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Oxidation vs. Corrosion Analysis in Copper Used in the Electronics Industry of Arid and Marine Environments

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Abstract

The process of oxidation (OP) that occurs on surfaces of copper (Cu), of electrical connections and connectors of electronic equipments installed in the electronics industry in the northwest of Mexico; is an important factor to determine the corrosion rate (CR) of this metal. The CR obtained from the installation of metallic copper specimens in the companies, one in Ensenada (marine environment) that manufactures video games, and one in Mexicali (arid zone), which manufactures personal computers; indicated the degree of deterioration of Cu. The CR in each city was determined by the gravimetric method, and increased or maintained of the CR was according to the type of thin films formed on the metals: porous and nonporous films. A correlation of CR with sulfates (SOX) and chlorides (Cl-) was made, and the data were obtained with the technique of sulfation plates (TPS) and the wet candle method (WCM). The analysis of CR in both cities showed an almost linear representation in Mexicali, indicating the rapidly growing of CR and in Ensenada a parabolic curve with a slow increase. The corrosion products were characterized by the scanning electron microscopy (SEM) and the Cu films formed with the technique of Auger Electron Spectroscopy (AES), representing the air pollutants that reacted with the copper surface in each city. The analysis of depth profiles show the increases and decreases in carbon, oxygen, sulfates, chlorides and copper, over a period of time, indicating the thickness of each film formed on the surface of Cu, for the OP in the two cities. The maximum value of CR in Ensenada was 188 mg/m2 year, and in Mexicali were 299 mg/m2 year.

Keywords

Corrosion; Climatic factors; Air pollutants; SEM and AES techniques

Introduction

Corrosion is a destructive attack of a material by reaction with the environment to which exposed. Serious consequences of corrosion are a problem of great significance worldwide [1]. An important aspect is knowing type and form of the materials which are deteriorate, the different types of corrosion that occurs in different environments, causing production downtime in the electronics industry [2-4], plus depreciation of resources or materials considered waste products, loss and contamination of products, reduction in production efficiency, maintenance costs, and large expenditures on design [3].

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The multidisciplinary aspects of corrosion problems, combined with associated liabilities and problems of increased complexity in devices and equipments, increases the cost of products by the phenomenon of corrosion [4]. The analysis and corrosion control are carried out to understand their mechanisms and the strength of materials, and the designs of new structures of electronic devices and methods of protection. Many industrial plants and government agencies are engaged in the corrosion control to determine the effect and the possible causes of each problem of this chemical process and detect the agents that generates the corrosion. The corrosion in the electronics industry causes large economic losses and human life sometimes. On this basis, a study was required by the two companies mentioned above, to understand the factors that generate chemical reaction mechanisms and effects of the presence of corrosion in both environments. Microcircuits, connectors and electrical contacts used in the electronics industry, are susceptible to atmospheric corrosion [5], which occurs in indoor plants, in Mexicali and Ensenada. In this study, uniform and localized corrosion (pitting) was occurred in electronic devices. When the CR was increased, electrical connections and electrical connectors was deteriorated, causing electrical failures in the industrial electronic systems. The formation of oxides at the Cu surface was an important factor in generating the two types of corrosion: uniform or pitting.

Functionality of electronic equipment

The efficiency of an industrial operation is based on productivity in a company that generates in the electronics industry. The main features that show the efficiency of production is the good appearance of the products, cost effectiveness, ease of operation and maintenance, safe use of articles manufactured and the number of operations. Electronic devices and equipment used in reception areas of materials, warehouse, production and shipping, are exposed to environmental factors, indoor and outdoor of industrial plants [6]. Climatic factors such as relative humidity (RH) and temperature in combination with chlorides and sulfates in Ensenada and sulfates in Mexicali, affects the operation of electronic systems. Sulfates come from external sources such as vehicular and industrial activities in Ensenada and chlorides of the sea breeze, and hydrogen sulfide and sulfate in Mexicali of the geothermal plant located at 25 km of the city, which cause corrosion and damage the metal surface of the Cu. The adhesion of air pollutants to the electrical connectors and these are deteriorated, originating a decrease in its operating equipments [7].

