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Studies on the presence of copper in the galvanized coating on weathering steel and the adherence characteristic of the protective copper complex formed on galvanized weathering steel

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Following the hot-dip process for zinc coating on weathering steel, the galvanizing bath was found to have picked up copper. The galvanizing bath was observed to pick up Cu from the weathering steel at an average rate of $1.83 \times 10^{-3}\%\ \mathrm{s^{-1} m^{-2}}$ at $452 \pm 2\,^{\circ}\mathrm{C}$. EDAX/SEM studies exhibited a concentration gradient of copper to exist across the thickness of the galvanized coating on weathering steel. XRD studies revealed the formation of a protective copper complex, $\{\mathrm{Cu}[(\mathrm{OH})_2\mathrm{Cu}]_3\}\mathrm{SO}_4$, on galvanized coating containing 0.739% Cu, when exposed in marine and industrial atmospheres. The adherence characteristic of the copper complex to the galvanized coating was found to be very satisfactory.

1. Introduction

With the aim of increasing the life of structural members in corrosive environments, copper-bearing steels (popularly known as weathering steels) were developed some time ago by BISRA [1]. In 1913, Buck [2] reported the beneficial effect of copper. This effect was attributed to a combination of copper with sulphur in steel, thus rendering sulphur innocuous [3]. Copson found that a protective complex of copper in the rust was formed on weathering steel during atmospheric exposure [4]. The complex was represented by the formula $\{\mathrm{Cu}[(\mathrm{OH})_2\mathrm{Cu}]_x\}\mathrm{SO}_4$, with maximum of $x = 3$. The complex is believed to be formed by the coordination mechanism of Werner [5], in the light of which, when the primary valency of copper is satisfied in the formation of normal CuSO_4, there remains the secondary valency directed towards building up the complex in which hydroxyl groups are arranged about a central Cu atom. The literature [6] suggests that the protective value of the complex is established long before the attainment of a maximum value of x. The content of copper in the steel also determines the value of x. A copper complex with $x = 3$ is therefore the most protective of the copper sulphate hydroxides.

The objective of the present work was to investigate whether the copper contained in galvanized coating responds similarly in producing the protective copper complex during industrial and marine exposures. This paper also deals with the ability of the copper complex to adhere to the surface of the galvanized coating.

2. Experimental procedure

Specimens of $50 \times 25 \times 3$ mm, cut from the weathering steel (C, 0.18%; Cu, 0.39%) sheet were degreased, pickled, pre-fluxed, dried and galvanized by hot dipping into the galvanizing bath maintained at $452 \pm 2\,^{\circ}\mathrm{C}$. The zinc taken was of 99.917% purity with 0.083% iron. The hot-dipping duration was 35 s for all the specimens.

X-ray diffraction (XRD) analysis of the zinc-coated surface and the corrosion products were carried out using an X-ray diffractometer (Siemens D-500), equipped with Tektronix console LA 100 digital microprocessor computer and PDP 11/23 recorder/plotter system. The study was carried out in steps of 0.03 degrees with 0.9 s per step using Cr-*K* radiation.

For EDAX/SEM studies, the galvanized weathering steel specimens of 4×10 mm were sectioned, ground up to 600 grade emery paper, polished against selvit cloth impregnated with a slurry of powdered alumina, cleaned ultrasonically and finally etched in 2% nitramyl etchant. The scanning electron microscope (CAMSCAN series 2, Link Analytical AN-1000, UK) was made to scan a number of regions belonging to different intermetallic layers of the galvanized coating on weathering steel for the presence of copper and also for plotting the X-ray scanning spectrum (map).

3. Results and discussion

The galvanizing bath before and after hot dipping 30 weathering steel specimens was chemically analysed, and the compositions are presented in Table I. The data indicate copper pick-up in the galvanizing bath to the extent of 0.170% from the weathering steel, under the influence of diffusion. The total surface area of 30 weathering steel specimens ($50 \times 25 \times 3$ mm) taken together amounted to $0.0885\ \mathrm{m}^2$ and the sum

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TABLE I Galvanizing bath compositions (%) before and after hot-dip operation

Element	Before hot dipping	After hot dipping
Zn	99.917	99.773
Fe	0.083	0.057
Cu	0	0.170

total of hot-dipping durations of all the specimens taken together was 1050 s. This suggests that Cu pick-up to the level of 0.17% for a period of 1050 s was at an average rate of $1.83 \times 10^{-3}\% \ s^{-1} m^{-2}$.

The X-ray diffractogram taken from the outermost layer of the galvanized coating exhibits a peak of Cu, indicating the presence of Cu in the galvanized coating on weathering steel (Fig. 1). The EDAX/SEM studies were also carried out on the last (30th) weathering steel specimen galvanized, to obtain the percentage Cu in different intermetallic layers of the galvanized coating on weathering steel and also within the weathering steel matrix close to the galvanized coating. The data obtained are shown in Table II. The EDAX/SEM scanning spectrum taken from the outermost layer of the galvanized coating is shown in Fig. 2. The spectrum exhibits the peaks of Cu, Zn and Fe.

