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CORROSION-RESISTANT HIGH-STRENGTH LOW-ALLOY STEELS

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ABSTRACT OF THE DISCLOSURE

Low-alloy steels having five to eight times the atmospheric corrosion resistance of carbon steels, 80,000 p.s.i. minimum yield strengths and an overall desirable balance of mechanical properties produced directly off the hot-mill have the following chemistry: carbon, 0.4% to .10%; manganese, .40% to 1.80%; sulfur, .03% maximum; aluminum, .015% minimum; chromium, .90% to 1.20%; copper, .30% to .50%; silicon, .50% to 1.20%; phosphorus, .10% to .15%; columbium, .015% to .040%; and zirconium, .04% to .12% or a total content of rare earth elements, such as cerium and lanthanum, such that the weight ratio of total rare earths to sulfur is at least 2.8 to 1. In processing the steel to strip or plate, it is hot-rolled so as to have a finishing temperature between its A_3 temperature and 1700° F., cooled at a rate between 20° F./sec. and 45° F./sec. and coiled or piled at a temperature of 1100° F.±100° F.

The present invention relates to high-strength low-alloy steels resistant to atmospheric corrosion.

A class of high-strength low-alloy steels known as "weathering" steels has been commercially available for the last few years. These steels typically possess yield strengths between 50,000 p.s.i. and 60,000 p.s.i. and exhibit resistance to atmospheric corrosion four to eight times as great as carbon steel. The weathering steels generally are alloyed with small amounts of several of the following elements: copper, chromium, phosphorus, silicon, and nickel. They achieve their corrosion resistance by forming, upon prolonged exposure, a tight non-flaking oxide coating and are used in bridges, buildings, sign and lamp posts, transmission towers, railroad cars, highway rails, architectural curtain walls, etc.

Use of the weathering steels has been limited by certain deficiencies in their mechanical properties. Thus, even at their relatively low strength levels (50,000 p.s.i. to 60,000 p.s.i. yield strengths), they possess limited formability and, in general, poor toughness. Except for a significantly more expensive class of alloy steels, e.g., quenched and tempered steels and so-called Ni-Cu-Cb steels, yield strengths in excess of 60,000 p.s.i. are not available in the weathering grades. Further, these more expensive alloy grades only have atmospheric corrosion resistance up to five times that of carbon steel.

An object of the present invention is to provide low-alloy weathering steels having 80,000 p.s.i. minimum yield strengths developed directly off a hot-strip mill. Another object of the invention is to provide such steels having five to eight times the atmospheric corrosion resistance of carbon steels and a desirable balance of mechanical properties, including formability, weldability, fatigue resistance, and toughness. Still another object of the invention is to provide such steels at low cost.

We accomplish the foregoing objects of our invention by providing steels of unique chemistry processed in a critical manner. The steels of our invention have the following chemistry: carbon, .04% to .10%; manganese, 0.40% to 1.80%; sulfur, 0.03% maximum; aluminum,

.015% minimum; chromium, .90% to 1.20%; copper, .30% to .50%; silicon, .50% to 1.20%; phosphorus, .10% to .15%; columbium, .015% to .040%; and zirconium, .04% to .12%, or rare earths in amounts such that the weight ratio of total rare earths to sulfur is at least 2.8 to 1. The steels are produced according to conventional steel making techniques with the various alloy additions typically being made to the steels in a ladle after they have been fully killed. In processing the steel to strip or plate, it is hot-rolled so as to have a finishing temperature between its A_3 temperature and 1700° F., cooled at a rate between 20° F./sec. and 45° F./sec. and coiled or piled at a temperature of 1100° F.±100° F. As set out in detail below, the composition of the steels and the method by which they are hot-rolled are critical to the formation of the desired balance of properties of corrosion resistance, strength, formability, toughness and weldability.

The steels of our invention derive their corrosion resistance from the elements phosphorus, copper, chromium and silicon. Nickel also can be used if desired. We have found that of these elements phosphorus is the most effective in enhancing corrosion resistance in all environments, i.e., rural, marine and industrial. Following phosphorus in order of effectiveness in both the rural and marine atmospheres are copper, silicon or nickel, and chromium. In the marine atmosphere, however, silicon is more effective than nickel. In an industrial atmosphere, copper, nickel, silicon and chromium follow phosphorus in order of corrosion resistance effectiveness.

