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Giuliani et al.

[54] BAINITIC STEEL RESISTANT TO HYDROGEN EMBRITTLEMENT

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- [58] Field of Search 75/124, 126 P, 126 C; 148/37

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[57] ABSTRACT

A bainitic steel resistant to hydrogen embrittlement, and therefore resistant to sulphide stress corrosion cracking and highly useful in the oil industry, consists essentially of 0.15–0.35 C; up to 0.8 Mn; 0.8–1.0 Si; 1.0–2.0 Cr; 0.1–0.5 Mo; 0.2–0.6 Al; up to 0.03 P; up to 0.03 S; up to 0.05 Cu; 0.002–0.004 B; up to 0.1 Ta, balance essentially iron. The ratio Si:Mn is 1–2 and the ratio Mo-Al is 1–3. The sum of $0.5 \times \%$ Cr + %MO + 100 $\times \%$ B is 1–2, preferably 1–1.5. The bainitic structure is obtained directly in the as-rolled condition by air cooling any of a wide range of plate thicknesses.

2 Claims, No Drawings

BAINITIC STEEL RESISTANT TO HYDROGEN EMBRITTLEMENT

The present invention relates to high strength steel ⁵ which is resistant to sulphide stress corrosion cracking. Such steel is particularly useful in the oil industry, for example for the fabrication of oil well casings and drill rig rods and for pipes through which crude oil is pumped. In oil well practice, the hydrogen sulphide and ¹⁰ other sulphur compounds in the oil liberate hydrogen in contact with the steel, which gives rise to hydrogen embrittlement; and the steel of the present invention is particularly resistant to this.

Steels used in the oil industry are subjected to enor-¹⁵ mous stresses, especially during drilling operations. These steels accordingly have an ultimate tensile strength of 600–100 kg/mm² or higher. However, such steels have a marked tendency to crack due to hydrogen embrittlement, and thus have a shorter life than ²⁰ lower strength steels.

It is believed that the cracking of high strength steels used in the oil industry results from microscopic structural inhomogeneities. It is believed that inclusions provide points of stress concentration: the larger the inclusion and the higher the strength of the matrix, the greater will be the stress concentration. Diffusion of hydrogen in steel seems to be related to the local stress concentration; and so the hydrogen tends to concentrate at the larger inclusions in the matrix. This results in sharp localized hydrogen concentration gradients, which in turn promotes fracture. Therefore, high strength steels for use in the oil industry should ideally be as resistant as possible to hydrogen embrittlement. 35

A steel widely used in the oil industry is known as N 80 and has the weight composition of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.03 S, up to 0.03 P, 0.12 Cu, balance essentially iron. Although this steel complies with API 5 LX, its average lifetime in oil industry application application of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.03 S, up to 0.03 P, 0.12 Cu, balance essentially iron. Although this steel complies with API 5 LX, its average lifetime in oil industry application of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.03 P, 0.12 Cu, balance essentially iron. Although this steel complies with API 5 LX, its average lifetime in oil industry application of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.03 P, 0.12 Cu, balance essentially iron. Although this steel complies with API 5 LX, its average lifetime in oil industry application of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.03 P, 0.12 Cu, balance essentially iron. Although this steel complies with API 5 LX, its average lifetime in oil industry application of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.03 P, 0.12 Cu, balance essentially iron. Although this steel complies with API 5 LX, its average lifetime in oil industry application of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.03 P, 0.12 Cu, balance essentially iron. Although this steel complies the transmission of 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.35-0.40 C, 1.5 Mn, 0.3 Si, 0.3 Mo, up to 0.35-0.40 Si 0.35-0.40 Mi steel complex to 0.35-0.40 Mi steel comp

Accordingly, it is an object of the present invention to provide a high strength steel particularly durable under conditions of the oil industry.

Another object of the present invention is the provision of a high strength steel having a bainitic structure in the as-rolled condition for a wide range of plate thicknesses.

Finally, it is an object of the present invention to provide a high strength steel which will be relatively simple 50 and inexpensive to produce and rugged and durable in use.

Other objects, features and advantages of the present invention will become apparent from a consideration of the following more particular disclosure.

The steel of the present invention has the following per cent composition by weight: 0.15-0.35 C, up to 0.8 Mn, 0.8-1.0 Si, 1.0-2.0 Cr, 0.1-0.5 Mo, 0.2-0.6 Al, up to 0.03 P, up to 0.03 S, up to 0.05 Cu, 0.002-0.004 B, up to 0.1 Ta, balance essentially iron. The Si:Mn ratio 60 is 1-2, and the Mo:Al ratio is 1-3. Cr, Mo and B satisfy the relation $0.5 \times %$ Cr + %Mo + 100 × %B = 1-2, preferably 1-1.5.

