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[54] **CORROSION RESISTANT STEELS HAVING IMPROVED WELDABILITY**

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Related U.S. Application Data

[60] Continuation-in-part of Ser. Nos. 2,695, Jan. 14, 1970, Pat. No. 3,733,195, and Ser. No. 237,215, March 22, 1972, abandoned, which is a division of Ser. No. 2,695.

[52] **U.S. Cl.** ..... **75/125,** 75/126 M, 75/126 N
[51] **Int. Cl.** **C22c 39/54,** C22c 39/20
[58] **Field of Search** ..... 75/126 L, 126 M, 126 N, 75/125, 128 R

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[57] **ABSTRACT**

Corrosion resistant steels having improved weldability particularly sea-water resistant steels comprising 0.001 – 0.25 percent of carbon, 0.7 – 1.1 percent of silicon, 0.3 – 2.0 percent of manganese, 0.5 – 2.0 percent of chromium, 0.1 – 1.5 percent of molybdenum. 0.1 – 0.29 percent of copper, less than 0.04 percent of phosphorus, two or more elements selected from the group consisting of arsenic, tin, beryllium, bismuth, lead, germanium, antimony, selenium and tellurium in an amount of 0.02 – 0.20 percent each, the balance being iron and unavoidable impurities.

1 Claim, No Drawings

CORROSION RESISTANT STEELS HAVING IMPROVED WELDABILITY

This is a continuation-in-part of copending applications Ser. Nos. 2,695, filed Jan. 14, 1970, now U.S. Pat. No. 3,733,195 and Ser. No. 237,215, filed Mar. 22, 1972, now abandoned, said application Ser. No. 237,215 being a division of said application Ser. No. 2,695.

BACKGROUND OF INVENTION

Conventional sea-water resistant steels have the following corrosion problems.

1. In case of marine structures such as base piles and buoys which are exposed and splashed with sea-water the corrosion of portions splashed with sea-water is as high as 3 to 7 times the corrosion of other portions (portions that are in the sea-water or above the sea), the corroded surface conditions are characterized by severe local corrosion and pit corrosion, and the corrosion products (rust) of the splashed portions have remarkable tendency of sticking as compared with the other portions.

2. In case of applications such as marine steel piping and floats which are immersed always in the sea-water, sevrre corrosion takes place particularly on portions of the structure which are 1 – 3m below the sea surface. This is due to the physiological action of sulphate-reducing bacteria which reduces sulphate ions in the sea-water into sulphur and corrode the steel remarkably. This action is greater in contaminated zones and warm districts of the sea.

3. In case of applications such as oil tankers, oil pipe lines which are exposed alternately or simultaneously with the sea-water and oils.

The corrosion is a complicated combination of whole-surface corrosion and local corrosion, the corrosion rate of the latter type being extraordinarily high. In general, corrosion in crude oil alone is very small, and for acceleration of corrosion, an electrolytic aqueous solution, such as sea-water and plain water contained in the crude oil plays an important role. Further acceleration of corrosion is effected by presence of sludge and bacteria in the crude oil.

In such marine applications as above, the corrosion of steel materials is due to the physiological action of sulphate-reducing bacteria during the reduction of sulphate ions contained in the sea-water into sulphur, and thus the corrosion mechanism is quite different from those of ordinary weather-resistant steel materials (particularly corrosion by industrial atmospheres) and is characterized by severe local corrosion and pit corrosion. This is the very reason why steel materials having

only weather-resistance alone cannot be used as sea-water resistant steel materials.

Presently, cathodic protection by using galvanic anode drainage using zinc, aluminum, magnesium etc. and corrosion inhibitors have been proposed for preventing such types of corrosion as above. But, all of these methods are only temporarily effective and require very large cost and labor for maintenance.

Further, steels as shown in Table 1 have been proposed for such marine applications and are improved in sea-water resistance as well as in mechanical properties by addition of phosphur, copper, chromium and aluminum.