Factors causing corrosion

Levels higher of 70% and 35°C of RH and temperature, are the principal factor of the corrosion. This generates a higher valence change in the state of active metals that are deteriorated faster [8]. Corrosion is caused by the chemical reaction of metals exposure to chlorides, sulfides, NOX, ammonia and organic compounds. This occurs when the oxide films formed on the surface of Cu, is not covered uniformly, and is covered only in some zones of the Cu surface, and where an instantaneous reaction with sulfates occurs. The use of copper in various industrial activities depends on how it is exposed to environmental conditions. In the corrosion process, the Cu suffers modifications that change their physicochemical properties [1]. The objective of this research was to know the process of CR in the Cu

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surface of electronic equipments in the arid and marine environments, showing after a period of six months, and causing electrical current down, which originates the electrical failures.

Experimental

Metallic probes of Cu were installed in indoors of the electronics industry, to the corrosion tests, by periods of one, three, six and twelve, months in both cities. The metal specimens were evaluated using the gravimetric method to ASTM G 1, G4, G31 [9-11], and the CR was correlated with the ranges of RH and temperature in different seasonal periods. The dimension of the rectangular specimens was 2.5 cm × 1 cm × 0.5 cm were cleaned with high purity isopropyl alcohol in ultrasound for 15 minutes. Immediately after cleaning the copper samples were placed in sealed plastic bags and ready to be installed in industrial plants. After each exposure period, samples were removed, weighed and cleaned, for determine the weight loss and CR [12-14]. The morphology of the corrosion products was examined with the Auger technique [15,16], to see if the types of films covering the entire surface of copper had a protective effect. To determine if the corrosion process was active or passive, was used the depth profiling analysis of AES technique [17]. Gaseous pollutants mentioned above, led to a deterioration of the surface of Cu. The most active gases were hydrogen sulfide (H_2S) and SOX in Mexicali and sulfates and chlorides in Ensenada. The H_2S is a corrosive and toxic pollutants originating from municipal wastewater and chemical or biological decomposition of organic matter containing sulfur. Air pollutants were evaluated as follows: H_2S by a portable device TGase 1021. The SO_2 in Mexicali with the Environmental Monitoring Stations (EMS), and sulfatation plates technique (SPT) [18]. Sulphides and chlorides in Ensenada were monitored by the SPT and the wet candle method (WCM) [19]. It was also determined in both cities, corrosivity levels (CL), which indicates the level of aggressiveness of the interior of the industrial plants evaluated. We analyzed two types of corrosion presented in the study: uniform and localized (pitting), with small spots in some areas of the Cu surface, which depended on the type of oxide films formed: non protective or protective films [20].

Results and discussion

The CR in the desert was higher than in marine environments. A comparative analysis of the four periods mentioned, represents a higher intensity of uniform corrosion in Ensenada and localized pitting corrosion and crevice corrosion in Mexicali. This is showed in the CL presented in Table 1, ISO / CD11844 [12,13].

Table 1: Corrosivity levels in indoor of the electronics industry of Mexicali and Ensenada.

