EFFECT OF LOW ALLOY ADDITIONS ON CORROSION OF STEEL IN DIFFERENT ATMOSPHERES

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Introduction

HE loss due to corrosion is one of the important problems that is drawing the attention of engineers. This is a universal problem which cannot be completely eliminated. Any bare metal corrodes under all types of atmosphere to which it is exposed, the effect under different atmospheres varying only in degrees. The loss can be minimized by giving suitable protection as in the form of coating or by the addition of alloying elements. The type and amount of alloying elements to be added depend largely on the conditions under which the material is to be used. In general, low percentages of Cu, Ni, Cr, etc., are added to steel for light structures, inaccessible components, parts subjected to irregular abrasion which damages the protective coatings and where minimum of painting and maintenance is desirable. This paper reviews the effect of low alloy additions on atmospheric corrosion of steel.

As a result of thorough investigations it has been found that the amount of moisture present in the atmosphere is very important as metals suffer slow attack below a certain value of humidity, known as critical humidity, but corrodes rapidly above this value. Moreover, the presence of sulphur either in the atmosphere or in the metal and that of chlorides, carbon dioxide and solid particles in the atmosphere influence the corrosion rate. That is why materials are more susceptible to corrosion when exposed to industrial and marine atmosphere than to rural atmosphere.

The merit and demerit of materials under specified conditions can be judged only after prolonged exposure. When first exposed all steels corrode at about the same rate, but with time the rate of corrosion decreases as shown in Table 1. Also relative corrosivity of different atmospheres varies with time. As given in Fig. 1¹ the loss in one year is higher in industrial than in marine atmosphere, but further period of exposure shows that though the initial loss is higher in the case of industrial atmosphere, the rate falls off more rapidly with time than in the marine atmosphere.

		STEEL		WT. LOSS IN GM./CM. ²					
Ni	Cr o/	Cu	Si %	Mo	Bayo	nne (Indus	Block Island		
70	70	70	/0	/0	1 yr.	3.0 yr.	5·1 yr.	1.1 yr.	5.0 yr.
1.18	0.65	-	_	_	3.70	4.42	5.10	_	_
1.00		1.05	_	_	3.48	4.49	5.32	_	
1.47		_		-	3.29	4.56	5.82		
_	1.20	0.50	0.83	_	-	_	_	2.04	4.83
1.18	0.65	-	_	-		—	_	2.03	5.53
1.84	-	-	_	0.24	×		_	2.07	5.66

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20 18 16 ONE Ωŭ. 14 so. 31 ,oct 12 ¢ B 10 WEIGHT LOSS, G 154 8 6 BAYONNE BLOCK 15 4 62 BAYONNE 2 0 2 0 1 з 5 6 TIME, YR

Fig. 1 — Weight loss versus time curves for three steels

The corrosion rate is also influenced by the conditions under which a material is used, i.e. whether they are inclined or vertical; completely exposed, partly exposed or completely sheltered; near the ground or above the ground; and also on the direction of the wind. Result of tests on specimens boldly exposed and sheltered is given in Fig. 2¹. Initially the loss is lower on sheltered specimens, but after about two years the loss becomes greater.

Mechanism of Corrosion — To understand the effect of alloying elements in retarding corrosion, it is necessary to study the mechanism of protective rust formation. That the nature of the rust itself and not the inherent improvement in the corrosionresistant properties of steel is responsible for low corrosion rate of low-alloy steels has been shown by Maurer and Heine² by an interesting experiment. The periodical removal of rust film from the exposed specimens, in three-year exposure test, failed to show any beneficial effect of adding copper or chromium. Examination of rust on corroding samples shows that those exhibiting best performance have relatively smooth, dense and tightly adhering rust, while fast-corroding steels have coarse, loose and porous rust. This is best illustrated in Fig. 3³. This difference in porosity affects the corrosion rate because it directly influences the quantity and quality of water reaching the surface through the pores. As the thickness of the layer of the corrosion product on the surface of the steel increases, the water directly reaching the surface becomes less. The solubility of corrosion product then comes into play. More soluble the corrosion product, higher is the rate of corrosion and vice versa. Moreover, greater the solubility of the corrosion product, more easily the product is washed off and thus makes the rust more porous, but if the corrosion product is less soluble, it is not easily washed off and thereby decreases the porosity of the rust. From analysis of rust given in Fig. 4⁴ it can be seen that the amount of sulphate and water in the rust increases with the addition of copper and nickel. From these results it is apparent that increase in corrosion resistance is paralleled by increase in sulphate in the rust. This increase in sulphate can be explained only by inferring the formation of a less soluble complex basic sulphate of iron, copper and nickel which accumulates to plug the pores in the rust. Though no comprehensive data on the analysis of rust in marine atmosphere could be found in the literature surveyed, a few analyses by Copson⁴ show the presence of low chloride concentration in the rust probably due to the high solubility of chlorides.