Table 1

C (%)	Si (%)	Mn (%)	P (%)	S (%)	Cu (%)	Cr (%)	others (%)
0.20	0.50	0.90	0.07 –0.15	0.04	0.2 –0.6	0.2 –0.8	
0.22	0.10	0.6 –0.9	0.08 –0.15	do.	0.5		Ni: 0.40 – 0.65
0.18	0.50	0.6	do.	<0.03	0.6 –1.5	0.5 –3.0	Al: 0.5 – 1.5
0.13	do.	0.5	0.03	0.025		3.9 –4.3	Al: 0.7 – 1.1

The above conventional sea-water resistant steels are improved in sea-water resistance chiefly by the addition of phosphorus and/or copper, but these additives present a critical defect that cracks at welded portions are remarkably increased in welded structures such as submarine pipe lines and buoys.

Further, many trials have been proposed for improving sea-water resistance of steels by the addition of special elements. For example, Hudson teaches in Journal of Iron and Steel Institute (JISI), 1955, July, vol. 180, pp.271 – 284 that chromium, phsophorus, silicon, aluminum, molybdenum, nickel and beryllium are useful while tin, antimony, arsenic, bismuth, lead, tungsten, niobium and vanadium are not useful.

However, Hudson's findings are limited to results obtained from studies on corrosion in sea-water and in plain water, and does not teach of corrosion caused by repeated splashing of the sea-water or corrosion under a condition where both crude oil and sea-water are present. The type and mechanism of corrosion under such conditions are quite different from those in sea-water or in plain water.

DESCRIPTION OF INVENTION

The present invention relates to corrosion resistance steels, particularly sea-water resistant steels, having improved weldability, useful for applications such as ship hulls, buoys, landing piers, base piles, dolphins (marine oil drilling platforms) which are exposed to splashing of sea-water, such as marine or submarine steel pipes and floats which are always immersed in sea-water, and such as parts of ship hull and oil pipe lines which are exposed alternately or simultaneously to oil, sea-water and plain water.

The basic composition of the present invention steels comprises 0.001 – 0.25 per cent by weight of carbon, 0.7 – 1.1 per cent by weight of silicon, 0.3 – 2.0 per cent by weight of manganese, 0.5 – 2.0 per cent by weight of chromium, 0.1 – 1.5 per cent by weight of molybdenum, 0.1 – 0.29 per cent by weight of copper less than 0.04 per cent by weight of phosphorus, two or

more elements selected from the group consisting of arsenic, tin, beryllium, bismuth, lead, germanium, antimony, selenium and tellurium in an amount of 0.02 – 0.20 per cent by weight each, the balance being iron and unavoidable impurities.

In the above preferred type of composition, the reasons for the limitations of each of the elements are as follows.

Silicon and manganese are well known as elements necessary for deoxidation in steel production, and chromium and copper are well known as elements necessary for improving strength and weather-resistance of steels.

However, in the present invention, when these elements are present in suitable amounts, a remarkably improved corrosion resistance, which cannot be expected from the addition of only one of these elements, can be obtained.

For example, when both silicon and chromium are present in the steel, corrosion in contaminated sea-water is remarkably reduced. In other words, the resistance against general corrosion increases, as the chromium content increases. On the other hand, the resistance against pitting corrosion decreases as the chromium content increases. Therefore, the possibility of improving both the resistance against general corrosion and pitting corrosion was studied by the addition of other elements to silicon and chromium. From experimental results, it was found that the addition of molybdenum is remarkably effective for reducing pitting corrosion and general corrosion.

Particularly, an increased content of silicon is effective for forming a silicate film on the surface of the corrosion product (metal oxides) and thus effective for preventing corrosion action of the sulfate-reducing bacteria in the sea-water.

The present inventive steel having a composition as above shows an excellent sea-water resistance in a contaminated sea zone or in a sea-water splashing zone, and the proportional range of each element is defined as above because a steel having a composition in the above range is useful from the points of corrosion resistance, manufacturing, mechanical properties and weldability.

