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[54] **HEAT TREATMENT FOR ALLOYS PARTICULARLY STEELS TO BE USED IN SOUR WELL SERVICE**

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[57] **ABSTRACT**

Steel characterized by high yield strength, e.g., over 90,000 p.s.i., is rendered greatly less susceptible to Sulfide Corrosion Cracking in sour oil wells or comparable environments through the use of a sequence of heat treating operations in which the steel is heated within its A_{c1} and A_{c3} region and thereafter heated below its A_{c1} temperature.

26 Claims, No Drawings

HEAT TREATMENT FOR ALLOYS PARTICULARLY STEELS TO BE USED IN SOUR WELL SERVICE

As those skilled in the art are well aware, the petroleum industry has, for close to 20 years, been confronted with a perplexing problem commonly referred to as "Sulfide Corrosion Cracking", a problem of no little magnitude. In point of historical origin, the dilemma seemingly first manifested itself (doubtless there were others) circa 1950 in connection with the unexpected failures of oil well tubing in sour oil wells located in Canada, the failures being unexpected to the extent that the steel from which the tubing was fabricated had given excellent service prior thereto, though, it appears, in sweet condensate wells. In any event, since that time investigations into the "causes" of such failures have been many, and extensive as well as intensive. And there have been a number of solutions advanced, many of which have been deemed impractical by reason of economic considerations while others have imposed such severe commercial limitations as to be unsuitable.

All the research notwithstanding, there ostensibly is not yet an unanimously accepted theory as to the mechanism responsible for Sulfide Corrosion Cracking. But there is a considerable body of authoritative opinion which reflects that both hydrogen embrittlement and stress corrosion cracking phenomena are involved. And there does seem to be virtual accord that steels of high yield strength, particularly above 90,000 pounds per square inch (psi), are exceptionally prone to Sulfide Corrosion Cracking. Too, it might be added that cracking of the type under consideration appears to be relatively spontaneous in occurrence, thus rendering detecting devices of doubtful value. This, of course, only accentuates the gravity of the difficulty, which has been expressed in terms that if either the casing or tubing in a high pressure sour well should fail, apart from other damage, the well itself might be lost.

As to the nature of the problem itself and assuming both hydrogen and stress to be involved, it has been considered that hydrogen in nascent form first penetrates the steel surface, steel exhibiting a rather striking affinity for hydrogen. The initial point of hydrogen entry seems concentrated at such sites as voids, discontinuities, inclusions, or other points of imperfection. In sour oil and/or gas wells and apart from other sources, the hydrogen can be introduced by corrosive attack of the steel (tubing, casing, etc.). Regardless of the source, the supply of atomic hydrogen is unfortunately ample.

It has been postulated that upon penetration of the steel surface, the nascent or atomic hydrogen tends to accumulate and form molecular hydrogen. This in turn is thought to bring about a volume expansion of hydrogen in the void, etc. Thus, a stress pattern is set up (the hydrogen aspect of the problem) which together with internally and externally induced pressures (the stress cracking part) causes the formation or extension of a crack which with time continues to propagate under pressure until failure.

As a practical matter, it is virtually impossible to prevent the occurrence of either internal or external stresses. For example, it is conventional to cold work tubing and the like simply to straighten the same and cold work is a classical method of inducing internal stress. Similarly, certain heat treatments are conducive to internal stressing, quenching from austenitizing being a prime example. As to external pressures, the weight of equipment and gas pressures are exemplary.

Accordingly, it has been proposed to use various inhibitors, coatings (prevent hydrogen penetration), liners (of special alloys to allow for permeation of the liner by atomic hydrogen such that the hydrogen transforms into the molecular state which is passive to steel), and different metals such as stainless steels and nickel-base alloys (proposals considered too expensive). None of these solutions, which are but illustrative, seem to have attained a point of acceptance at least with regard to steels having yield strengths above 90,000 psi.

Therefore, there has been a distinct commercial need for low cost steel characterized by high yield strength e.g., 90,000 psi or more, which greatly resists Sulfide Corrosion Cracking.