Though the above mechanism explains the role of copper and nickel in the corrosion of low-alloy steels, but the same cannot be said to be applicable to other alloying



FIG. 2 - EFFECT OF SHELTER ON SPECIMENS EXPOSED VERTICALLY AT BAYONNE

elements in the absence of supporting experiments.

Many other mechanisms on the beneficial effect of low alloy additions have been proposed. Carius⁵ suggested that the formation of copper or copper-rich alloy on the surface of copper steel is the reason for its low corrosion, but the analysis of the rust fails to show any copper concentration in outer loose rust, adherent rust or on the surface after descaling. It has also been proposed that rust on poor steel being more hygroscopic remains wet for a longer period. But this alone does not explain properly the vast difference in corrosion rate of good and bad steels.

Effect of Alloying Elements — Corrosion experiments show in general that certain metals used as alloying elements for lowalloy steels such as copper, chromium, nickel, etc., have pronounced effect in increasing the resistance to corrosion while others like carbon, manganese, etc., have no marked influence and that elements like silicon, aluminium, phosphorus, etc., are not effective when added singly, but they do exert influence when added in combination with nickel, chromium, etc. Low alloy additions decrease both pit depths and number of pits, but the greatest improvement is found in case of weight loss.

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Effect of various elements singly or in combination is discussed next.

Effect of Copper — Additions of copper improve the resistance of steel to atmospheric corrosion. Addition of very small amount of copper markedly lowers the corrosion rate. It can be seen from Fig. 5⁶ that up to about 0.2 per cent, copper has big effect in lowering the corrosion rate, but with increase of copper the effect is less marked. A.S.T.M.⁷ and ISI⁸ Corrosion Committee have also reported 0.25-0.50 per cent of copper addition as C-MARKED AND



FIG. 3 — COMPARATIVE CORROSION RESISTANCE OF FIVE STEELS IN INDUSTRIAL ATMOSPHERE. PHOTO-GRAPHS SHOW APPEARANCE OF RUST FILMS AT THE TIMES INDICATED FOR THE DIFFERENT SAMPLES. (Data and photographs by courtesy of Carnegie-Illinois Steel Corp., Pittsburgh)

the optimum value to get the maximum beneficial effect. Same conclusion has also been arrived at by Copson⁹, Hudson¹⁰, Taylersen¹¹ and several other authors. From the result (as given in Table 2) obtained by Taylersen¹¹ by exposing varieties of low-alloy Cu-bearing steels to industrial plus marine, marine and rural atmosphere, it can be seen that the addition of copper is also effective in reducing the rate of corrosion even in industrial plus marine atmosphere. Additions of other alloying elements like nickel, chromium, etc., further improve the resistance to corrosion of Cu-bearing steels.

Effect of Nickel — It has already been mentioned that the beneficial effect of copper reaches its maximum value somewhat at about 0.2-0.5 per cent copper. But that of the nickel steel, however, increases continuously with rise in nickel content as

						T A	BLF	2						
Steel	IN	DUSTR	IAL AN	D MARI	NE			MARIN	Е			Ru	RAL	
Cu	Duration of exposure (in yr.)			Duration of exposure (in yr.)				Duration of exposure (in yr.)						
%	0.5	1	2	3	5	0.5	1	2	3	5	0.5	2	3	5
0.03	20-1	31.1	40.2	44.9	56.6	15.0	24.8	32.9	38.5	50.6	4.1	11.3	14.6	19-7
0.26	14-2	21.8	27.1	29.1	33.6	11.3	19.7	24.9	28.3	36.8	3.9	10.0	12.8	16.5
0.54	12.7	19.7	23.5	25.9	29.4	11.8	18.1	22.5	25.6	31.7	3.9	9.6	12.0	14.9

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Fig. 4 — Percentage H_2O , iron and SO_4 in loose three-year rust from groundward surface of Bayonne steels

shown in Figs. 6 and 7⁹. The improvement increases with time and is higher in marine than under industrial conditions.

