

Corrosion risk of SO₂ on silver plating of electric components

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Abstract. With the miniaturization and high integration of electronic devices, the reliability of the devices will be seriously reduced by the small corrosion of silver plating. As common corrosion pollutants, SO₂ have strong corrosion sensitivity to silver. Using the G1 limit in ANSI/ISA 71.04 as the baseline, hour-by-hour SO₂ concentration data for 210 cities show that the SO₂ ranges from 1-993 μg/m³, with an average of 20.80% of days ratio and 8.04% of hours ratio exceeding G1 level requirements, indicate a momentary high corrosion risk in the actual running environment. For silver plating, the corrosion risk of independent parameters conforms to the law of power function. Under the comprehensive influence of multiple factors, the corrosion thresholds of some parameters will decrease and the corrosion risk of electronic devices in service will increase.

Keywords: Electric component; Ag plating; SO₂; corrosion.

1. Introduction

Silver has good electrical and thermal conductivity and is the most commonly used plating material for electronic devices. But silver has strong activity in the environment containing sulfur pollutants, which is easily subjected to atmospheric corrosion. With the corrosion of microelectronic devices used in the automotive industry increasing, the corrosion of silver coating on electronic devices poses a risk to vehicle safety.

The electrical behavior of a material in an electronic device is a function of ambient humidity and the amount of contaminants [1], with the most active gas being SO₂. When the surface of silver plating is covered with wetting film, the SO₂ pollutant dissolves and produces uniform corrosion, while microdroplets attached to the surface, SO₂ pollutant can cause pitting corrosion. Both uniform corrosion and pitting corrosion can accumulate corrosion products between the connection points of the silver plating, and reduce the electrical conductivity of the device, which can cause the failure of the automotive electronic system.

With the miniaturization of electronic and electrical systems, the separable electrical pin and voltage are lower than before, leading that few amount of corrosion products can cause the failure of electronic equipment. As integrated circuits and devices are exposed to various environment conditions, the situation of corrosion failure becomes more complicated. Based on the SO₂ hourly data of 210 cities, this paper briefly discusses the corrosion risk of SO₂ on electronic devices, and explores the galvanic corrosion possibility and corrosion mechanism of silver plating. Combined with the collaborative corrosion and prediction methods of different gas mixtures, the changes of gas corrosion threshold and device corrosion risk under multi-factor working conditions are analyzed.

2. Atmospheric corrosion risk

According to the concentration conversion method described in "GB/T 2423.51 Environmental test Part 2: Test method Test Ke: Corrosion test of Flow Mixed Gas", "ANSI/ISA-71.04 Environmental Conditions for Process Measurement and Control Systems: Airborne Contaminants" G1 level requirements SO₂&SO₃<10ppb=26.3 μg/m³. The hourly data of SO₂ pollutants in 210 cities in China in 2022 were analyzed, and the concentration range was 1-993 μg/m³, with an

average value of 8.88 $\mu\text{g}/\text{m}^3$. According to the SO_2 concentration described in ANSI/ISA 71.04 (Level G1) as the limit value, the SO_2 concentration of each city is collected by hour, and the statistical dimension is hour ratio and day ratio. The hours ratio: 24h per day in each city, if the hourly data exceeds the limit value, the number of hours in the city is included, summarized, and divided by the recorded number of hours. The days ratio: if the maximum concentration exceeds the limit value, the number of days in the city is included, summarized and divided by the recorded number of days. Typical cities are shown in table 1.

The hourly SO_2 concentration data showed that all of the cities had hourly SO_2 concentration exceeding G1 level, and Baiyin city accumulated 2877h above G1 level, accounting for 33.09% in the whole year. Wuhai, Shizuishan, Panzhihua, Datong accounted for more than 20%, and three cities had accumulated 4 hours records exceeding the concentration described in GB/T 2423.51 method 4 ($\text{SO}_2=200\text{ppb}=526 \mu\text{g}/\text{m}^3$).

Table 1. Hours and days ratio of ISA 71.04(leven G1) at SO_2 concentration in 210 cities