In the steel of the present invention, the chromium helps to make the structure more uniform and suppres- 65 ses surface anodic activity of the steel facilitating oxidation of the sulphur from S⁻⁻ to S⁰. This latter action is also performed by silicon, although to a lesser extent.

Manganese must be held to a low limit, because of its high bonding with S^{--} and because it locks the austenite in a metastable form which, upon further transformation, gives rise to martensite that is very sensitive to hydrogen embrittlement.

Copper must be held to a low limit, because it raises the electrode potential in the presence of sulphur and favors the release of hydrogen, thus increasing the hydrogen concentration at the surface and hence its gradient inside the metal. It is to be noted that low copper is in contrast to the prior art in which it is higher.

The silicon performs the function of promoting diffusion of hydrogen, thereby tending to eliminate sharp gradients of hydrogen concentration.

The aluminum and chromium are synergetic at low stress; while the silicon and molybdenum are synergetic at high stress. This improves the behavior of the steel in contact with hydrogen.

As a result, the steel according to the present inven-20 tion has longer life in a hydrogenating environment, and this life is less subject to variation according to applied load, than is true of the prior art.

The steel of the present invention also has good mechanical properties, including a tensile strength of, for example, 90 kg/mm², a yield strength of, for example, 65 kg/mm², in the normalized condition, good creep resistance, and improved wear resistance.

A very important characteristic of the present invention is that the bainitic structure is obtained directly in ³⁰ the as-rolled condition for a wide range of plate thicknesses. The preferred range of plate thickness is 10–30 mm; although thicknesses up to 60 mm can be rolled if a decrease of about 10 kg/mm² in the values of the ultimate tensile strength and the yield strength can be ac-³⁵ cepted. No special heat treatment is needed: the bainitic structure may be obtained directly by, for example, air cooling from a rolling temperature of, say, 850°C. However, an increase in ultimate tensile strength and yield strength can be achieved by temper-⁴⁰ ing at about 650°C for a time of about 90 minutes.

EXAMPLE

A large number of test specimens were machined from 20 mm. plate rolled at 850°C. and air cooled, with tempering for 90 minutes at 650°C., and having the weight per cent composition 0.22 C, 0.65 Mn, 0.8 Si, 1.0 Cr, 0.41 Mo, 0.20 Al, 0.012 S, 0.011 P, 0.02 Cu, 0.002 B and 0.03 Ta, balance essentially iron. The test specimens were similar in shape to standard round test specimens according to A.S.A. specifications, but with special characteristics for stress-corrosion testing, namely, overall length: 150 mm.; length of end section: 64 mm.; length of reduced cylindrical section: 7 mm.; radius of fillet: 14 mm.; diameter of end section: 10 mm.; diameter of reduced section: 4 mm.; both ends threaded for a length of 18 mm. A like number of specimens of the same size and shape were cut from N 80 steel. These specimens were immersed in a solution of 0.03 M sodium sulphide in 0.5 M acetic acid. This solution is a known test solution that accelerates the effects of oil well environment on steel.

The specimens were subjected to various static tensile loads while immersed in the above solution, and the life of the specimens to failure was noted. Fifty specimens of each steel for each load were tested, and the results, both in terms of the absolute tensile load, and in terms of the percentage of the tensile strength that that load amounts to, are set forth in the following tables.

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TABLE I	
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			Life of the s	teel in hou	rs		
Tensile strength	N 80 steel			Steel according to the invention			5
4	min.	max.	average	min.	max.	average	
56	710	900	830	1330	1550	1460	
65	300	650	450	770	1030	920	
72	220	410	350	590	880	710	
80	120	290	220	430	750	550	
90	50	250	120	200	480	320	10

TABLE II

	Average life of the steel in hours		
Applied load kg/mm ²	N 80 Steel	Steel according to the invention	
44	830		
49.5		1460	
52	450		
59		920	
57	350		
64	220	710	
72		550	
76	120		
81		320	

From a consideration of the foregoing disclosure, therefore, it will be evident that all of the initially recited objects of the present invention have been achieved.

⁵ Although the present invention has been described and illustrated in connection with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit of the invention, as those skilled in this art will ⁰ readily understand. Such modifications and variations are considered to be within the purview and scope of the present invention as defined by the appended claims.

Having described our invention, we claim:

1. A bainitic steel resistant to hydrogen embrittlement, having the weight per cent composition 0.15-0.35 C, up to 0.8 Mn, 0.8-1.0 Si, 1.0-2.0 Cr, 0.1-0.5 Mo, 0.1-0.6 Al, up to 0.03 P, up to 0.03 S, up to 0.05 Cu, 0.002-0.004 B, up to 0.1 Ta, balance essentially iron, the ratio Si:Mn being 1-2, the ratio Mo:Al being 1-3, and the sum of $0.5 \times \%$ Cr + %Mo + 100 × %B being 1-2.

2. A bainitic steel as claimed in claim 1, said sum being 1-1.5.

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