As already described, the weathering steel specimen used for galvanizing contained 0.390% Cu. The data cited in Table II indicate the presence of 0.201% Cu in the region of the weathering steel matrix close to the galvanized coating. This shows a depletion of Cu from 0.390 to 0.201% in the aforementioned region. This drop in percentage Cu is attributed to diffusion of copper from the weathering steel into the galvanized coating. It is also evident from Table II that percentage Cu increases from the matrix to the outermost layer. This suggests that a concentration (percentage) gradient of copper exists across the thickness of the galvanized coating on weathering steel.

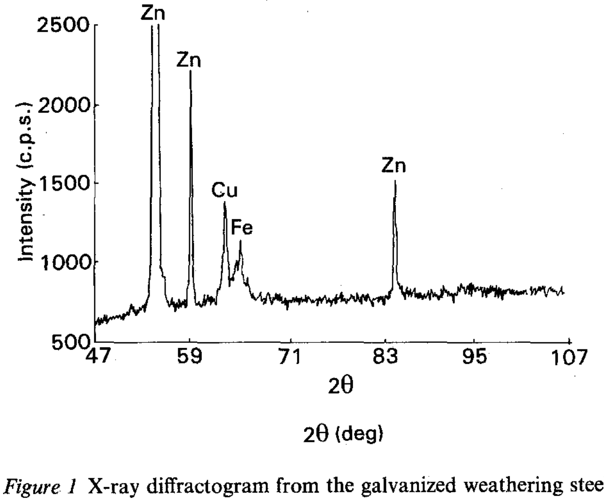

Figure 1 X-ray diffractogram from the galvanized weathering steel surface.

TABLE II Variation of percentage Cu in different regions of galvanized weathering steel

MT	TD	CP	PU	OM
0.201	0.466	0.592	0.801	1.098

MT = weathering steel 'matrix' close to the galvanized coating; TD = 'thin and dark' etched intermetallic layer of the galvanized coating adjacent to the weathering steel (substrate) surface; CP = 'compact and palisade' intermetallic layer next to the thin and dark-etched one; PU = 'penultimate' intermetallic layer of the galvanized coating; OM = 'outermost' layer of the galvanized coating.

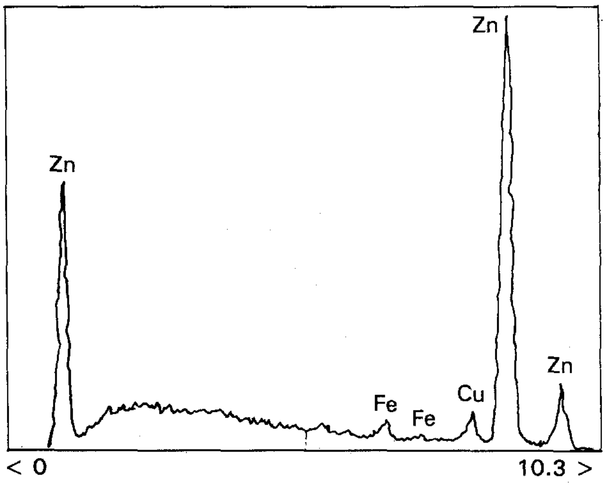

Figure 2 EDAX/SEM scanning spectrum of the outermost layer of galvanized coating on weathering steel.

XRD studies were carried out separately on the rust layers formed in marine and industrial environments. These studies revealed the formation of a basic complex of copper $\{Cu[(OH)_2Cu]_3\}SO_4$ in the white rust on galvanized weathering steel in both of these environments. The data are presented in Table III and the corresponding X-ray diffractograms are shown in Figs 3 and 4. The copper complex formed in this study corresponded to the maximum value of x ($x = 3$) in the general formula of the complex. Again, from Table II, the galvanized coating contained an average of 0.739% Cu, considering layers from TD to OM. The galvanized coating containing 0.739% Cu thus responded to the formation of the protective complex of copper on the surface of the coating during atmospheric exposures. The copper sulphate hydroxide so formed is believed to fill in the pores of the rust [6], giving a more compact and hence a more corrosion-resistant rust layer on galvanized weathering steel. For good corrosion protection, the adherence of corrosion products, especially of the copper complex, to the galvanized weathering steel surface is desirable. If the complex adheres poorly to the galvanized weathering steel surface, the pores of white rust layer on the steel filled in by it may preferentially become sites of localized attack. In this study, the corrosion-product layer formed on the surface of galvanized weathering steel showed a satisfactory adherence, in that it could not be washed away by running water to any measurable extent. However, heating in ammonium acetate solution removed the corrosion products to a large extent.

The satisfactory adherence characteristic of the copper complex is well demonstrated by the XRD study carried out on the corroded galvanized weathering

TABLE III Details of XRD peaks, representing $\{Cu[(OH)_2Cu]_3\}SO_4$

Parameter	Marine environment	Industrial Environment			
		Peaks from white rust layer 'as-obtained' on exposure		Peaks after removal of white rust layer by applying razor blade abrasion	
		I	II	I	II
Intensity (% HP[a])	5.90	64.10	70.10	32.40	35.30
Peak position (on 2θ scale)	53.986	42.183	51.240	42.232	51.332
d_{hkl} (nm) (experimental)	0.25208	0.31913	0.26778	0.31953	0.26767
d_{hkl} (nm) (from JCPD File [7])	0.25210	0.31900	0.26780	0.31900	0.26780
hkl [5]	122	400	420	400	420

[a] Percentage height of peak.