	Days ratio	Hours ratio		Days ratio	Hours ratio		Days ratio	Hours ratio
Baiyin	95.07%	33.09%	Shangluo	24.66%	2.66%	Daqing	5.48%	0.83%
Wuhai	70.68%	27.78%	Jilin	13.42%	2.66%	Fushun	8.22%	0.81%
Shizuishan	79.45%	24.95%	Changzhi	23.01%	2.65%	Guiyang	4.66%	0.81%
Panzhuhua	80.00%	23.00%	Baise	20.27%	2.65%	Linxia	8.22%	0.80%
Datong	69.59%	23.12%	Qitaihe	22.47%	2.62%	Nanchang	6.85%	0.78%
Jinchang	77.81%	18.83%	Ordos	21.92%	2.59%	Shuangyashan	10.41%	0.77%
Guoluo	55.62%	18.87%	Shihezi	16.99%	2.52%	Guangan	10.14%	0.77%
Yangquan	66.58%	17.35%	Huhot	14.25%	2.41%	Zhaoqing	10.14%	0.77%
Jinzhong	62.47%	16.35%	Qianxinan	13.97%	2.42%	Weinan	8.77%	0.76%
Huludao	56.44%	16.34%	Jinhua	16.71%	2.35%	Quzhou	10.14%	0.75%
Xining	67.12%	15.30%	Jingdezhen	25.21%	2.34%	Qujing	8.77%	0.73%
Jiayuguan	72.60%	14.62%	Jingmen	20.55%	2.32%	Dazhou	7.95%	0.72%
Baotou	64.38%	14.07%	Guangyuan	21.92%	2.20%	Hegang	8.77%	0.71%
Fuxin	56.44%	14.03%	Longnan	11.78%	2.15%	Cangzhou	6.30%	0.68%
Tonghua	52.60%	11.80%	Huangshi	19.18%	2.10%	Heihe	7.67%	0.67%
Lanzhou	50.68%	11.70%	Loudi	22.74%	2.04%	Deyang	7.40%	0.67%
Shangrao	51.78%	11.39%	Zunyi	8.49%	1.96%	Qinhuangdao	7.12%	0.67%
Xinyu	57.53%	11.17%	Haibei	16.44%	1.92%	Xiangyang	4.38%	0.67%
Wuzhong	54.52%	10.62%	Puyang	13.97%	1.92%	Pingliang	9.04%	0.65%
Qiqihar	28.49%	10.12%	Bortala	15.89%	1.85%	Ganzhou	9.04%	0.64%
Yingtian	51.78%	9.37%	Ezhou	16.16%	1.82%	Jining	5.48%	0.64%
Binzhou	47.67%	9.29%	Lvliang	15.07%	1.81%	Siping	6.03%	0.63%
Harbin	21.10%	9.13%	Zhoukou	12.05%	1.82%	Fangchenggan	7.40%	0.62%
Pingxiang	43.01%	9.02%	Laibin	22.47%	1.80%	Liangshan	7.67%	0.61%
Baishan	41.92%	9.01%	Chaozhou	17.53%	1.78%	Luohe	6.03%	0.61%
Shuozhou	37.53%	8.81%	Chengde	15.62%	1.77%	Ziyang	5.75%	0.61%
Dongying	38.90%	8.79%	Dezhou	8.49%	1.66%	Songyuan	4.93%	0.61%
Shenyang	40.82%	8.85%	Yanbian	16.99%	1.65%	Jieyang	6.85%	0.59%
Yinchuan	51.51%	8.43%	Suining	18.36%	1.64%	Leshan	9.04%	0.57%
Jinzhong	35.62%	8.08%	Luzhou	16.44%	1.64%	Xiangtan	7.40%	0.57%
Yulin	39.45%	7.80%	Pingdingshan	16.16%	1.64%	Rizhao	5.21%	0.56%
Chifeng	39.18%	7.80%	Tieling	16.99%	1.62%	Maanshan	8.77%	0.55%
Yunfu	37.81%	6.77%	Handan	11.78%	1.55%	Hami	7.40%	0.55%
Honghe	34.79%	6.63%	Shaoguan	15.89%	1.54%	Taian	7.12%	0.55%
Anshan	36.99%	6.48%	Ili	13.70%	1.74%	Lianyungang	4.66%	0.55%