Namely, carbon is an element necessary for required strength of the present inventive steel. However, more than 0.25 percent of carbon causes embrittlement of the steel and lowers weldability and sea-water resistance, while less than 0.001 percent of carbon lowers steel strength and gives poor economy and productivity caused by a longer refining time. Silicon is necessary for deoxidation in steel production, and 0.7 – 1.1 percent of silicon in combination with chromium and manganese improves sea-water resistance. In the amounts of silicon less than 0.7 percent, these effects are not substantial. On the other hand, the addition of silicon over 1.1 percent is disadvantageous for weldability. Manganese is useful as a deoxidizer and desulfurizer in steel production and is useful for improving steel strength. In the present inventive steel more than 0.3 percent of manganese is necessary for the required strength, but too much manganese will cause embrittlement of the steel and is thus limited to 2.0 percent. Molybdenum coexistent with silicon and chromium is effective for reducing the pitting corrosion in marine atmosphere. This effect can not be expected with less than 0.1 percent of molybdenum and more than 1.5 percent of molybdenum will cause embrittlement. Copper is useful for improving sea-water resistance. This effect can not be expected with less than 0.1 percent of copper, and more than 0.29 percent of copper will cause embrittlement and lowers weldability without any remarkable improvement in sea-water resistance. Therefore, the content of copper is limited to 0.1 – 0.29 percent. An excess amount of phosphorus embrittles the steel, and severely deteriorates joint portions of welded structures such as sub-marine pipe lines and buoys. Thus, the upper limit of phosphorus is 0.04 percent. Sulphur, an unavoidable impurity, severely lower sea-water resistance and weldability, and should be maintained as low as possible. A permissible upper limit of sulphur is 0.035 percent.

A second preferred composition according to the present invention further comprises in addition to the first type of preferred composition one or more elements selected from the group consisting of zirconium, vanadium and tungsten, in an amount of 0.01 – 0.50 percent by weight with respect to zirconium and vanadium alone or combination; and 0.1 – 1.5 percent by weight with respect to tungsten alone or in combination.

For the types of preferred composition according to the present invention, addition to the basic composition (chromium, silicon, manganese, copper, carbon, phosphorus and molybdenum) of the second group of alloying elements (zirconium, vanadium and tungsten) or addition of the first group of alloying elements (arsenic, antimony, tin, lead, selenium, beryllium, bismuth, tellurium and germanium) is usefal to some degree for the desired corrosion resistance, but the addition of these two groups of alloying elements in combination gives remarkably improved and unique corrosion resistance which cannot be expected from the addition of either of the two groups alone.

The elements of the basic composition and second group by themselves are effective to reduce hydrogen embrittlement, prevent intergranular corrosion and improve corrosion fatigue, but their effects are remarkably enhanced when added in combination of the elements of the first group. This is due to the fact that the elements of the first group lower the activity coefficient of nitrides or carbides of the basic composition and second group elements to convert them into a useful state and give a strong protection against severe corrosion attach by the co-presence of crude oil and sea-water, as well as remarkably reduce corrosion on portions splashed with sea-water and corrosion by bacteria in a contaminated sea zone.

The addition of the first group elements by themselves is effective to reduce corrosion due to their toxicity to bacteria. Their effects are increased two-fold when added in combination of the second group elements, and further a remarkably improved resistance against local corrosion is given by a unique effect which reduces the ability of corrosion products to form a cathode.

Particularly, chromiun and silicon and useful for the above combined effect. Silicon and manganese have a specific ability to remarkably reduce corrosion on portions splashed with sea-water or corrosion under the condition where crude oil and sea-water are present, particularly when added in combination with copper.

Therefore, in view of economy, productivity, and practical utility, silicon, chromium, manganese, copper

and molybdenum are indispensible elements in the present invention. As for carbon and phosphorus, they are necessary for desired workability and weldability.

The reason for addition of two or more elements of the first alloying group is that although addition of arsenic alone, for example, gives good corrosion resistance, such element cannot be added in a large amount in view of weldability and mechanical properties. On the other hand, with the addition of a decreased amount of arsenic together with other element such as tin, improved weldability can be obtained without sacrifice of corrosion resistance. Thus, taking one consideration with another, it is advantageous to add two or more of the first group of alloying elements.

