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63-1-4

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# TRANSLATION

CORROSION OF COPPER AND ITS ALLOYS IN  
HYDROFLUORIC ACID

By

E. I. Antonovskaya and Yu. N. Vil'k

## FOREIGN TECHNOLOGY DIVISION

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English Pages: 6

Source: Khimicheskaya Promyshlennost', No. 6,  
1961, pp. 61-62.

SC-1257  
SOV/64-61-0-6-3/3

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## CORROSION OF COPPER AND ITS ALLOYS IN HYDROFLUORIC ACID

E. I. Antonovskaya and Yu. N. Vil'k

In the manufacture and storage of hydrogen fluoride and its aqueous solution, i.e., hydrofluoric acid, equipment made of copper and its alloys is used [1 through 8]. At the same time, in the literature there are no data on the corrosion of copper and its alloys in boiling hydrofluoric acid.

It is well known that the corrosion of copper and its alloys depends to a considerable degree upon the contamination of the hydrofluoric acid by atmospheric oxygen, and also the presence in it of other oxidizing agents and impurities ( $H_2SO_4$ ,  $SO_2$ ,  $H_2S$ ,  $H_2O_2$ , and others). Therefore, we studied first of all the effect of these impurities and of atmospheric oxygen upon the corrosion of M-1 copper and copper alloys BrA5, BrAN and L62 in boiling hydrofluoric acid.

The samples were tested in a laboratory column made of M-1 copper (Figure). Into the 100-ml vessel 1 was poured 40% hydrofluoric acid and heated in an oil bath. The temperature was controlled by a thermoregulator within the limits from 110 to 114°. Six samples, hung on a fluoroethylene-4 tape, were placed in the acid and at the vapor-liquid interface. The system was checked for tightness, and before the experiment was flushed with the gas in which the experiment

was conducted. The duration of the experiments was 100 hours. The admixtures were introduced in the given quantities along with the hydrofluoric acid and their content was analyzed by the methods given in the Technical Specifications of the Ministry of the Chemical Industry 3846--53. The results obtained are given in Tables 1, 2 and 3.

From this data it is apparent that the presence of oxygen in pure hydrofluoric acid has the more negative influence on copper corrosion, especially at the vapor-liquid interface, where corrosion cracking occurred along the boundaries of the crystals as well as through them. Precipitation of copper sponge also took place at the affected places. This effect, the mechanism of which is being studied at the present time, was also noted by Lingnau [9]. In the liquid phase copper corrodes uniformly.

When from 5 to 15% sulfuric acid is added to 40% hydrofluoric acid, the nature of copper corrosion is changed. This, together with other factors, is apparently explained by the change in the ratio of  $H_2O$  to HF and the formation of fluosulfonic acid [10, 11], which lowered the corrosive activity of the mixture, and also by the higher boiling point of the mixture at the vapor-liquid interface. Corrosion cracking is reduced, and the corrosion first of all becomes pitting (on addition of 10%  $H_2SO_4$ ), and then uniform (on addition of 15%  $H_2SO_4$ ), but the rate of over-all corrosion is increased.

The presence of  $H_2S$  affects copper corrosion more than an admixture of  $SO_2$ ; cracking becomes greater and the corrosion rate increases. This was noted by Byrne and Vahn [12] for copper in other media. When adding to hydrofluoric acid  $SO_2$  in concentrations encountered in the manufacture of hydrogen fluoride, the corrosion

rate of copper was not increased; the nature of the corrosion also did not change.

When hydrogen peroxide was added, the rate of the over-all corrosion of copper was increased. This is explained by the catalytic decomposition of  $H_2O_2$  on the surface of the copper ( $H_2O_2 \rightleftharpoons H_2O + \frac{1}{2} O_2$ ); the oxygen formed causes the corrosion [13].

The copper alloys BrA5, BrAN and L-62 show higher rates of over-all corrosion and corrosion cracking at the vapor-liquid interface than does copper. The corrosion destruction of alloys is accompanied by "dealuminizing" of BrA5 and BrAN and "dezincing" of L-62 brass. In the corrosion of BrA5 it is mainly aluminum that goes into the corrosion products; corrosion cracking and precipitation of copper sponge are observed in the vapor phase and at the vapor-liquid interface at the affected places.

When brass corrodes, a zinc-rich component ( $\beta$ -phase) passes into the acid and cracking and precipitation of copper sponge occur.

Metallographic studies of bronze and brass samples, and also of their corrosion products confirm the results obtained.

#### Conclusions

1. The corrosion rates of M-1 copper, L-62 brass and BrA5 and BrAN bronze in boiling hydrofluoric acid were determined.
2. A study was made of the effect of oxygen,  $H_2SO_4$ ,  $SO_2$ ,  $H_2S$  and  $H_2O_2$  upon the corrosion of copper and its alloys in 40% hydrofluoric acid at 110 to 114°.
3. It was shown that oxygen, hydrogen peroxide and hydrogen sulfide heighten copper corrosion under the above conditions. In the concentrations studied,  $SO_2$  did not exert a substantial influence on the resistance of the copper. The addition of sulfuric acid im-

proved the nature of copper corrosion, but increased the rate of over-all corrosion.