Dingxi	32.60%	6.33%	Yulin	13.42%	1.48%	Bengbu	6.85%	0.53%
Liaoyang	38.63%	6.27%	Jian	15.89%	1.46%	Longyan	3.01%	0.53%
Haidong	41.10%	6.24%	Tongliao	15.07%	1.46%	Tangshan	4.38%	0.52%
Taiyuan	33.70%	6.14%	Wujiaqu	14.79%	1.46%	Hengshui	5.21%	0.49%
Chuxiong	45.75%	6.07%	Tongchuan	15.34%	1.45%	Baoji	6.30%	0.48%
Zibo	33.70%	6.05%	Zhaotong	15.34%	1.45%	Wuwei	6.30%	0.48%
Yushu	36.16%	5.97%	Yichun	13.70%	1.43%	Kaifeng	5.75%	0.45%
Anshun	24.66%	5.78%	Xuchang	13.42%	1.39%	Naqu	7.40%	0.44%
Ulanqab	40.00%	5.62%	Jiuquan	19.18%	1.37%	Zhangye	6.30%	0.44%
Dehong	41.10%	5.55%	Jiaozuo	13.97%	1.34%	Neijiang	3.84%	0.44%
Linyi	25.48%	5.50%	Jinan	8.49%	1.33%	Ningde	4.38%	0.40%
Linfen	25.75%	5.39%	Liuzhou	11.23%	1.26%	Jingzhou	4.11%	0.41%
Yingkou	30.41%	5.30%	Heze	9.86%	1.26%	Altay	3.84%	0.39%
Dandong	24.38%	5.19%	Jincheng	9.59%	1.23%	Yichun	5.21%	0.38%
Panjin	28.22%	5.17%	Hebi	12.88%	1.22%	Quanzhou	4.38%	0.37%
Ankang	38.36%	5.11%	Tongling	11.78%	1.22%	Zigong	4.66%	0.37%
Maoming	29.32%	5.04%	Xingtai	13.42%	1.19%	Changde	5.48%	0.33%
Xinzhou	36.71%	4.91%	Suihua	11.51%	1.19%	Meishan	5.48%	0.33%
Hetian	29.59%	4.80%	Weifang	9.86%	1.18%	Jiamusi	4.11%	0.32%
Zhongwei	36.16%	4.77%	Huanggang	12.60%	1.14%	Bozhou	3.56%	0.32%
Benxi	32.88%	4.74%	Anyang	12.60%	1.12%	Wenshan	4.66%	0.29%
Guilin	28.77%	4.50%	Changchun	7.67%	1.13%	Kunming	3.29%	0.29%
Liaocheng	30.68%	4.43%	Fuzhou	10.68%	1.11%	Changji	3.56%	0.28%
Zaozhuang	31.78%	4.12%	Huangnan	13.97%	1.08%	Haixi	3.84%	0.26%
Gannan	39.73%	3.73%	Nanchong	12.33%	1.08%	Baicheng	2.74%	0.25%
Zhanjiang	21.92%	3.61%	Tianshui	11.51%	1.03%	Nujiang	4.11%	0.24%
Hengyang	26.85%	3.55%	Da Hinggan Ling	9.86%	1.02%	Shangqiu	3.01%	0.23%
Chaoyang	25.48%	3.45%	Danzhou	13.42%	0.99%	Yuxi	3.84%	0.21%
Chenzhou	25.21%	3.34%	Qingyang	11.23%	0.98%	Liupanshui	3.29%	0.18%
Jixi	20.00%	3.17%	Yongzhou	11.23%	0.98%	Huaian	2.74%	0.18%
Huaihua	19.18%	3.00%	Ngari	11.23%	0.91%	Kizilsu Kirgiz	2.74%	0.18%
Liaoyuan	28.22%	2.89%	Mudanjiang	6.85%	0.87%	Zhenjiang	2.19%	0.18%
Yuncheng	17.81%	2.88%	Sanming	10.96%	0.86%	Kashgar	3.56%	0.17%
Bayan Nur	28.22%	2.86%	Sanmenxia	8.77%	0.84%	Guiyang	3.29%	0.16%
Shaoyang	20.55%	2.83%	Wuzhou	9.04%	0.83%	Xinxiang	3.29%	0.16%

Among 210 cities, the concentration of SO₂ analyzed an average of 20.80% of days ratio and 8.04% of hours ratio exceeding G1 level requirements, or even exceeds the concentration requirements described in the accelerated corrosion test. When silver plating and devices are used in the that harsh environment, factors in some areas show strong corrosion risk [2], and combined with factors such as temperature and humidity, the corrosion risk is higher [3-4].

3. Plating material corrosion

Due to the difference in working environment of electronic devices, silver plating materials may face more corrosion risks. By analyzing the plating structure and summarizing the corrosion threshold of the plating materials, the corrosion prediction under different working conditions can be realized.

3.1 Board corrosion

At room temperature, above the critical value of 50%RH, the silver is covered by physical adsorption of more than 3 molecular water monolayer. This water layer acts as an electrolyte, absorbing and dissolving SO₂. The critical relative humidity of metals in a sulfur-rich environment [5] is between 50% and 90%, and some pollutants may cause creep [6].

Under dry conditions, no obvious oxides are formed on the silver surface under the action of temperature and pressure around. However, under humid conditions with high pH value and in the presence of strong oxidants, Ag₂O is stable only in a small condition range, and atmospheric corrosion grows a thin and small layer of metal oxides on the surface. Exposed for 60 days at a temperature of 19-27 °C and relative humidity of 32-64% RH, different degrees of corrosion will occur indoors and outdoors according to the difference in sulfide content [5].