The emphasis is on yield strength as well as resistance to cracking because such strength levels are most desirable for the deeper sour wells since the external pressures are greater. Of course, as mentioned herein, it has been the higher strength steels which have proven to be the most susceptible to attack. For this reason the National Association of Corrosion Engineers (NACE) recommended that steels to be used in sour wells be tempered such that the yield strength thereof not exceed 90,000 psi, and the American Petroleum Institute (API) introduced a specification to this effect in 1963. Insofar as we are aware, this remains the practice currently prevailing, a point seemingly confirmed by a recent article which indicated that at yield strengths above 100,000 psi no known alloy except a certain copper-nickel alloy completely resists the onset and failure by way of Sulfide Corrosion Cracking. All steels failed. It is to this problem which the present invention is primarily addressed.

It has now been discovered that the capability of steels characterized by high yield strengths, 90,000 psi and above, e.g., 100,000 psi, to resist Sulfide Corrosion Cracking are markedly enhanced provided the steels are subjected to a special sequence of heat treating operations as described herein.

It is an object of the invention to provide steels of yield strengths on the order of 90,000 psi and higher which, despite their strength, display a greatly improved ability to resist the degradation effects of Sulfide Corrosion Cracking.

Other objects and advantages of the invention will become more apparent from the following description.

Generally speaking, the present invention contemplates subjecting a steel to a two-stage heat treatment in which the steel is first brought to a temperature within its A_{c1} and A_{c3} region (often referred to herein as the intercritical temperature), cooled, and thereafter again heated but to a temperature below its A_{c1}, the steel again being cooled. (It is to be understood, of course, the first stage heat treatment can be preceded by other treatments including such conventional treatments as normalizing or austenitizing and quenching.)

Upon heating above the A_{c1} temperature, a phase change takes place in which a portion of the metal structure is converted into austenite which upon cooling transforms whereby a metal matrix is formed containing a decomposition production of austenite. This decomposition product, for example, martensite, should not constitute more than about 50 percent, by volume, of the metal matrix. For, in carrying the invention into practice, should the first stage temperature be too high, the microstructure upon cooling therefrom is one obtained in which the matrix is predominantly influenced by the austenite decomposition product, e.g., martensite, and it has been found, as will be illustrated herein, that in such instances the steel can be rendered susceptible to Sulfide Corrosion Cracking. Accordingly, it is advantageous that the intercritical temperature be controlled such that not more than about 30 percent or 40 percent of the austenite decomposition product is formed upon cooling therefrom. (Of course, the exact intercritical temperature will vary from steel to steel since, as is well known to those skilled in the art, A_{c1} temperature (also A_{c3}) depends upon composition. However, it is merely a routine matter to determine the point at which, for example, more than about 50 percent martensite forms for any given composition.) On the other hand, the intercritical temperature should be sufficiently high, i.e., above the A_{c1} temperature, so as to provide a microstructure containing at least about 5 percent, and beneficially at least 10 percent, of the decomposition product upon cooling.

With regard to the duration a steel should be held within its A_{c1} – A_{c3} temperature range, long holding periods should be avoided since they only add to cost. A suitable period would be up to 4 hours, e.g., 15 minutes to 2 hours. Cooling from the A_{c1} – A_{c3} temperature should be carried down past the temperature necessary to transform the austenite, for example, below the M_s and preferably below M_f temperature in the case of martensite. Other operations can be carried out to effect maximum transformation, e.g., cold treating as by refrigeration down to below, say $-100°$ F.

Concerning the second stage treatment, the temperature used, of course, should not exceed the A_{c1}, lest the first stage be simply repeated. Preferably, the temperature should be at least 25° F. or 50° F. below A_{c1}, a range of 50° F. to 300° F. below A_{c1} being suitable. However, for nickel steels, particularly high nickel steels, e.g., 5 percent or more, a temperature of at least 100° F. below, and preferably at least 200° F. below, A_{c1} should be used. Cooling can be conducted by air, oil quenching, water quenching, etc. (This also applies to cooling from the intercritical temperature.)