Time, months	Corrosivity levels	
	Ensenada	Mexicali
1	1	1
3	2	2
6	2	3
12	2	3

Influence of climatic factors and air pollutants in the CR

The values of RH and temperature in Mexicali were above 70% and 45°C in summer and a minimum of 20% and 5°C in winter, with warm desert winds in summer. In contrast, in Ensenada, the climatic factors showed maximum levels of RH and temperature of 90% and 35°C in summer and minimum 30% and 5°C in winter. High levels of RH in Mexicali, accelerates the CR causing pitting corrosion. In summer in both cities, in the first six months of exposure, the CR increase lowly, but from this period, we observed an increase in the CR. In both cities in the range of 25 to 35°C with a RH level of 30% to 70%, the CR was the highest. Moreover, in winter, temperatures around 15°C to 25°C and RH was 35% to 75%, water was condensed on the surface of Cu and forming the protective films and the CR was low, however when temperatures were above 35°C, and generated some wetted zones of Cu surface and later observed originated isolated stains and pits, crevices and cracks. Another important factor were the levels of air pollutants such as sulfur in both cities, which exceeded the permitted levels of air quality standards, and variations of RH and temperature described in the range of 30% to 80% 0°C and 35°C, originated from corrosion. In Ensenada, at temperatures above 35°C with RH levels from 50% to 85%, protective films were formed in the Cu surface. Therefore, the CR was much higher, affecting the electrical conductivity of Cu in the connections and electrical connectors of electronic equipment [3]. In Tables 2 and 3 show the effect of copper exposure to air pollutants: H_2S SO_2 and Cl-to Ensenada, and H_2S, NOX, and SO_2 to Mexicali, and the RH and temperature levels, concentration of air pollutants and the CR. In Ensenada, the highest value was 188 CR mg/m2.año with values of 95.1% RH, temperature of 17.2°C and levels of chloride concentration of 21.4 mg/m^2.año. For the city of Mexicali, the highest value was 299 VC mg/m^2.año at 86.7% RH values, temperature of 30.1°C and concentration levels of 0.56 ppm of H_2S.

Table 2: Correlation of CR with climatic factors and air pollutants in Ensenada (2010).

Climatic factors	Sulfhidric acid (H_2S)				Sulfur oxides (SO_2)				Chlorides (Cl^-)			
	RH[a]	T[b]	C[c]	CR[d]	RH[a]	T[b]	C[c]	CR[d]	RH[a]	T[b]	C[c]	CR[d]
Max	83.243.5	28.3	0.13	147	88.4	22.3	0.32	143	77.8	23.3	17.7	162
Min		14.2	0.06	111	49.8	13.7	0.19	87	42.3	15.4	8.9	145
Summer												
Max	94.3	38.5	0.11	157	89.8	37.8	0.42	124	89.9	38.7	14.5	148
Min	56.5	21.9	0.09	124	49.7	27.9	0.13	102	47.8	20.9	5.3	125
Winter												
Max	92.4	21.4	0.38	169	90.4	19.8	0.61	147	95.1	17.2	21.4	188
Min	38.3	12.5	0.21	132	56.7	10.7	0.21	1116	56.7	10.9	11.2	154

Note: [a] RH. Relative humidity, %, [b] T. Temperature, ºC, [c] C. Air pollution concentration (C), ppm, [d] CR. Corrosion rate, mg/m^2.año

Table 3: Correlation of CR with climatic factors and air pollutants in Mexicali (2010).

Climatic factors	Sulfhidric acid (H_2S)				Sulfur oxides (SO_2)				Nitrogen oxides (NOX)			
	RH[a]	T[b]	C[c]	CR[d]	RH[a]	T[b]	C[c]	CR[d]	RH[a]	T[b]	C[c]	CR[d]
Spring												
Max	72.127.8	38.1	0.17	198	83.3	27.8	0.47	185	66.7	29.9	0.3	183
Min		17.8	0.09	143	42.1	17.3	0.28	102	31.3	19.2	0.2	135
Summer												
Max	90.2	43.2	0.15	216	80.2	44.3	0.58	181	80.6	45.2	0.5	193
Min	44.3	25.6	0.12	195	39.3	27.8	0.19	132	36.3	26.5	0.2	156
Winter												
Max	86.7	30.1	0.56	299	84.5	25.6	0.86	169	90.2	33.3	0.8	196
Min	30.1	22.3	0.28	199	34.8	14.3	0.29	128	48.7	17.9	0.4	169

Note: [a] RH. Relative humidity, %, [b] T. Temperature, ºC, [c] C. Air pollution concentration (C), ppm, [d] CR. Corrosion rate, mg/m2.año

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AES analysis

The AES technique was used to determine the types of corrosion [21]. The AES spectra showed the surface analysis evaluated in three points of different areas of Cu surface. Figure 1 shows two images of the specimens of Auger map. The nanophotographs of corrosion products covering the complete surface of Cu in Ensenada (Figure 1a), and was formed the protective film, and thus the CR was slow. Figure 1b shows a Cu sample installed in Mexicali, with isolated spots. Auger analysis showed the presence of Cl-and SOX, which reacted with the Cu surface, made with the technique in the vacuum chamber, which requires two steps: using a mechanical pump oil to reduce the ambient pressure to 50 milli torr and then using a turbo molecular pump with the mechanical pump combined with the mechanical pump to reduce the pressure at 1 torr [16].