Silver plating is 10 times more sensitive to SO₂ than H₂S and COS, and Ag₂SO₄ can be formed by contact between Ag and SO₂ in humid condition, but only when the concentration of SO₂ is 2-3 orders of magnitude higher than that in the surrounding environment [7-8]. Oxidizing substances such as O₃, NO₂ and Cl₂ can promote the formation of Ag₂SO₄. The specific mechanism of the oxidant reaction has not been determined, it is possible that the oxidant promotes the transformation of S(IV) into S(VI), thereby increasing the acidity of the water monolayer and the dissolution rate of Ag, or it is possible that the oxidant participates in the surface process and then reacts with Ag.

3.2 Galvanic corrosion

In the suitable external environment, substrate and silver plating, silver plating and other connecting parts can form electrochemical galvanic cells, leading to galvanic corrosion in the structure. According to the electrochemical potential data (Table 2), silver possess a higher electrochemical potential than other materials, and the formation of electric couple with other materials will cause corrosion of other metal materials.

Table 2. Electrochemical potential of PCBA materials[9-10]

	10% Flux solutiong	10%Sweat solution
	mV	mV
Ag-Rol bonded	167	156
Cu-electroplated	39	-31
Ni-electroless coatings	-241	-287
Sn-surface finish	-329	-462
SAC solder-HASL	-418	-474
Al-Sputter coated	-502	-583

Electroplating creates intermetallic compound (IMC) between substrate and silver plating, the corrosion resistance of IMC is a major problem. Even if the outer layer is protected by resin (EMC), water can penetrate the EMC, react with the hydrolyzed ions of the pollutants, and release H⁺. Water and SO₂ ions diffuse to the silver electric couple interface, causing IMC corrosion. The by-product H₂ is also generated during the corrosion process, and the precipitation of H₂ gas leads to the formation of micro-cracks in the corrosion zone.

In the corrosion mechanism of IMC silver electric couple structure, pollutant ion level is a dominant factor. During the corrosion process, several intermediates are formed [11-12], repeated reduction and oxidation reactions form voids, cracks and oxides in the corrosion area [11], which will weaken the plating material and increase the contact resistance. Extreme conditions such as being too wet or too dry (e.g. vacuum, closed/semi-closed cavity) can lead to corrosion, and moisture and SO₂ under bias [6] can create an ideal environment for electromigration of silver.

Galvanic corrosion of the plating material is a common phenomenon, which is caused by the difference of electrochemical potential between the metals. Studies have shown that when the potential difference between two metal materials exceeds 400mV, it is very easy to cause galvanic corrosion. SO₂ in the environment can decrease galvanic corrosion threshold to half, and most of the device materials can not be avoided.

3.3 SO₂ synergistic corrosion

ISA mixed gas can be used to analyze the corrosion behavior of silver plating[13], and the average corrosion of single gas was more than 76% lower than that of copper plating. Corrosion of two or three component gas mixture with SO₂ shows weak corrosion affection than the sum of single reactions. Meanwhile, the four component gases produced the highest level of corrosion (1539A), about 2.5 times of the expected corrosion.

Hydration intermediates play different roles in the corrosion mechanism of silver. When the concentration of SO₂ is low, the corrosion behavior of silver plating changes monotonically. When the concentration of SO₂ is very high, the sensitivity of silver and SO₂ to corrosion reaction decreases. The synergistic corrosion rate may be 4.6 times that of monomer addition [16].

D. W. Rice[1] took a single pollutant as the control variable (70%RH, 25.0°C), found that the corrosion of silver plating by SO₂ generally presents a power function rule ($r=AC^n$), and with the increase of gas composition, the corrosion threshold of SO₂ decreases and the corrosion threshold of silver materials decreases significantly. Under the coordinated corrosion of SO₂, H₂S[7], Cl₂, HCl, NO₂, O₃ and NH₃, the stress threshold decrease to range of 0.2-0.7ppb (SO₂= 0.53-1.84 µg/m³), all 210 cities are above this threshold.

4. Summary

With the miniaturization and high integration of electronic devices, even small corrosion pits on the surface of silver plating can seriously reduce the reliability of devices. The SO₂ corrosion risk of silver plating materials was summarized and the following conclusions were reached:

(1) The annual mean of SO₂ is 8.88 µg/m³, which is less than the limit of G1 level in ANSI/ISA 71.04, but the hourly data shows an average of 20.80% of days ratio and 8.04% of hours ratio exceeding G1 level requirements. Some cities exceed the concentration described in GB/T 2423.51 method 4, and electronic devices have a greater probability of facing more severe corrosion risks at some moments;

(2) The corrosion risk of silver plating materials for electronic devices by independent parameters is in line with the power function law. Under multi-factor conditions, the SO₂ corrosion threshold decreases (SO₂=1ppb), and the device corrosion risk increases significantly;

(3) With the silver plating material as the target, limiting the type of corrosion parameters, reducing the level of pollutants and other methods can be used as measures to improve the corrosion resistance of electrical appliances.

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