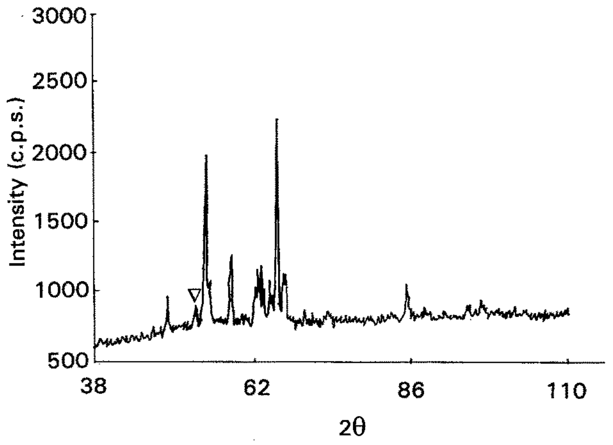

Figure 3 X-ray diffractogram from corroded surface of the galvanized weathering steel, exposed in marine atmosphere. The marked (▽) peak corresponds to $\{Cu[(OH)_2Cu]_3\}SO_4$.

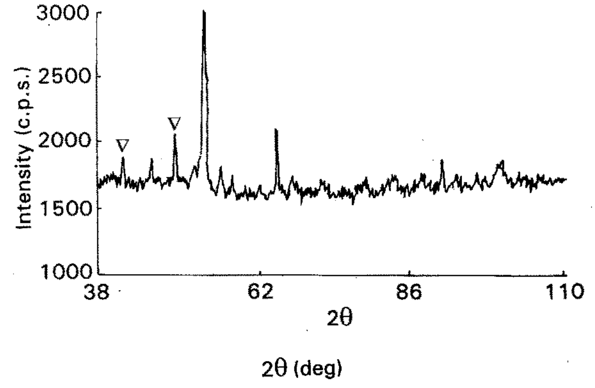

Figure 4 X-ray diffractogram from corroded surface of the galvanized weathering steel, exposed in industrial atmosphere. Marked (▽) peaks correspond to $\{Cu[(OH)_2Cu]_3\}SO_4$.

steel specimen, stripped of corrosion products as far as possible by razor-blade abrasion. Interestingly, even after that severe abrasion the XRD peak representing the copper complex is found to remain present at an intensity (% HP) of about half of that present before abrasion. This can be seen by comparison of the two X-ray diffractograms (Figs 4 and 5) taken from a corroded galvanized weathering steel specimen before and after abrasion (See Table III).

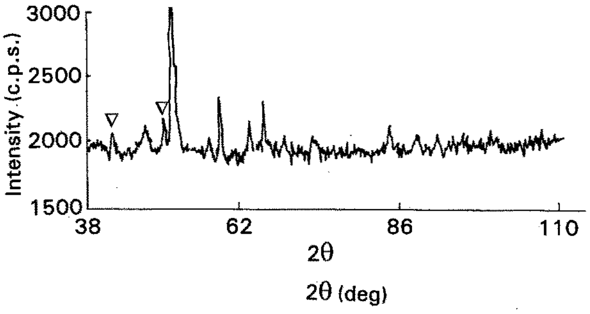

Figure 5 X-ray diffractogram after removal of corrosion products as far as possible from the corroded galvanized weathering steel. Marked (▽) peaks correspond to $\{Cu[(OH)_2Cu]_3\}SO_4$.

Thus the most protective complex of copper sulphate hydroxides, formed in the rust layer on galvanized weathering steel during exposure to both industrial and marine environments, it expected to contribute considerably to reducing the corrosion rate of galvanized weathering steel during atmospheric exposure because of the well known pore-plugging action, coupled with very good adherence characteristics of the copper complex.

4. Conclusions

1. The galvanizing bath was found to pick up Cu from the weathering steel at an average rate of $1.83 \times 10^{-3}\% \ s^{-1} m^{-2}$ of weathering steel hot-dipped into the bath at $452 \pm 2\,^{\circ}C$.
2. EDAX/SEM studies demonstrated the presence of Cu in each of the intermetallic layers belonging to the galvanized coating on weathering steel.
3. A composition gradient of Cu was found to exist across the thickness of the galvanized coating on weathering steel.
4. The protective copper complex, $\{Cu[(OH)_2Cu]_3\}SO_4$, was found to have formed on the galvanized coating containing an average of 0.739% Cu during exposures in marine and industrial environments.
5. The adherence of the corrosion products, and especially of the copper complex, to the galvanized coating was found to be very satisfactory.

6. The galvanized coating on weathering steel, as compared to that on mild steel or any other steel containing no Cu, is expected to have a longer lifetime during marine and industrial exposure applications in view of the protective nature, coupled with very satisfactory adherence characteristics of the copper complex that forms during atmospheric exposures.

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