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STEELS FOR HYDROCRACKER VESSELS CONTAINING ALUMINUM, COLUMBIUM, MOLYBDENUM AND NICKEL

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9 Claims

ABSTRACT OF THE DISCLOSURE

Steel which contains nickel, aluminum, molybdenum, columbium and low carbon offers a desirable combination of mechanical characteristics at elevated temperature and also resists temper embrittlement and hot hydrogen attack. Such properties in a steel are attractive in the fabrication of hydrocrackers.

As is generally known to those skilled in the art, hydrocracking involves a process of hydrogenation coupled with catalytic cracking wherein petroleum feed stock is treated with hydrogen gas under pressure (about 1000 to 2000 p.s.i.g.) at relatively high temperatures (600° F. to 850° F.) in the presence of a catalyst to produce gasoline or other high grade distillate. While the basic concept spans a period of nearly forty years, it has only been during the last decade that commercial exploitation of any consequence has been undertaken. But within this short period the impact industrially has been striking, a point perhaps best illustrated by a recent report which indicated that 38 gallons of gasoline were extracted from a 42-gallon barrel of crude using hydrocracking as opposed to but 21 gallons utilizing more conventional processing. This underscores the reasons for the expected expansion of hydrocracking.

In respect of the hydrocracker vessels per se, a common characteristic to all is their "massiveness." Installed, a by no means unusual vessel is on the order of 100 feet in length, 10 feet in diameter (internal), and 7 inches thick, with a weight of one million pounds. As can be appreciated, the very magnitude of such dimensions, particularly wall thickness, not only gives rise to fabricating difficulties but renders transportation and erection (situated) particularly troublesome. Presently, these vessels are fabricated from a normalized and stress-relieved, low strength 2¼% chromium-1% molybdenum steel (ASTM, A387D). Now, it is the low strength thereof (60,000 to 80,000 p.s.i. ultimate) which is primarily responsible for the exceedingly thick walls necessary to resist the relatively high pressures encountered in operation. Accordingly, there is a more than definite commercial interest in utilizing higher strength steels whereby wall thickness, overall weight, etc., would be reduced, thereby minimizing the difficulties now experienced.

But the problem is somewhat more complex than one of simply using a steel of high strength. By way of explanation, the hydrocracking reaction is conducted at elevated temperature, thus requiring a steel which not only retains high strength at elevated temperature but which also exhibits high temperature stability, i.e., the steel must perform without degradation of mechanical properties over long periods. This focuses emphasis on the fact that the steel must be tough and ductile at ambient and operating temperatures and resistant to temper embrittlement. It has been proposed to use the 2¼% chromium-1% molybdenum steel in the quenched and tempered (as opposed to the normalized and stress-relieved) condition, thereby increasing tensile strength; however, the steel would have a bainitic structure, a structure

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known to be particularly susceptible to temper embrittlement.

Further, as a consequence of hydrogenation, a steel, irrespective of its structural constitution, must manifest the capability of resisting hot hydrogen attack. If a steel is unable to cope with hot hydrogen, it thus becomes subject to blistering or fissuring even though clad with austenitic stainless. In this regard the interior surface of hydrocracker vessel walls are, for the most part, clad with austenitic stainless. Because of the very substantial wall thickness of vessels now in use, this must be accomplished by the weld overlay procedure, a costly and undesirable technique since it must be performed after fabrication of the vessel. But with appropriate high strength steels and accompanying thinner walls, the advantages of standard roll cladding could be realized.

It has now been discovered that a combination of desired mechanical characteristics, including high strength at ambient and elevated temperatures, toughness, ductility, resistance to both hot hydrogen attack and temper embrittlement, high temperature stability, etc., can be attained with steels of low carbon content and containing nickel, aluminum, molybdenum, and, advantageously, columbium, as described more fully herein.

It is an object of the invention to provide new and improved steels having characteristics which render the steels suitable for use in the fabrication of hydrocracker vessels.