While phosphorus is very effective with respect to imparting corrosion resistance and also inexpensive, phosphorus additions are limited by metallurgical considerations. Thus, high phosphorus levels cause a small decrease in ductility and can also cause weld embrittlement due to the strong effect of phosphorus on steel hardenability, especially at carbon contents above about .10%. Accordingly, the steels of the invention include .10% to .15%, preferably .13%, phosphorus, and, to counteract any detrimental effects of the phosphorus, the carbon level preferably is maintained at or below .08%.

Nickel which is only moderately effective in promoting corrosion resistance in rural, marine and industrial atmospheres is expensive, and, in addition, nickel does not result in any significant improvement in the other properties of ferrite-pearlite steels. For these reasons, we prefer not to include nickel in the steels of the invention, although, if desired, it can be added in amounts up to about 1%.

The steels of the invention include .50% to 1.20%, preferably .60%, silicon. We have found silicon to be as effective in preventing corrosion resistance as nickel but much less expensive. Silicon also is a solid solution strengthener, and, in amounts recommended for the steels of the invention, has no detrimental effects on the other desired mechanical properties of the steels. But, because of the high silicon content, the steels are aluminum-killed before silicon additions are made to prevent the formation of massive silicate inclusions.

.30% to .50%, preferably .35%, copper and .90% to 1.20%, preferably 1.00%, chromium are considered by us to be necessary to impart the desired degree of corrosion resistance to the steels. Copper also results in some precipitation strengthening of the steels, but included in amounts greater than about 0.60% can cause hot-shortness. Nickel additions to high-copper steels prevent hot shortness, but where the steels are free of nickel, as in our preferred chemistry, copper contents should be kept at or below 0.50%.

We have determined that to secure maximum atmospheric corrosion resistance at a reasonable cost, the phos-

phorus, silicon, copper and chromium contents of the steels, besides being within the ranges set out above, must be such as to satisfy the following relationship:

$$6.2 \leq 21.50(\%P) + 4.50(\%Cu) + 1.20(\%Cr) + 2.20(\%Si) \leq 7.1$$

The steels of our invention derive their high yield strengths through solid solution strengthening, grain refinement and precipitation strengthening. Solid solution strengthening is provided by the corrosion resistant elements discussed above and by manganese additions in the range of 0.40% to 1.80%. Grain refinement is achieved by a controlled hot-rolling practice, as discussed below, using columbium as the grain refining agent.

Columbium also acts to strengthen the steels by the precipitation of CbC during hot rolling. The role of columbium as both a grain refining and precipitation strengthening agent in conjunction with carbon is shown in Table I. The heats of Table I were processed to simulate a finishing temperature of 1650° F., a coiling temperature of 1100° F. and a cooling rate between finishing and coiling of between 30° F./sec. and 45° F./sec.

TABLE I

Heat No	4682	4684	22-5
Chemical analysis (weight percent):			
Carbon	.08	0.7	.03
Manganese	.77	.88	.62
Sulfur	.014	.013	.011
Aluminum	.040	.041	.040
Chromium	1.16	1.14	.93
Copper	.44	.44	.40
Silicon	.53	.48	.46
Phosphorus	.12	.13	.12
Cerium (other rare earths not analyzed)	.019		
Zirconium		.089	.11
Columbium	.026	.002	.022
Yield strength (p.s.i.)	84,900	52,700	68,800
Tensile strength (p.s.i.)	101,500	74,800	79,800
Percent total elongation in 2"	21.3	34.5	30.5
50% FATT (° F.)[1]:			
Longitudinal	+6	+40	−15
Transverse	0	+40	N.A.
Shelf energy (ft.-lb.)[1]:			
Longitudinal	35	32	64
Transverse	23	18	N.A.

[1] Impact data obtained on ½-inch V-notch Charpy specimens.

