BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 743—744 (1974)

The Effect of Copper(II) on the Formation and Thermal Change of Synthetic β-FeOOH

Katsuya INOUYE, Hiroyuki IMAMURA, Katsumi KANEKO, and Tatsuo ISHIKAWA
Department of Chemistry, Faculty of Science, Chiba University, Chiba 280

(Received July 10, 1973)

Synopsis. The effect of Cu(II) added to β-FeOOH in various ratios up to 6% Cu/Fe was examined by X-ray diffraction, electron microscope, BET surface area, DTA, TGA and chemical analyses. Differing from other cases reported previously, Cu(II) showed no effect, but thermal changes of the Cu-doped samples indicated a reinforcement of bonding by Cu.

In order to obtain a more definitive fundamental elucidation of the role of copper added to anti-weathering steels, which have been widely recognized to be appreciably anti-corrosive in atmospheric and, perhaps in a lesser extent, marine environments, the present authors have examined the effect of Cu(II) doped in every component of the corrosion product. These studies have covered the following cases: oxide-oxyhydroxide mixtures produced by the air oxidation of $Fe(OH)_2$,[1,2] magnetite from mutual interaction between $Fe(OH)_2$ and $Fe(OH)_3$ colloids,[3] magnetite from the self-decomposition of $Fe(OH)_2$[4] and α-FeOOH produced by the hydrolysis of a Fe(III)-sulfate solution.[5] The explanation of the phenomena observed as the copper effects is by no means simple, but it appears plausible to conclude that Cu(II) invariably impedes the formation and growth of those oxides and/or oxyhydroxides.

The present study is concerned with an examination of the similarly-expected copper effect on the crystallization of β-FeOOH, together with some thermal changes in Cu-doped β-FeOOH. It is interesting to note that β-FeOOH, as one of the corrosion products of iron-base alloys, is produced only when the Cl^- ion (or possibly other halide ions) is present and further, that the β-FeOOH crystal embraces chlorine as a genuine component.[6–8] It thus appears that the behavior of chlorine is an essential problem in any case involving the characteristics of β-FeOOH.

β-FeOOH was prepared from solutions of 0.2 M $FeCl_3$ added by 0.2 M $CuCl_2$ in 0, 1, 2, 3, 4, 5, and 6 Cu/Fe atomic % through hydrolysis with and without the addition of urea (30 g per 500 ml of a mixed solution) at 95—99 °C for 5 hr; up to this temperature range the solution was warmed at the rate of 1 °C/min. When aged, the suspension was kept at 30 ± 0.5 °C for various times up to 10, 20, 30, and 50 days. During the aging procedure, the pH values of the suspensions were kept at 7.5—8.0 with daily stirring. The suspensions were then filtered, and the crystals thus obtained were washed thoroughly with distilled water and dried at 80 °C for 2 hr.

The Fe, Cu, and Cl contents were conventionally determined after dissolving β-FeOOH in HCl by $K_2Cr_2O_7$ titration, by colorimetry in the presence of Cupferazone, and by Volhard method respectively, based on the crystal dried at 105—110 °C for 1 hr. Correction for the co-existing Cu(II) on Fe determination was done by means of a calibration curve. X-Ray diffraction, BET surface area determination, electron microscopy, differential thermal analysis (DTA), and thermal gravimetric analysis (TGA) were carried out by procedures similar to those described in preceding reports.[3–5,7,8]

It is noteworthy, first, that any Cu(II) over 6% Cu/Fe added to the original solution is excluded from the precipitates into medium during the course of hydrolysis, though the reason why 6% is the limit has not yet been understood.

The electron micrographs of each sample, with or without addition of Cu(II) and after aging at 30 °C for various durations, showed almost identical rod-like crystals approximately $1.8—1.9 \times 10^{-5}$ cm in length. The specific BET surface area measurements also gave almost identical values, ranging from 41 to 51 m^2/g. X-Ray diffraction patterns were exactly the same, irrespective of the variation in Cu content and aging time. There is no recognizable shift in any diffraction peak of the samples with different amounts of Cu present. The crystallite size calculated showed no appreciable variation with regard to the Cu content and aging time, giving values mostly in the range of 250—290 Å.

These results were inconceivable on the basis of our knowledge of previous experimental results, which indicated comprehensively that Cu is more or less destructive in the formation of oxyhydroxides or oxides. The disappearance of the Cu effect in the present case was thought at first to be possibly due to the presence of urea in the hydrolysis because of the homogeneous precipitation. The preparation of β-FeOOH without

TABLE 1. CHEMICAL COMPOSITION OF β-FeOOH

Aging time (day)	Cu/Fe, intended (%)	Cu/Fe, analyzed (%)	Cl/Fe, analyzed (%)	Cl/(Fe+Cu), calculated (%)
0	0	0.0	8.2	8.2
	1	0.9	8.2	8.1
	3	2.9	8.7	8.4
	6	5.8	9.2	8.7
20	0	0.0	8.7	8.7
	1	0.9	8.9	8.8
	3	3.1	9.3	9.0
	6	5.2	9.3	8.8
50	0	0.0	8.3	8.3
	1	0.8	8.8	8.7
	3	2.8	9.1	8.8
	6	5.5	9.0	8.5

the addition of urea under conditions otherwise the same was attempted in order to confirm the effect of urea. The X-ray diffraction patterns and other examinations of the resultant crystals showed them to be entirely identical with those which came out of suspensions upon the addition of urea.