While the exact mechanism which might explain the theory involved is not yet completely at hand, the effect of the above-described two-stage heat treatment might be considered unusual. To simply double temper a steel below its A_{c1} temperature does not result in any significant improvement in respect of Sulfide Corrosion Cracking (failure obtains). Moreover, conventional double tempering at best usually results in a loss of strength accompanied by a slight increase in toughness. This focuses attention upon heat treating between the A_{c1} and A_{c3} temperatures. From what has heretofore appeared in the literature, it would seem that such a heat treatment should not be employed. To explain — it has been previously said that the formation of martensite is an excellent way to actually promote Sulfide Corrosion Cracking. However, the intercritical treatment contemplated herein encompasses the intentional formation of martensite. But when the matrix so formed is tempered below the A_{c1} temperature, what might otherwise have been a crack-prone steel becomes a steel greatly resistant to sulfide corrosion cracking.

Actually, it has been found that in respect of certain steels the dual step heat treatment in accordance herewith contributes to higher strength levels notwithstanding the fact that the second heating is a tempering treatment in which a loss in strength and an increase in ductility would be expected. The increase in ductility is readily understandable since hard austenite decomposition products, such as martensite, formed upon cooling from the intercritical temperature are softened by tempering. More difficult to explain, however, is the simultaneous increase in strength. In any case, it is considered that the mechanism involves stress-strain behavior. It has been noted that in single tempering below the A_{c1} temperature of such steels, a sharp yield point is observed which disappears as the temperature is raised to just above A_{c1}, yield strength also decreasing. A further increase in temperature above A_{c1}, but well below A_{c3}, results in a substantial strength increase; however, the yield point does not reappear. This behavior indicates a straining of the matrix by transformation of the austenite region. Thereupon, tempering below A_{c1} enables strain aging to occur in the plastically deformed regions of the matrix and restores the yield point whereby strength is increased. (This overall behavior is often referred to herein as "intercritical strengthening".)

Intercritical strengthening occurs particularly in respect of nickel-containing steels, and more particularly as to those steels which also contain at least one temper resistant element such as molybdenum, chromium, silicon, vanadium, tungsten, etc. The nickel content can be as high as 10 percent although a range of from 1 to 5 or 7.5 percent is satisfactory. Up to 3% molybdenum, up to 4% chromium, up to 3% silicon, up to 3% vanadium, up to 1% carbon (and preferably at least 0.2% carbon) as well as other desired constituents can be present in the steels. Such other constituents include age hardening con-

stituents such as copper, aluminum and titanium in the following percentages: up to 3% copper, up to 2% aluminum and up to 2% titanium. Further, columbium and boron may be present in amounts up to 2% and up to 0.25%, respectively. A steel containing from 1 to 10% nickel and at least one or more temper resistant constituents in the following ranges is deemed suitable: 0.05 to 2% molybdenum, 0.5 to 3% chromium, 0.2 to 1% silicon, 0.1 to 1% vanadium, 0.1 to 0.5% carbon, 0.05 to 2% tungsten, the balance being essentially iron. A particularly satisfactory steel contains from 0.3 to 0.5% carbon, from 0.4 to 1% manganese, from 1.25 to 2.5% nickel, 0.4 to 1.25% chromium, 0.1 to 0.75% molybdenum. Another illustrative steel contains about 0.05 to 0.2% carbon, from 1.75 to 2.75% chromium, from 0.5 to 1.5% molybdenum. As contemplated herein, the nickel content can be replaced in whole or in part by an equivalent amount of manganese. Moreover, it is considered that the subject invention could be used in connection with certain stainless steels containing from about 11 to 14 percent chromium.

In order to give those skilled in the art a better understanding of the invention the following illustrative data are given.

A series of commercially produced steels, C–75, AISI 4140 and AISI 4340, the composition of which are given in Table I, were heat treated in accordance with the invention and, for purposes of comparison, by other heat treatments, the heat treatments being set forth in Table II. Alloy C75 was an open hearth heat from which 2% inch O.D. tubing had been formed. Specimens were longitudinally cut therefrom for test. The AISI steels 4140 and 4340, which had been produced using an electric furnace, were hot rolled from 1 1/8 inch round bar stock and 4× 4 inch squares, respectively, to ⅜ inch plate from which specimen blanks were cut.