NOTE.—FATT=Fracture Appearance Transition Temperature.

We have found with respect to the effect of columbium on yield strength that yield strengths in excess of 80,000 p.s.i. can consistantly be obtained at columbium contents between about .02% and .03%. However, columbium levels as low as about .015% can be employed provided higher cooling rates are used. Conversely, we do not consider it necessary to add columbium in excess of .04%.

The steels of the invention exhibit superior formability and transverse toughness. Thus, typically, subjected to the ASTM E290 bend test (bend axis perpendicular to the direction of rolling with machined-edge specimens), the steels of our invention can be bent without cracking about an inside radius as small as that equal to the thickness of the steel. Of course, in most commercial fabricating operations, the bend axis is often parallel to the direction of rolling, and the edges are not machined, but usually sheared. Under these conditions, the minimum inside bend radius of our steels is as small as two times the steel thickness (for thicknesses .250" and less). These properties are established through the incorporation into the steels of an inclusion shape-control agent comprising zirconium or rare earths. Rare earths which can be employed are cerium, lanthanum, praseodymium, neodymium, yttrium, scandium and mischmetal (a mixture of rare earths). The inclusion shape-control agents cause the sulfide inclusions in the steels to retain a spherical form, resulting in a significant improvement in the formability and transverse toughness of the steels. In the absence of an inclusion shape-control agent, certain inclusions occurring in the steels become elongated during hot rolling and aligned parallel to the rolling direction to adversely affect the formability and transverse toughness of the steels.

We have found that when using rare earths, a minimum weight ratio of total rare earths to sulfur of 2.8 to 1 is required to establish the desired degree of formability in the steel. Also, when using rare earths, the sulfur content of the steels is preferably maintained below 0.015% although the sulfur content can be as high as .030%. Zirconium can also be used as the inclusion shape-control agent. The amount of zirconium required depends on the nitrogen content of the steel. The steels of our invention typically contain about .006% nitrogen, and we have found that zirconium contents of .04% to .12%, preferably .08%, are required to provide the desired degree of formability.

As previously noted, the steels of the invention are subject to a controlled hot-rolling practice to bring about the desired mechanical properties directly off the hot mill. In this regard, we have determined that the finishing temperature, the cooling temperature and the rate of cooling between finishing and coiling are all critical to the establishment of the desired strength and toughness in the steels.

To possess yield strengths in excess of 80,000 p.s.i., the steels of the invention must be hot-rolled finished below about 1700° F. This is shown in Table II which lists the processing practice and physical properties for steel samples having the following chemistry: carbon, .08%; manganese, .77%; sulfur, .014%; aluminum, .040%; chromium, 1.16%; copper, .44%; silicon, .53%; phosphorus, .12%; columbium, .026%; cerium, .019% (other rare earths not analyzed).

TABLE II

Case	1	2
Processing practice:		
Finishing temperature, ° F	1,650	1,750
Cooling rate, ° F./sec	30–45	30–45
Coiling temperature, ° F	1,100	1,100
Yield strength (p.s.i.)	84,900	74,000
Tensile strength (p.s.i.)	101,500	88,800
Percent total elongation in 2"	21.3	32.0
50% FATT (° F.):		
Longitudinal	+6	+14
Transverse	0	+30
Shelf energy, ft.-lb.:		
Longitudinal	35	46
Transverse	23	32

As can be seen, finishing temperatures above 1700° F., in addition to causing the yield strength to fall below 80,000 p.s.i., impair somewhat the fracture appearance transition temperature (FATT). To minimize production liabilities as a result of low line speeds required when using low finishing temperatures, the finishing temperature is usually maintained above about 1550° F.

We have determined that the steels of the invention must be cooled between the end of hot rolling and coiling at a rate in excess of about 20° F./sec. to consistently develop yield strengths in excess of 80,000 p.s.i. This is shown in Table III.