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

Generally speaking and in accordance with the present invention, alloys contemplated herein contain (in percent by weight) carbon in an amount up to less than 0.04%, about 5% to 10% nickel, about 0.7% to 1.2% aluminum, from 0.5% to 2% molybdenum, up to 1.5% chromium, up to 1% manganese, up to 1% silicon, up to 0.12% columbium, and most advantageously from 0.008% to 0.08% columbium, the balance being essentially iron. Constituents such as nitrogen, oxygen, sulfur and phosphorus should be maintained at low levels consistent with good commercial steelmaking practice. However, other elements may be present as follows: up to 5% cobalt, up to 1% or 2% copper, up to 0.01%, e.g., up to 0.005% boron, and up to 0.2% tantalum. Tungsten can be used in lieu of molybdenum on an atom for atom basis, two parts of tungsten for one part of molybdenum; however, molybdenum is appreciably more effective than tungsten and is much preferred. Elements such as vanadium and titanium are quite unnecessary, although up to 0.2% of each can be tolerated. High amounts thereof detract from toughness.

In carrying the invention into practice, the carbon content of the steels should be less than 0.04% and it is beneficial that it not exceed 0.03%; otherwise, the risk is increased that nascent hydrogen evolved during the hydrocracking operation (and which permeates a stainless cladding) will combine or react with carbon present in the form of iron carbides. This reaction establishes the environment for methane gas to form at grain boundaries and other discontinuities. Eventually sufficient pressure may be built up from the trapped gas to cause fissuring or cracking. But as will be shown herein, relatively low carbon per se is not necessarily a complete panacea since other low carbon steels have been tested with resulting failure.

Nickel is required to confer adequate hardenability. Suitable nickel ranges are from 5% to 7% and, for optimum hardenability, 8% to 9.5%. Aluminum is a potent hardening and strengthening constituent, but excessive amounts thereof, e.g., 1.5%, should be avoided if the ability of the steels to absorb impact energy is not to be drastically impaired. Molybdenum confers strength

and resistance to temper embrittlement and a particularly satisfactory range thereof is from 0.75% to 1.5%. Columbium, it has been found, imparts strength without adversely affecting toughness, provided that amounts appreciably above 0.12% are avoided. Too, it is deemed that columbium is effective in resisting fissuring, i.e., it is capable of combining with carbon to form carbides which are less readily attacked by hydrogen.

For the purpose of giving those skilled in the art a better understanding of the invention, the following description and illustrative data are given:

A series of alloys were prepared by either vacuum

The compositions of the alloys are given in Table I, the age hardening Alloys 1 through 5 being within the invention whereas Alloys A, B and C are outside the scope thereof (Alloy A conforms to the aforementioned hydrocracker 2¼% Cr1% Mo steel). In Table II room temperature (R.T.) and elevated temperature properties are reported. The Yield Strength (Y.S.) at 0.2% offset and Ultimate Tensile Strength (U.T.S.) are given in pounds per square inch (P.S.I.), the Elongation (El.) and Reduction in Area (R.A.) values in percent (%) and the Charpy V-notch impact toughness (C.V.N.) determinations in foot-pounds (ft.-lbs.).

TABLE I

Alloy	C, percent	Ni, percent	Mo, percent	Al, percent	Cr, percent	Mn, percent	Si, percent	Other, percent	Fe percent
1-----	0.008	9.05	0.98	1.02	n.a.	n.a.	n.a.	-----	Bal.
2-----	0.008	9.15	1.02	0.96	0.008	n.a.	n.a.	-----	Bal.
3-----	0.017	9.27	1.03	1.08	0.008	n.a.	n.a.	-----	Bal.
4*-----	0.020	9.40	1.00	1.07	0.06	0.09	0.05	-----	Bal.
5-----	0.02	9.10	0.94	1.0	0.08	0.54	0.22	-----	Bal.
A-----	0.15	-----	0.93	-----	-----	0.54	0.32	2.28 Cr----	Bal.
B*-----	0.02	0.91	-----	(**)	0.03	0.38	0.18	1.47 Cu----	Bal.
C*-----	0.18	2.58	0.60	0.02	n.a.	0.76	0.16	0.11 V, 3.00 Cr.	Bal.

n.a.=not added.

*=air melted.

**=added for deoxidation purposes.

Bal.=balance plus impurities.