The second type or steel of the present invention further comprises, in addition to the above composition, one or more elements selected from the second group of alloying elements in an amount of 0.01 – 0.50 percent by weight with respect to Zr, and V, and 0.1 – 1.5 percent by weight with respect to W, to give further improved corrosion resistance and mechanical properties. The lower limits of the above additional elements are shown as limits for tangible resistance against corrosion, while the upper limits are shown as limits beyond which detrimental effect begin to appear on steel-making, or mechanical properties, weldability and other practical properties.

The present inventive steels having a composition as defined above may be used "as hot rolled", "as annealed" or "as tempered."

The present invention will be better understood from the following example.

Example

Table 1 shows results of corrosion tests on the present inventive steels and conventional steels produced in a converter or electric furnace, cast into ingots and hot rolled.

A. shows general corrosion rates after rust removal determined on the specimens of 4 mm thickness × 50 mm width × 100 mm length, polished on all surfaces with No. 320 emergy and immersed horizontally for one month alternately in a tank filled with crude oil and then in a tank filled with sea-water. The corrosion rates shown in (A) represents the ratio of the weight loss due to general corrosion of the present inventive steel to that of the ordinary carbon steel.

B. shows the highest corrosion rates observed in the above mentioned specimens.

The highest corrosion rates in (B) represents the ratio of the pit depth due to pitting corrosion of the present inventive steel to that of the ordinary carbon steel.

As seen from the Table, the present inventive steels show excellent corrosion resistance.

Table 2

No. of Specimens	Chemical Composition (Weight %) C	Si	Mn	P	S	Cu	Cr	Mo	As	Sn
Ordinary carbon steel										
1	0.14	0.03	0.85	0.009	0.013					
Inventive steel										
1	0.07	0.80	0.42	0.013	0.010	0.19	1.24	0.50		0.02
2	0.10	0.71	0.80	0.015	0.020	0.21	1.02	0.15	0.01	
3	0.05	0.85	0.50	0.020	0.008	0.25	1.16	0.20		0.01
4	0.06	0.91	0.82	0.009	0.009	0.27	1.00	0.18		0.02
5	0.05	0.76	0.85	0.012	0.013	0.27	1.08	0.15	0.01	0.02
6	0.08	0.78	0.45	0.015	0.011	0.25	1.98	0.20	0.02	
7	0.06	0.85	1.15	0.016	0.018	0.24	1.75	0.18	0.02	0.01
8	0.11	0.80	0.80	0.015	0.013	0.18	1.82	0.15		
9	0.08	0.91	1.10	0.008	0.009	0.26	1.95	1.0		

No. of Specimens	Sb	Se	Te	Be	Bi	Pb	Ge	Sea water Corrosion Rate (%) A	B
Ordinary carbon steel 1								100	100
Inventive steel									
1	0.03							59.8	49.1
2		0.02				0.01	W;0.15	57.6	47.8
3			0.02		0.03			59.7	47.5
4		0.01		0.01				55.7	47.1
5							V;0.03	56.8	48.7
6		0.01				0.01		43.5	41.1
7							Zr;0.05	41.6	38.6
8				0.02			0.01	48.7	41.5
9	0.01			0.02				39.2	30.6

What is claimed is:

1. A corrosion resistant steel having improved weldability consisting of 0.001 – 0.25 percent by weight of carbon, 0.70 – 1.1 percent by weight of silicon, 0.3 – 2.0 percent by weight of manganese, 0.5 – 2.0 percent by weight of chromium, 0.1 – 1.5 percent by weight of molybdenum, 0.1 – 0.29 percent by weight of copper, less than 0.04 percent by weight of phosphorus, and two or more elements selected from the group consisting of arsenic, tin, beryllium, bismuth, lead, germanium, antimony, selenium and tellurium in an amount of 0.02 – 0.20 percent by weight each, the balance being iron and unavoidable impurities.

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