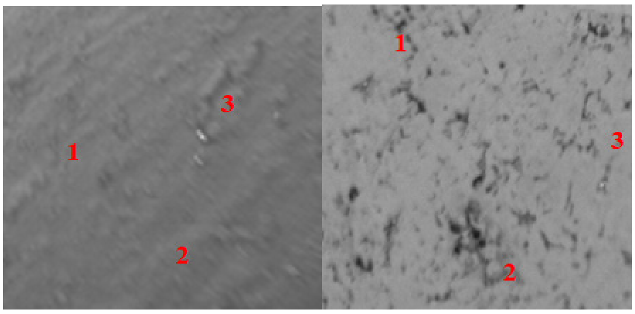

Figure 1: Auger map of corrosion products in: (a) Ensenada y (b) Mexicali.

Auger spectra of Cu samples were generated by an electron beam with a voltage of 5 keV, which shows the chemical composition of corrosion products in the samples of Ensenada (Figure 2) and Mexicali (Figure 3). In both cities, the peaks of Cu, sulfates, chlorides, carbon and oxygen appear in the spectra at different levels of intensity of kinetic energy. For the analysis of data, the program Origin Pro 6.1 was used. The spatial resolution of this technique was 100 nm and a resolution of 1 nm in depth [15]. The depth profiles were obtained from samples tested in both cities, showed in Figures 4 and 5. The technique of depth profiling is defined by alternating cycles of ion Ar+ sputtering method, to remove a thin layer of 5 to 10 Å of air pollutants [15] and its characterization in some regions [22]. In Figure 4, the chlorine and sulfur located between the carbide particles were bombed during the first cycle of sputtering method (10 Å). A small proportion of chloride and sulfur persisted with more carbide particles (point 2). In Figure 5, the depth profile indicates a low presence of sulfur between the carbide particles.

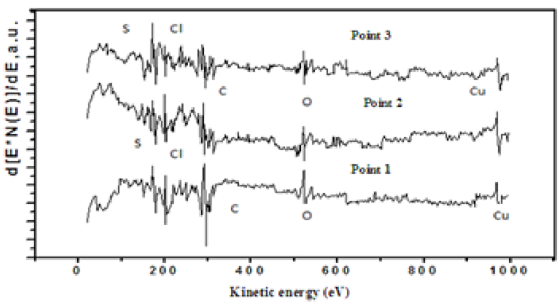

Figure 2: AES analysis of corrosion products after six months of exposure in Ensenada.

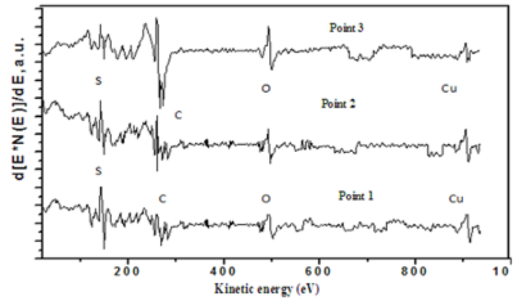

Figure 3: AES analysis of corrosion products after six months of exposure in Mexicali.

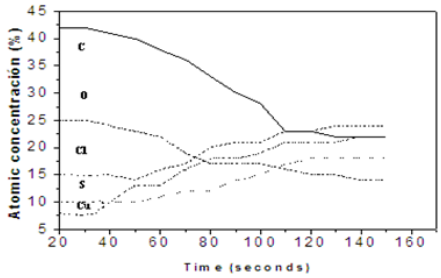

Figure 4: Depth profile analysis on Cu surface after six months of exposure in Ensenada.

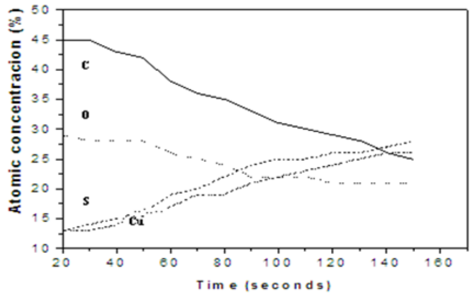

Figure 5: Depth profile analysis on Cu surface after six months of exposure in Ensenada.