After testing for mechanical properties, (results reported in Table II) specimens were finished machined to a dimension of approximately 3× ¼ × ⅛ inch. Notch beam specimens were then made, the notch being cut transversely to the direction of hot rolling with an included angle of 45° and a notch radius of 0.010 inch. Two specimens for each condition of heat treatment were deflected to the yield deflection in three-point loaded fixtures, a common testing procedure. The deflection necessary to approximately reach the onset of plastic deformation was determined using instrumented bend tests.

The loaded specimens were then immersed in a 5-liter flask containing an aqueous solution of 5% NaCl and 0.5% acetic acid, nitrogen being passed through the solution for about 30 minutes to purge the system of oxygen. The solution was then saturated with H_2S which was continuously bubbled therethrough. Prior to opening the flask for examination of the specimens, the nitrogen purge was again repeated. Inspections were carried out after the second and seventh days and every seven days thereafter (as to uncracked specimens) until a predesignated period of thirty days (total) elapsed, after which the test was discontinued. To avoid accumulation of corrosion products (which might have otherwise interfered with accuracy of the results) and to also keep the pH constant at about 3.8, the solution was changed after each inspection. In various instances threshold stress values were determined, i.e. threshold values at or below yield deflection. With respect to specimens which exhibited early failure, the threshold evaluation was one of reducing the percent of yield deflection to successively lower levels until a stress level was reached (± 5000 psi) at which no failure occurred within an exposure period of 30 days.

TABLE I.—CHEMICAL COMPOSITION

Alloy	C, percent	Mn, percent	Si, percent	Ni, percent	Cr, percent	Mo, percent	Al, percent	P, percent	S, percent	Fe, percent
C-75	0.47	1.47	n.d.	n.d.	0.04	0.21	n.d.	n.d.	n.d.	Bal.
4140	0.38	0.79	0.34	0.15	1.01	0.17	n.d.	0.009	0.027	Bal.
4340	0.44	0.71	0.28	1.82	0.79	0.25	0.025	0.008	0.01	Bal.

n.d. = Not determined.
Bal. = Balance iron plus impurities.

TABLE II

Alloy: Heat treatment hours at ° F.	Yield point, p.s.i.	Yield stress, p.s.i.	Elon., percent	R.A., percent	Specimen failures percent	Days	Threshold stress, p.s.i
C-75							
1/1600, W.Q		95,700	23.6	61.5	100	2	n.d.
Plus 1/1,325, A.C		99,300	20.0	63.0			n.d.
C-75							
1/1,600, W.Q	88,500	83,600	25.5	62.0	0		89,50C
Plus 1/1,325, A.C	90,200	83,600					
Plus 1/1,200, A.C							
C-75							
1/1,600, W.Q	110,300		20.0	60.0	100	2	50,000
Plus 1/1,350, A.C	100,300		20.0	61.0			
C-75							
1/1,600, W.Q	96,400	89,400	25.4	64.5	0		97,500
Plus 1/1,350, A.C	98,600	89,200	23.6	64.0			
Plus 1/1,100, A.C							
AISI4140							
1/1,650, O.Q		78,200	21.0	44.0	100	2	62,500
Plus 1/1,400, A.C		78,200	21.0	50.0			
AISI4140							
1/1,650, O.Q	88,200	84,200	26.0	66.5	0		88,500
Plus 1/1,350, A.C	88,700	84,700	26.0	66.5			
Plus 1/1,100, A.C							
AISI4340							
1/1,650, O.Q	124,600	123,000	22.0	66.0	100	8-14	n.d.
Plus 1/1,200, A.C	124,000	123,400	22.0	67.0			
AISI4340							
1/1,650, O.Q	106,200	97,800	24.0	53.5	50	8-14	96,500
Plus 1/1,250, A.C	108,800	98,400	25.0	54.0			
AISI4340							
1/1,650, O.Q		91,800	24.0	55.5	100	2	46,000
Plus 1/1,325, A.C		93,000	23.0	54.0			
AISI4340							
1/1,650, O.Q	103,600	97,800	25.0	66.5	0		103,000
Plus 1/1,325, A.C	111,600	98,200	25.0	69.0			
Plus 1/1,100, A.C							
AISI4340							
1/1,650, O.Q		95,200	21.0	52.5	100	2	<76,000
Plus 1,350, A.C		95,000					
AISI4340							
1/1,650, O.Q	107,200	112,400	25.0	70.0	0		107,000
Plus 1/1,350, A.C	107,300	112,400	25.0	67.5			
Plus 1/1,100, A.C							
AISI4340							
1/1,650, O.Q		102,800	12.0	28.0	100	2	<30,000
Plus 1/1,375, A.C		97,200					
AISI4340							
1/1,650, O.Q	107,800	100,200	26.0	67.5	100		
Plus 1/1,375, A.C	115,800	112,400	25.0	67.5			
Plus 1/1,100, A.C							

