produce razor blade stock from Alloy B:

Step 1.

Alloy B plate (4 in. × 12 in. × 0.6) was hot rolled at 2,100° F. to produce a coiled band approximately 0.008 inch thick and 4 inches wide.

Step 2.

The coil was austenitized at from 2,000° to 2,200° F. for **1** hour, cooled to and held for one hour at 1,900° F., cooled to ambient temperature and further cooled to and held for 1 hour at −100° F.

Step 3.

The coil was then tempered at 500° F. for 2 hours, cold rolled to a thickness of approximately 0.004 inches (50% reduction) and then retempered at 800° to 1,100° F., preferably 1,000° F., for 2 + 2 hours.

The resulting razor blade stock was found to be harder than all commercial stainless steel razor blades tested and markedly more corrosion resistant.

A number of factors render the steels of this invention particularly attractive for use in automobile bumpers. First, unlike other stainless steels of similar strength, these new steels can be heat-treated (Condition I) to possess the high ductility required in the formation of bumpers. Second, the steels of this invention

are inherently corrosion resistant and therefore do not require the platings necessary on conventional bumper steels. Third, because these steels harden locally on impact, the effect of a collision is spread over the entire bumper and local damage is reduced.

What is claimed is:

1. A heat-treated stainless steel consisting essentially of:

Element	Weight Percent
Carbon	0.12 to 0.20
Nitrogen	0 to 0.07
Chromium	12 to 16
Molybdenum	0 to 7
Vanadium	0 to 0.6
Cobalt	12 to 16
Nickel	0.5 to 1.5
Niobium	0.1 to 0.3
Iron	Balance

said steel having been subjected to the following sequence of heat treatments:

a. austenitized at a temperature of from 1,600° to 1,800°F. and cooled to ambient temperature; and

b. austenitized at a temperature of from 1,950° to 2,300°F., cooled to and held at a lower temperature of from 1,800° to 2,000°F., and cooled to ambient temperature; and

c. tempered at a temperature of from 500° to 1,100°F.

2. A steel according to claim **1** which, after having been subjected to treatment (b) and before having been subjected to treatment (c), has been cooled to and held at a temperature of from −65° F. to −150° F.

3. A steel according to claim **1** which in step (b) was air cooled or oil quenched to ambient temperature.

4. A steel according to claim **2** which in step (b) was air cooled or oil quenched to ambient temperature.

5. A heat-treated stainless steel consisting essentially of:

Element	Weight Percent
Carbon	0.13 to 0.18
Nitrogen	0.02 to 0.05
Chromium	13.5 to 14.5
Molybdenum	4.7 to 5.1
Vanadium	0.1 to 0.4
Cobalt	13.2 to 14.2
Nickel	0.85 to 1.25
Niobium	0.17 to 0.25
Iron	Balance

said steel having been subjected to the following sequence of heat treatments:

a. austenitized at a temperature of from 1,600° to 1,800°F. and cooled to ambient temperature; and

b. austenitized at a temperature of from 1,950° to 2,300°F., cooled to and held at a lower temperature of from 1,800° to 2,000°F., and cooled to ambient temperature; and

c. tempered at a temperature of from 500° to 1,100°F.

6. A steel according to claim **5** which, after having been subjected to treatment (b) and before having been subjected to treatment (c), has been cooled to and held at a temperature of from −65° to −150° F.

7. A steel according to claim **5** which in step (b) was air cooled or oil quenched to ambient temperature.

8. A steel according to claim **6** which in step (b) was air cooled or oil quenched to ambient temperature.

* * * * *