TABLE II

Alloy Number	Heat Treatment	Test Temp., F.	Y.S., p.s.i.	U.T.S., p.s.i.	El., percent	R.A., percent	C.V.N. ft.-lbs.
1-----	A-----	R.T.	98,800	111,600	21	80	184
	B-----	R.T.	149,900	154,900	21	71	10.5
	C-----	800	105,200	114,300	22	75	-----
2-----	A-----	R.T.	98,100	113,500	19	82.5	181
	B-----	R.T.	150,500	155,500	19.5	70.8	17
	C-----	800	107,800	115,000	23	75	-----
3-----	A-----	R.T.	100,000	124,200	20	82.5	224
	B-----	R.T.	153,400	167,600	19	68.5	47
	C-----	800	114,700	129,700	20	75.0	-----
4-----	A-----	R.T.	140,100	143,500	21	76	115
	B-----	650	113,100	118,100	21	75	-----
	C-----	850	91,200	101,000	25	80.8	-----
5-----	A-----	R.T.	160,100	199,200	16.5	59.5	30
	B-----	650	145,900	179,000	18.5	65.0	-----
	C-----	850	132,400	162,200	17.0	59.8	-----
A-----	Q & T	R.T.	108,400	134,000	18	63.8	16
	Q & T	650	99,600	149,200	17	47.2	-----
	Q & T	850	88,000	134,600	19	49.0	-----
B-----	E-----	R.T.	82,600	100,100	27	72.2	80.3
	F-----	650	67,200	83,200	23.5	59.5	-----
	G-----	850	54,800	67,500	23.5	49.0	-----
C-----	H-----	R.T.	121,950	136,950	19.5	68.8	79.0
	I-----	650	102,000	116,200	17.5	60.0	-----
	J-----	850	90,300	104,700	20.5	70.2	-----

Q & T=Quenched and Tempered.

induction or air melting processing. Ingots were forged and thereafter hot rolled to ¾-inch rounds or ⅝-inch square bars (Alloy 5, Table I in form of ½-inch plate), which, prior to testing were then given one or more of the following heat treatments:

Heat Treatment A:

- (1) Heat treated at 1600° F. for 1 hour, air cooled.

Heat Treatment B:

- (1) Heat treated at 1600° F. for 1 hour, air cooled.
- (2) Heated to 1000° F. and held for 2 hours followed by air cooling.

Heat Treatment C:

- (1) Same as "B" except steels water quenched after heating to 1600° F.

Heat Treatment D:

- (1) Heat treated at 1600° F. for 1 hour, then fan cooled to simulate cooling rate of a water quenched 4-inch thick plate.

- (2) Heated to 950° F., held for 3 hours, air cooled.

Heat Treatment E:

- (1) Aged 1 hour at 1050° F.

Heat Treatment F:

- (1) Same as "D" except heated to 1050° F., held for 4 hours and air cooled.

With regard to the data in Table II, the alloys within the invention manifested satisfactory room and elevated temperature mechanical properties, a tensile strength of nearly 200,000 p.s.i. and an impact strength of 30 ft.-lbs. (Alloy 5) at room temperature and a strength of over 160,000 p.s.i. at 850° F. being deemed quite satisfactory. It should be explained the reason for the low impact energy levels of Alloys 1 and 2 (Heat Treatment "B") at room temperature stems from fact these alloys were low in carbon; consequently, entrapped oxides exerted a detrimental influence, an influence readily obviated with commercial processing, or with higher carbon alloys as illustrated by Alloy 3. Raising the strength of the normalized and stress-relieved 2¼% Cr-1% Mo standard (Alloy A) from 60,000-80,000 to 134,000 p.s.i. by quenching and tempering rather substantially detracted from toughness. In this connection, recent published reports concerning the 2¼% Cr-1% Mo steel in the quenched and tempered condition indicated that a tensile strength of about 160,000 p.s.i. could be obtained; however, the Charpy V-Notch impact strength was quite low, to wit, 6-7 ft.-lbs.

Alloys 5, B and C were also tested to ascertain their behavior regarding long term stability, temper embrittlement and resistance to hydrogen under pressure. The results of this more discriminate and informative testing are set forth in Table III.