n.d.=not determined; W.Q.=Water Quenched; A.C.=Air Cooled; O.Q.=Oil Quenched—Approximate A$_{c1}$ and A$_{c3}$ temps. for C-75, 1,301° F. and 1,401° F.; for AISI 4140, 1,351° F.-1,401° F. and 1,501° F.; for AISI 4340, 1,251° F.-1,275° F. and 1,401° F.-1,451° F.

In perusing the data given in Tables I and II it will be observed that in each instance in which a steel specimen was treated in accordance with the invention complete resistance to Sulfide Corrosion Cracking obtained over the full 30 day period of test. This is in marked contrast to the failure characteristic of all specimens treated in a manner beyond the scope of the invention (but not inconsistent with conventional practice). It should also be particularly noted that in many instances the yield strength (yield point or yield stress) exceeded 100,000 psi and yet Sulfide Corrosion Cracking did not occur. This is thought to be quite significant inasmuch as the testing procedure used is considered to be one of considerable severity. Note should be taken of the AISI 4340 specimens heated to the intercritical temperature of 1,375° F. While this temperature is below the A$_{c3}$ for the steel, nonetheless, it represents a situation referred to above herein in which the amount of martensite formed upon cooling from the 1,375° F. temperature was excessive (above 50 percent) such that upon subsequent tempering Sulfide Corrosion Cracking resulted. A most desirable microstructure as contemplated herein consists of a ferritic matrix containing relatively uniformly distributed carbide particles and tempered martensite.

With particular regard to AISI 4340, a steel which contained nickel together with such temper resistant constituents as molybdenum and chromium, the yield strength actually increased upon the second stage (tempering) treatment. This is reflected by the data concerning the intercritical temperature of 1,350° F., the yield stress being raised by a value of about 7,000 psi. Normally, as indicated previously a loss in strength would be expected as a result of the tempering (softening) treatment below A$_{c1}$. Together with the increase in strength, ductility was also considerably improved as can be seen from a comparison of the tensile elongation (Elong., percent) and reduction in area (R.A., percent) figures.

This result whereby strength is improved by a tempering treatment, or is not impaired but toughness is considerably enhanced, is also reflected by the data given in connection with the steels set forth in Tables III and IV.

TABLE III.—CHEMICAL COMPOSITION

Alloy	C, percent	Mn, percent	Si, percent	Ni, percent	Cr, percent	Mo, percent	Al, percent	Fe, percent
9 Ni-A	0.007	0.7	0.2	9.0	·0.2	0.09	0.07	Bal.
9 Ni-B	0.05	0.88	0.21	9.17	0.23	n.a.	0.03	Bal.
9 Ni-C	0.11	0.86	0.19	9.05	0.22	n.a.	0.17	Bal.
7 Ni	0.12	0.86	0.17	7.15	n.a.	n.a.	n.d.	Bal.
3.5 Ni	0.10	0.44	0.23	3.50	n.a.	n.a.	0.02	Bal.

n.a.=not added.
n.d.=not determined.
Bal.=balance iron plus impurities (phosphorus, sulfur, etc.).