Copper and chromium additions further improve the resistance of nickel steels, the general trend of corrosion, however, remains unchanged. Maximum effect is achieved at a copper content of 2 per cent in the presence of 4 per cent nickel. Study of corrosion-time relationship by electrical resistance method shows that the relationship between log of the amount of corrosion and the log of time is a straight line as shown in Fig. 8¹². This indicates that the resistance to corrosion increases with increased duration of exposure.

Addition of chromium to Ni or Ni-Cu steels further increases the resistance to THE REPORT OF TH

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Fig. 5 — Effect of copper on corrosion of lowcarbon steels exposed to the atmosphere for three years f(x) = 0

corrosion, as shown in Table 3^{13} ; though the effect is marked, it is not additive. Addition of molybdenum to Ni-Cr steels gives better result than that with copper. Addition of 0.5 per cent molybdenum instead of 0.5 per cent Cu to 3 per cent Ni - 1 per cent Cr steel reduces the corrosion from 1.6 mils./yr. to 1.4 mils./yr.¹³.

TABLE 3

Sl. No.		MATE	TOTAL		
	Ni	Cu	Cr	Si	mils./yr.
1		0.02	_	0.3	2.6
2	3.1	0.02	-	0.2	2.3
3	3.1	0.50		0.3	2.4
4	3.1	0.01	1.0	0.2	2.1
5	3.0	0-50	1-1	0.3	2.0

Effect of Chromium — Addition of low percentage of chromium (about up to 3 per cent) to steel improves its resistance to atmospheric corrosion considerably as shown in Table 4¹³. With further addition of chromium above 10-12 per cent the corrosion rate reaches low values. This

TABLE 4						
Sl. No.	Approx. Cr, %	Corrosion in Mils./yr.				
1	Nil	3-7				
2	1.0	2-6				
3	1.5	2-5				
4	2.0	2.1				
5	2.5	2-0				

considerable improvement is also supported by the results of other research workers on the line.

Addition of copper to chromium steels further lowers the rate of corrosion, the effect being not additive in this case also. Presence of 0.5 per cent Cu in 1 per cent Cr steels reduces the corrosion rate by one-third

Cr-Si-Cu¹² steel gives maximum corrosion resistance in all the three types of atmosphere, e.g. industrial and marine, marine and rural atmosphere. Effect of C content on low-alloy steel containing Cr is negligible.



FIG. 6 — Weight loss versus nickel content of certain steels at Block Island



FIG. 7 — WEIGHT LOSS VERSUS NICKEL CONTENT OF CERTAIN STEELS AT BAYONNE

Effect of Aluminium — Aluminium, added singly to steel, does not materially affect the rate of corrosion of steel. Exposure test shows that with 1.30 per cent Al the rate falls from 0:110 lb./sq.ft./yr. to 0.080 lb./sq. ft./yr.¹⁴. Electrolytic iron was used to prepare the alloy. Aluminium when added in combination with chromium gives strikingly better result as shown in Table 5¹³.

T A	BLE	5
Cr, %	Al, %	Average corro- sion rate, mils./yr.
_		6.4
-	1.6	3.3
2.6	-	2.4
2.6	0.1	2.3
2.8	1.4	1.5
	T A Cr, % 	T A B L E Cr, Al, $\%$ $\%$ $$ $$ $$ $1 \cdot 6$ $2 \cdot 6$ $$ $2 \cdot 6$ $0 \cdot 1$ $2 \cdot 8$ $1 \cdot 4$

Effect of Manganese — The general conclusion is that the addition of Mn to steel has no marked effect on the resistance to corrosion, but Copson⁹ has shown beneficial effect of Mn in 0.3 per cent Cu steel both in marine and industrial atmospheres. The effect in marine atmosphere is, however, more pronounced.