TABLE III

Heat No	4682	4609
Chemical analysis (weight percent):		
Carbon	.08	.08
Manganese	.77	.65
Sulfur	.014	.016
Aluminum	.040	.040
Chromium	1.16	.97
Copper	.44	.43
Silicon	.53	.42
Phosphorus	.12	.12
Columbium	.026	.023
Cerium (other rare earths not analyzed)	.019	
Zirconium		.099
Processing practice:		
Cooling rate, ° F./sec	30–45	10
Finishing temperature, ° F	1,650	1,650
Coiling temperature, ° F	1,100	1,100
Yield strength (p.s.i.)	84,900	62,700
Tensile strength (p.s.i.)	101,500	82,600
Percent total elongation in 2"	21.3	30.5
50% FATT (° F):		
Longitudinal	+6	+45
Transverse	0	N.A.
Shelf energy, ft.-lb.:		
Longitudinal	35	47
Transverse	23	N.A.

Cooling rates below about 20° F./sec. result in low yield strengths and increased transition temperatures.

We prefer to maintain the cooling rates at between about 20° F./sec. and 45° F./sec. because at these rates yield strengths of 80,000 p.s.i. are assured. It is, of course, possible to employ higher cooling rates, particularly when the columbium content is as low as about .015% or if yield strengths of 90,000 p.s.i. or greater are desired; but uniform elongation decreases with increasing cooling rates and existing commercial requirements do not demand yield strengths in excess of about 80,000 p.s.i.

The yield strengths of the steels of the invention fall off above and below a coiling temperature of about 1100° F. in a manner such that unless the coiling temperature is maintained at 1100° F.±100° F., yield strengths lower than 80,000 p.s.i. will result. This is shown in Table IV which lists the processing practice and physical properties for steel samples having the following chemistry: carbon, .08%; manganese, .77%; sulfur, .014%; aluminum, .040%; chromium, 1.16%; copper, .44%; silicon, .53%; phosphorus, .12%; columbium, .026%; cerium, .019% (other rare earths not analyzed).

TABLE IV

Case	1	2	3
Processing practice:			
Coiling temperature, ° F.	900	1,100	1,300
Finishing temperature, ° F.	1,560	1,650	1,650
Cooling rate, ° F./sec.	30–45	30–45	30–45
Yield strength (p.s.i.)	59,400	84,900	62,000
Tensile strength (p.s.i.)	96,700	101,500	79,500
Percent total elongation in 2"	26.8	21.3	32.0
50% FATT (° F.):			
Longitudinal	−2	+6	+40
Transverse	0	0	+40
Shelf energy, ft.-lb.:			
Longitudinal	47	35	26
Transverse	34	23	25

We have found the steels of the invention to have good welding properties. The joint efficiencies approach 100% with no excessive hardness increase or reduction in toughness in the heat affected zone. Welded samples of the steels with sheared edges can be bent over an inside radius equal to 1.5 times plate thickness with the bend axis parallel to the rolling direction without the occurrence of cracking. In addition, toughness of the heat affected zone is comparable to the base metal.

We claim:

1. Low-alloy steels characterized by having 80,000 p.s.i. minimum yield strengths, five to eight times the atmospheric corrosion resistance of carbon steels, and improved formability and toughness directly off a hot-rolling mill and having the following chemistry: carbon, .04% to .10%; manganese, .40% to 1.80%; sulfur, .03% maximum; chromium, .90% to 1.20%; copper, .30% to .50%; silicon, .50% to 1.20%; phosphorus, .10% to .15%; columbium, .015% to .040%; sufficient aluminum to kill the steel; an inclusion shape-control agent selected from the group consisting of .04% to .10% zirconium and rare earths in amounts such that the weight ratio of total rare earths to sulfur is at least 2.8 to 1; and balance essentially iron, the phosphorus, copper, chromium and silicon contents being such as to satisfy the relationship:

$$6.2 \leq 21.50(\%P) + 4.50(\%Cu) + 1.20(\%Cr) + 2.20(\%Si) + \leq 7.1$$

2. The steels of claim 1 wherein the inclusion shape-control agent comprises .04% to .10% zirconium.

3. The steels of claim 1 wherein the inclusion shape-control agent comprises rare earths in amounts such that the weight ratio of total rare earths to sulfur is at least 2.8 to 1.

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