TABLE IV

Heat Treatment		0.2% Offset Y.S., p.s.i.	U.T.S., p.s.i.	Elong., percent	R.A., percent	C.V.N., ft.-lbs. (−320° F.)
Alloy:						
9 Ni-Std.		85,000–95,000				25
9 Ni-A	1/1600, W.Q. plus 1/1050, A.C. plus 1/600, A.C.	110,000	114,000	22	78.5	23
9 Ni-A	1/1600, W.Q. plus 1/1100, A.C. plus 1/600, A.C.	105,800	111,200	23	78	58
9 Ni-A	1/1600, W.Q. plus 1/1150, A.C. plus 1/600, A.C.	97,200	105,100	24	80	129
9 Ni-A	1/1600, W.Q. plus 1/1250, A.C. plus 1/600, A.C.	97,200	112,000	20	78	120
9 Ni-A	1/1650, W.Q. plus 1/1350, A.C. plus 1/600, A.C.	119,900	129,000	17	77	115 / 37
9 Ni-B	1/1600, W.Q. plus 1/1150, A.C. plus 1/950, A.C.	108,600	113,400	23	74.5	20
9 Ni-B	1/1600, W.Q. plus 1/1150, A.C. plus 1/600, A.C.	107,600	112,200	23	76	54.5
9 Ni-C	1/1600, W.Q. plus 1/1150, A.C. plus 1/950, A.C.	99,400	130,700	26	64.5	28
9 Ni-C	1/1600, W.Q. plus 1/1150, A.C. plus 1/600, A.C.	99,400	130,900	28	68	44
7 Ni	1/1450, W.Q. plus 1/1100, A.C.	98,000	105,200	25	73.5	28
7 Ni	1/1450, W.Q. plus 1/1100, A.C. plus 1/850, A.C.	130,000	133,900			
7 Ni	1/1450, W.Q. plus 1/1200, A.C. plus 1/850, A.C.	113,300	124,500	21	70	36
3.5 Ni	1/1600, W.Q. plus 1/1300, A.C.	62,700	116,800	25	55.5	[1] 8.0
3.5 Ni	1/1600, W.Q. plus 1/1300, A.C. plus 1/800, A.C.	82,000	93,600	29	71	[1] 55

[1] Cut in different direction and tested at −200° F.
9 Ni-Std.=Standard 9% nickel steel.

Apart from the strength and/or toughness being improved, in connection with the steels set forth in Tables III and IV it should be particularly mentioned that with regard to the series of the 9 percent nickel steel the results were significantly better when the second stage heat treatment was conducted more than 100° F. below the A_{c1} temperature. (The A_{c1} temperatures for Alloys 9 Ni-A, 9 Ni-B and 9 Ni-C are on the order of 1050° F., 1025° F. and 1000° F., respectively.)

While the invention as described above has been primarily directed to resisting Sulfide Corrosion Cracking in steels of yield strengths of 90,000 psi or above, it is to be understood, of course, that steels of lower yield strength can be treated in accordance herewith. However, to minimize the possibility of Sulfide Corrosion Cracking, it is preferred to use a steel in which the yield strength is less than 120,000 psi. Castings may be given the double stage heat treatment as well as wrought products. In this regard, it is contemplated that cast irons may also be so treated in which case the carbon content can be as high as 4 or 5 percent together with the conventional elements commonly found in cast irons, e.g., nickel, manganese, chromium, molybdenum, vanadium, etc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for improving the resistance of steel to sulfide corrosion cracking which comprises "bringing into contact with a sulfide corrosion cracking environment a steel which has been, (a) heated" above its A_{c1} temperature but below its A_{c3} temperature to effect a phase change in which part of the metal structure transforms to austenite, the temperature being controlled such that upon cooling not more than about 50 percent of an austenite decomposition product is formed, (b) cooled such that a metal matrix is formed containing the decomposition product of austenite, (c) heated to a temperature below its A_{c1} temperature, and (d) thereafter cooled to form a metal matrix containing relatively uniformly distributed carbide particles and a tempered decomposition product of austenite.

2. A process in accordance with claim 1 in which the steel upon cooling from the second stage heating has a yield strength of at least about 90,000 psi.

3. A process in accordance with claim 2 in which the yield strength of the steel is less than 120,000 psi.

4. A process in accordance with claim 1 in which the amount of austenite decomposition product formed is at least about 5 percent and the second stage heat treatment is conducted more than 100° F. below the A_{c1} temperature.

5. A process in accordance with claim 1 in which the amount of austenite decomposition formed is not more than about 40 percent and the second stage heat treatment is conducted more than 100° F. below the A_{c1} temperature.