TABLE III

Alloy	Condition	Y.S., p.s.i.	U.T.S., p.s.i.	El., percent	R.A., percent	C.V.N., ft.-lb.
5-----	Before Exposure-----	160,100	199,200	16.5	59.5	30
	After 500 hrs. at 750° F-----	168,800	198,300	15	54.0	25
	After 5,000 hrs. at 750° F-----	173,800	198,500	16.5	59.8	22
	After 500 hrs. at 850° F-----	169,200	200,000	14	50.0	24.5
	After 500 hrs. at 750° F. and 1,000 p.s.i.g. H ₂ -----	168,800	198,300	15	54.0	25
	After 500 hrs. at 850° F. and 1,000 p.s.i.g. H ₂ -----	169,200	200,000	14.5	50.0	24.5
B-----	Before Exposure-----	82,600	100,100	27	72.5	80.3
	After 5,000 hrs. at 650° F-----	81,800	98,000	24	72	48
	After 5,000 hrs. at 850° F-----	85,300	100,000	25	69.5	33
	After 1,000 hrs. at 850° F. and 1,000 p.s.i.g. H ₂ -----	66,300	76,800	7	7	1
C-----	Before Exposure-----	121,950	136,950	19.5	68.8	79.0
	After 5,000 hrs. at 750° F-----	142,750	155,750	18.5	66.0	22
	After 5,000 hrs. at 850° F-----	131,200	145,000	16.5	57.8	3

Whereas Alloy 5 behaved quite well, Table III, Alloys B and C performed poorly. Low carbon Alloy B manifested susceptibility to temper embrittlement and also was exceedingly prone to hydrogen attack. Examination revealed severe grain boundary attack. Similarly, Alloy C lost virtually all ability to absorb impact after prolonged exposure to 850° F.

A further compositional range suitable for hydrocracker applications is as follows: carbon up to 0.03%, 5% to 9.5% nickel, 0.75% to 1.2% aluminum, 0.75% to 1.5% molybdenum, 0.008% to 0.08% or 0.1% columbium, up to 1% chromium, up to 0.75% manganese, up to 0.5% silicon, and the balance essentially iron. A particularly satisfactory steel consists essentially of about 0.02% carbon, about 9% nickel, about 1% aluminum, about 0.9% molybdenum, about 0.06% to 0.1% columbium, about 0.5% manganese, about 0.2% silicon, with the balance being iron.

Although the present invention is specifically addressed to hydrocrackers, the subject steels can otherwise be used in sundry environments, particularly applications where steels affording both relatively high strength and good toughness are required. The steels can be produced and used in the form of plate, bar, rod, forgings, 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.

I claim:

1. A novel alloy steel adapted for use in fabricating a hydrocracker vessel therefrom, said steel consisting essentially of less than 0.04% carbon, about 5% to 10% nickel, about 0.7% to 1.2% aluminum, from 0.5% to 2% molybdenum, columbium present up to 0.12%, up to

1.5% chromium, up to 1% manganese, up to 1% silicon, up to 5% cobalt, up to 2% copper, up to 2% tungsten, and the balance essentially iron.

2. A steel in accordance with claim 1 containing at least 0.008% columbium.

3. A hydrocracker vessel formed from the steel of claim 1.

4. A hydrocracker vessel formed from the steel of claim 2.

5. A steel in accordance with claim 1 in which the nickel content is from 5% to 7%.

6. A steel in accordance with claim 1 in which the nickel content is from 8% to 9.5%.

7. A steel in accordance with claim 1 and consisting essentially of carbon up to about 0.03%, 5% to 9.5% nickel, about 0.75% to 1.2% aluminum, about 0.75% to 1.5% molybdenum, from 0.008% to 0.08% columbium, up to 1% chromium, up to 0.75% manganese, up to 0.5% silicon, and the balance essentially iron.

8. A hydrocracker vessel formed from the steel of claim 7.

9. A steel in accordance with claim 7 consisting essentially of about 0.02% carbon, 9% nickel, about 1% aluminum, about 0.9% molybdenum, about 0.06% to 0.1% columbium, about 0.5% manganese and about 0.2% silicon.

References Cited

UNITED STATES PATENTS

3,284,191	11/1966	Hydrear	75—124
3,262,823	7/1966	Sadowski.	
3,303,023	2/1967	Dulis.	
3,368,887	2/1968	Clark	75—124 X

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U.S. Cl. X.R.

75—128