Effect of Phosphorus — Addition of small amount of phosphorus in combination with other elements has beneficial effect. The effect is more marked over shorter period of exposure than longer one. Though in chromium steels it has not much effect, increase of P from 0.02 to 0.14 per cent in Cu-Si-Cr steels markedly improves the corrosion resistance⁶.

Effect of Silicon — Silicon, when added singly, improves the resistance of steel to corrosion, but as high-Si steel is brittle this is not much used. Low addition of silicon¹ improves the corrosion resistance of chromium steel, but in copper steel silicon has no beneficial effect.

Effect of Arsenic and Cobalt — Small amount of arsenic increases the corrosion resistance of steel. Steels containing 0.1 per cent arsenic and 0.1 per cent Cu show equal or better resistance than those containing 0.22 per cent Cu only¹⁰.

Co and Ni, in spite of having close relationship of many properties, do not show much resemblance in atmospheric corrosion tests. Though there is a general tendency of decreasing rate of corrosion, the effect with certain amount of Co is below what is got from the same amount of nickel¹⁴.

Effect of Other Alloying Elements — The effect of alloying elements like Ag, Sn, W, Bi, Be, etc., on corrosion resistance of low-alloy steel has also been studied. Of all the elements the presence of Be produces a striking result. 0.4 per cent Be reduces the corrosion index of steel containing 0.2 per cent Cu from 3.3 mils./yr. to 1.8 mils./yr¹³.

Systematic investigations on atmospheric corrosion of metals and alloys have been started from June 1955 in the National

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FIG. 8 --- CORROSION-TIME RELATIONSHIP

Metellurgical Laboratory to study the corrosion in industrial atmosphere and have yielded interesting data. But these experiments are to be extended over a long period, say, 5 years, before any definite conclusions can be arrived at.

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- Some Recent Advances in the Study of Transformations in Alloy Steels, by G. MAYER.
- Development of Creep-resistant Alloy Steels, by G. P. CHATTERJEE.
- 4. The Welding of Special and Alloy Steels, by J. HINDE.
- 5. The Stress-corrosion Cracking of Austenitic Stainless Steels in Aqueous Chloride Solution, by T. P. HOAR & J. G. HINES.
- Effect of Low Alloy Additions on Corrosion of Steel in Different Atmospheres, by K. P. MUKHERJEE, A. K. LAHIRI & T. BANERJEE.

MR. D. GILL-DAVIS (Staybrite Works, Sheffield)

With the additions of stabilizers to stainless steels weld decay is readily prevented. This is a wellknown fact. Welding of austenitic stainless steels is simplest on earth provided expert opinion is taken, which is readily available from the British Welding Research Institute. They have recently published a book on welding of austenitic stainless steels for corrosion and heat-resistant work.

MR. E. H. BUCKNALL (Director)

I am not sure that the majority of martensite stainless cutlery does not contain welds. A document of 'Curtain walls' passed to me during the meeting emphasizes that type 430 (16-18 per cent Cr) is the steel in largest use. One hears much of the inevitable defectiveness of the all-austenitic weld. It is a fact: What is the explanation? Cases of weld cracking from Sindri investigated at the National Metallurgical Laboratory have not exhibited weld decay, but stress effects due to use of force fits in welding.

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MR. S. VISVANATHAN (Tata Iron & Steel Co. Ltd.)

Anything in ferrous metals can be welded provided necessary precautions are taken. Welding in the field or at the site is quite different than at the fabrication shops. Certain precautions which can be taken in the shop cannot be adopted in the field. I have had to do with welding for quite a long time. Mild steel is easily weldable if the sections are below 2 in. I would refer to some experiments which have been carried out in the plant on welding 7 in. buck stays. We have tried lowhydrogen electrodes and shielded-arc electrodes; we have tried all sorts of electrodes produced in America and England, but the result is pretty disappointing. It shows that even in mild steel if the sections are heavy and components are large, this easily weldable material is also very difficult to weld.