Formation of thin films on the Cu surface

The mechanism of film formation process in the form of deposits covered by oxides on the surface of Cu was formed principally for humidity and temperature that provide the Time of Wetness (TOW). The TOW is very important because it allows to know whether a surface is completely covered by thin film of water visible or non-visible, maintaining a wet surface, and generate a oxidation on the Cu surface, which is a protective film, that inhibit or decrease the corrosion phenomenon, that occurred in Ensenada. Other case occurred in Mexicali with Cu surfaces covered in some zones of wet thin film, which promotes and increases the CR. An analysis of weight loss of Cu specimens evaluated in each city was made. Figure 6 shows the behavior of CR in Ensenada, which was represented by a parabolic curve, indicating a protective oxide film on the Cu surface, because the transport of ions through the oxide is slow Figure 7 shows an analysis in Mexicali, with a transport of ions in the oxide faster, with an almost linear graph, and indicating that the film will tend to be porous and

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will not entirely cover the surface of Cu, and increase the CR.

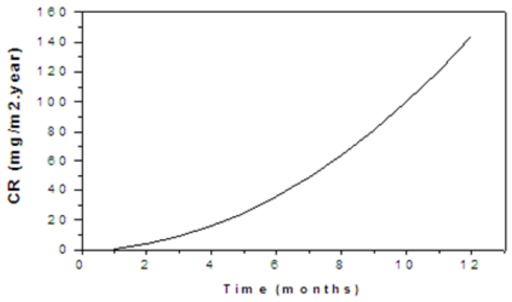

Figure 6: CR analysis of one year of exposure in Ensenada.

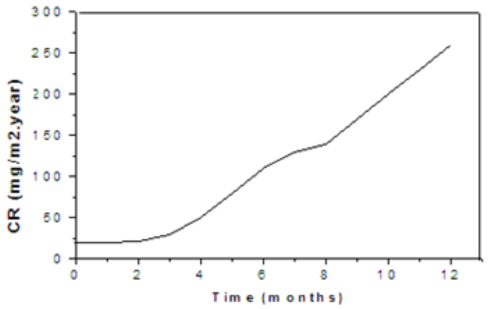

Figure 7: CR analysis of one year of exposure in Mexicali.

According to the mathematical relationship of Pilling-Bedworth (PB)

$$P.B. = \frac{\text{Volume of oxide film produced by the oxidation}}{\text{Volume of meal consumed by the oxidation}} \quad (1)$$

numerical values was obtained in range from 0 to 1 as porous and non-protective film, 1 to 4 as a layer that is broken and is not protective, but if it is equal or closest to 1, the film is protective [21].

Conclusions

The generation of corrosion in the electronics industry installed in the north west of Mexico, has been an important factor in the last 30 years. The complexity of electronic devices and equipment was increased and the corrosion too, which is characterized by market demand, its performance and reliability. Profitability is governed by the manufacture of electronic devices and equipment, increasing the need to develop most of the operations and reduce its size at a low cost. This has been the main effect of changing the designs of the smaller spaces between electronic devices and the use of new materials in electrical connectors and connections of electronic devices and equipment. Other factors in indoor of industrial plants are the lack of climate control and humidity and temperature, which promote and increase the CR. In most cases companies do not know the phenomenon of corrosion and not are considered as an important factor, until it causes a failure in some electronic devices and equipment, and stops the manufacturing process. Currently, the AES technique is a high reliability of surface analysis, used in most industrial processes to detect air pollutants that react with the Cu surface. Results of this technique, represents the chemical reaction of atmospheric agents that forms thin films on Cu surface. According to the objective of this research we can conclude that without an indoor climate control in the industrial electronics, and with of RH and temperatures values higher than 70% and 35°C, promote the CR very fast, with pitting and crevice corrosion in arid zones and uniform corrosion in marine environments with RH values and temperatures lower than 50% and 25°C, forming a protective oxide on the surfaces of Cu and connectors electrical electronics of the electronic industry. This study is of great importance to consider these factors and avoid economic losses or accidents.

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