6. A process in accordance with claim 4 in which the amount of decomposition formed is not more than about 30 percent and the second stage heat treatment is conducted more than 200° F. below the A_{c1} temperature.

7. A process in accordance with claim 1 in which nickel is present in an amount up to about 10 percent.

8. A process in accordance with claim 1 in which the steel contains at least one temper-resistant constituent in the following ranges: up to 3% molybdenum, up to 4% chromium, up to 3% silicon, up to 3% vanadium and up to 3% tungsten.

9. A process in accordance with claim 7 in which the nickel is from 1 to 7.5 percent.

10. A process in accordance with claim 8 in which the steel contains at least one temper-resistant element in the following ranges: 0.05 to 2% molybdenum, 0.5 to 3% chromium, 0.2 to 1% silicon, 0.1 to 1% vanadium and 0.05 to 2% tungsten.

11. A process in accordance with claim 7 in which the steel contains carbon in an amount of at least 0.2 percent.

12. A process in accordance with claim 8 in which the steel contains carbon in an amount of at least 0.2 percent.

13. A process in accordance with claim 1 in which the steel contains about 0.3 to 0.5% carbon, about 0.4 to 1% manganese, about 1.25 to 2.5% nickel, about 0.4 to 1.25% chromium and about 0.1 to 0.75% molybdenum.

14. A process in accordance with claim 1 in which the steel contains about 0.05 to 0.2 percent carbon, about 1.75 to 2.75% chromium and about 0.5 to 1.2% molybdenum.

15. A process in accordance with claim 1 in which the decomposition product of austenite is substantially martensite.

16. A process in accordance with claim 5 in which the austenite decomposition product is substantially martensite.

17. A process in accordance with claim 7 in which the austenite decomposition product is substantially martensite.

18. A process in accordance with claim 8 in which the austenite decomposition product is substantially martensite.

19. A process in accordance with claim 15 in which the microstructure obtained upon cooling from below the A_{c1} temperature consists of a ferritic matrix containing relatively uniformly distributed carbide particles and tempered martensite.

20. A process in accordance with claim 16 in which the microstructure obtained upon cooling from below the A_{c1} temperature consists of a ferritic matrix containing relatively uniformly distributed carbide particles and tempered martensite.

21. A process in accordance with claim 17 in which the microstructure obtained upon cooling from below the A_{c1} temperature consists of a ferritic matrix containing relatively uniformly distributed carbide particles and tempered martensite.

22. A process in accordance with claim 18 in which the microstructure obtained upon cooling from below the A_{c1} temperature consists of a ferritic matrix containing relatively uniformly distributed carbide particles and tempered martensite.

23. A process in accordance with claim 7 in which the second stage heat treatment is conducted more than 100° F. below the A_{c1} temperature when the steel contains at least 5 percent nickel.

24. A process in accordance with claim 9 in which the second stage heat treatment is conducted more than 100° F. below the A_{c1} temperature when the steel contains at least 5 percent nickel.

25. A process in accordance with claim 17 in which the second stage heat treatment is conducted more than 100° F. below the A_{c1} temperature when the steel contains at least 5 percent nickel.

26. A process in accordance with claim 11 in which the steel contains about 1 to about 10 percent nickel.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,465   Dated April 11, 1972

Inventor(s) EDWIN SNAPE and FRANK W. SCHALLER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Table II, Yield point, p.s.i., line 23, for "111,600" read "101,600";

Yield stress, p.s.i., line 6, for "110,300" read "100,300";

Yield stress, p.s.i., lines 27 & 28, for "112,400" read 102,400"

Table II notation, second line,

for "C-75,1,301°F. and 1,401°F.; for AISI 4140, 1,351°F.-1,401°F. and 1,501°F.; for AISI 4340, 1,251°F.-1,275°F. and 1,401°F.-1,451°F."

read "C-75, 1,300°F. and 1,400°F.; for AISI 4140, 1,350°F.-1400°F. and 1,500°F.; for AISI 4340, 1250°F.-1,275°F. and 1,400°F.-1,450°F."

Claim 1, lines 2 and 4, delete quotations.

Signed and sealed this 22nd day of January 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

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