The chemical analyses of each sample give us the Cu/Fe and Cl/Fe atomic ratios which are tabulated in Table 1. It seems that in crystals Fe is replaced by Cu at each intended ratio, except in the cases of 6% Cu/Fe, when only somewhat lower ratios were obtained. As for the Cl/Fe atomic ratio, values were observed in only the limited range of 8—9%, although a slight increase with the rise in the Cu/Fe ratio was observed. However, a constant Cl content was obtained by calculating Cl/(Fe+Cu). It is thus implied that Cl interacts not only with the Fe but also with the Cu included in the crystal.

According to Mackay,[6] β-FeOOH has the α-MnO_2 or hollandite ($BaMn_8O_{16}$) structure in a tetragonal system with a=10.48 Å and c=3.023 Å. Channels parallel to the *c*-axis are contained in crystals, where Cl^- and H_2O can be accomodated and sometimes mutually exchanged. In other words, the β-FeOOH structure is like a bundle of fine tubes, the walls of which are composed of O^- and OH^- ions surrounding the Fe^{3+}. Each Fe^{3+} is surrounded octahedrally by six (O^-, OH^-) ions. The octahedra are linked to form tubes parallel to the *c*-axis, sharing edges and some corners of the octahedra. In this context, therefore, it may be concluded that β-FeOOH crystals are so strongly stabilized by the presence of Cl^- that the destructive action of replacing Cu does not show up.

TGA curves in Fig. 1 on pure β-FeOOH and the 6% Cu/Fe sample illustrate the difference in the temperature region where the weight loss increases steeply, corresponding to the evolution of $FeCl_3$ sublimed, accompanied by a transformation of β-FeOOH to α-Fe_2O_3.[7,8] The shift in the "decomposition temperature" with the Cu indicates an increase in the bonding in the Cu-doped crystals. From the DTA curves in Fig. 2, we can conceive a bonding between the Cu added and the Cl constitutionally present. After the evolution of H_2O and the degradation of the β-FeOOH crystals to an amorphous state below 300 °C, a rather sudden recrystallization to α-Fe_2O_3 occurs at the temperatures characteristic of the Cu content; the recrystallization temperature corresponds to the sharp exothermic DTA peak, which shifts to higher temperatures proportionally with the increase in the Cu/Fe ratio. It is noted further that shallow endothermic DTA peaks appear in Fig. 2 just below 500 °C, presumably as a result of the melting of the resulting $CuCl_2$ (mp 498 °C).

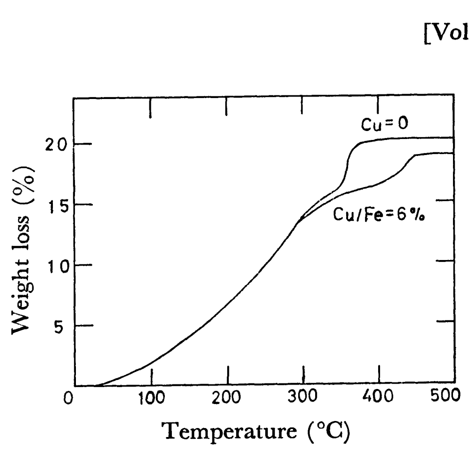

Fig. 1. TGA curves of β-FeOOH with 6% Cu/Fe and without addition of Cu.

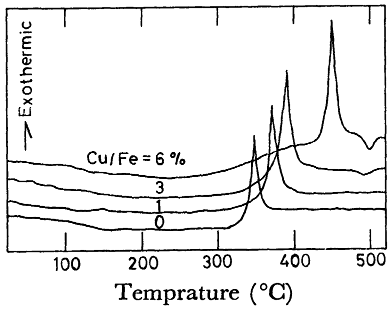

Fig. 2. DTA curves showing the shift of exothermic peaks.

All the facts observed seem to coincide with the unexpectedly high consistency of β-FeOOH crystals doped with Cu(II), if one accepts that it is likely to produce an interaction between Cu and Cl.

This work has been partly supported by the Government Science Research Fund of the Ministry of Education.

References

1) K. Inouye, *J. Colloid Interface Sci.*, **27**, 171 (1968).

2) K. Inouye and T. Ishikawa, *Corrosion Engineering, Japan*, **20**, 460 (1971).

3) K. Inouye, T. Hozumi, and T. Ishikawa, *Kolloid-Z. Z. Polym.*, **250**, 262 (1972).

4) K. Inouye, K. Murata, and T. Ishikawa, *Z. Anorg. Allg. Chem.*, **386**, 340 (1971).

5) K. Inouye, S. Ishii, K. Kaneko, and T. Ishikawa, *ibid.*, **391**, 86 (1972).

6) A. L. Mackay, *Miner. Mag.*, **32**, 545 (1960).

7) T. Ishikawa and K. Inouye, This Bulletin, **45**, 2350 (1972).

8) T. Ishikawa and K. Inouye, Paper presented at the 25th Symposium of Colloid and Interface Chem., Chem. Soc. Jap., Nov., 1972.