4. Copper alloys (BrA5, BrAN and L-62) corrode under the cited conditions more vigorously than does M-1 copper.

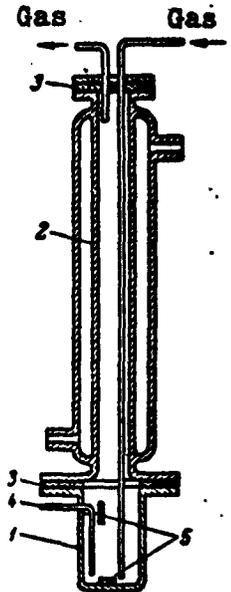


Figure. Diagram of laboratory apparatus for testing alloy samples: 1--vessel; 2--column with water jacket; 3--fluoroethylene-4 gasket; 4--thermocouple housing; 5--test samples.

Table 1  
The influence of oxygen on the corrosion rate of M-1 copper in 40% hydrofluoric acid,  $\text{g/m}^2 \cdot \text{hr}$

| Gaseous medium | Liquid phase* | Vapor-liquid interface | Nature of corrosion at interface                   |
|----------------|---------------|------------------------|--|
| Air . . . . .  | 3.38          | 5.90                   | Corrosion cracking, precipitation of copper sponge |
| Nitrogen with: |               |                        |  |
| 3% oxygen      | 0.19          | 0.12                   | " "  |
| 0.02% oxygen   | 0.05          | 0.05                   | Precipitation of copper sponge                     |

\*In the liquid phase corrosion was uniform in all experiments.

Table 2

The influence admixtures on the corrosion rate of M-1 copper in 40% hydrofluoric acid,  $\text{g/m}^2 \cdot \text{hr}$  (Gaseous medium: nitrogen + 0.02% oxygen)

| Admixtures to 40% HF                  | Liquid phase* | Vapor-liquid interface | Nature of corrosion at interface                              |
|---------------------------------------|---------------|------------------------|---|
| Without admixtures                    | 0.05          | 0.05                   | Precipitation of copper sponge                                |
| 5% $\text{H}_2\text{SO}_4$ . . . . .  | 0.14          | 0.12                   | Pitting, precipitation of copper sponge                       |
| 10% $\text{H}_2\text{SO}_4$ . . . . . | 0.40          | 0.36                   | Negligible pitting  |
| 15% $\text{H}_2\text{SO}_4$ . . . . . | 0.61          | 0.71                   | Uniform corrosion   |
| 0.02% $\text{SO}_2$ . . . . .         | 0.05          | 0.01                   | Precipitation of copper sponge                                |
| 0.21% $\text{SO}_2$ . . . . .         | 0.08          | 0.09                   | Corrosion cracking, precipitation of copper sponge            |
| 0.01% $\text{H}_2\text{S}$ . . . . .  | 0.27          | 0.36                   | " "   |
| 0.1% $\text{H}_2\text{O}_2$ . . . . . | 0.30          | 0.11                   | Precipitation of copper sponge                                |
| 0.5% $\text{H}_2\text{O}_2$ . . . . . | 0.81          | 0.13                   | Negligible corrosion cracking, precipitation of copper sponge |
| 1% $\text{H}_2\text{O}_2$ . . . . .   | 1.13          | 0.49                   | Corrosion cracking, precipitation of copper sponge            |

\* In the liquid phase corrosion was uniform in all experiments.

Table 3

The corrosion rate of copper alloys in 40% hydrofluoric acid,  $\text{g/m}^2 \cdot \text{hr}$   
(Gaseous medium: nitrogen + 0.02% oxygen)

| Alloy   | Liquid phase* | Vapor-liquid interface | Nature of corrosion at interface |
|---|---------------|------------------------|----------------------------------|
| Pure hydrofluoric acid                          |               |                        |                                  |
| M-1 . . .                                       | 0.05          | 0.05                   | Precipitation of copper sponge   |
| BrAN . .  | 0.21          | 0.06                   | " "                              |
| BrA5 . .  | 0.26          | 0.15                   | Negligible corrosion cracking    |
| Hydrofluoric acid + 15% $\text{H}_2\text{SO}_4$ |               |                        |                                  |
| M-1 . . .                                       | 0.61          | 0.71                   | Uniform                          |
| BrA5 . . .                                      | 0.03          | 0.05                   | Corrosion cracking               |
| L-62** . .                                      | 1.80          | 2.8                    | " "                              |

\*In the liquid phase corrosion was uniform in all experiments.

\*\*Before the experiment the brass samples were annealed at  $250^\circ$  for relief of internal stresses.

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