



Research on the Corrosion Phenomenon of Iron Parts in the Internal Micro-environment of Relay

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Abstract

With the continuous improvement of reliability requirements of relay products, more attention has been paid to the influence of varied micro-environment caused by the production of arc during the operation. In this paper, the corrosion phenomenon of iron parts of relays after electric life test has been analyzed, and it is confirmed that the formation of acidic substances is the primary cause of the corrosion of iron parts, where the acidic substances are the reaction production of water vapor (H_2O) and compounds of nitrogen and oxygen (N_xO_y) produced in air atmosphere under the action of arc. According to the corrosion mechanism, the varied internal micro-environment of relays during the electric life test has been simulated, and a rapid method for the evaluation of the corrosion resistance of the iron parts has been carried out.

1 Introduction

Material corrosion refers to the deterioration caused by chemical changes in the environment. According to the reaction mechanism, corrosion can be divided into chemical corrosion and electrochemical corrosion. The former is based on chemical reaction in dry atmosphere or non-electrolyte environment, while the latter is based on the formation of two electrodes of metal and electrolyte to form corrosive primary battery. Corrosion can be divided into local corrosion and overall corrosion according to the form, and local corrosion can be divided into pitting corrosion, galvanic corrosion, crevice corrosion, abrasion corrosion, etc. The mechanisms of different corrosion forms are different^[1]. The causes of material corrosion include environmental factors (external factors) and material factors (internal factors).

Xiaofeng Zhu and others^[2] analyzed that the main reason for the corrosion of relay components in the switch mechanism box of the series in the substation is the high temperature and high humidity in the mechanism box, and verified that the most important factor affecting the corrosion of metal materials is humidity. Chongfeng Liang and others^[3] analyzed the harm of humidity to electrical equipment and the corrosion mechanism of electrical equipment in humid environment. Kai Liu and others^[4] analyzed the harm of condensation in terminal box to power equipment corrosion, and studied the condensation mechanism.

The corrosion of the internal iron parts of the relay to a certain extent will bring harm to the relay, as Fig.1: it will affect the appearance of the relay, resulting in the reduction of the over travel and the

excessive actuation voltage. With the continuous improvement of reliability requirements of relay products, people pay more and more attention to the surface corrosion of iron parts caused by micro-environment changes caused by arcing in the process of relay operation. However, based on the micro-environment changes of relay, the mechanistic analysis and application research of the corrosion of iron parts in relay are inadequate.

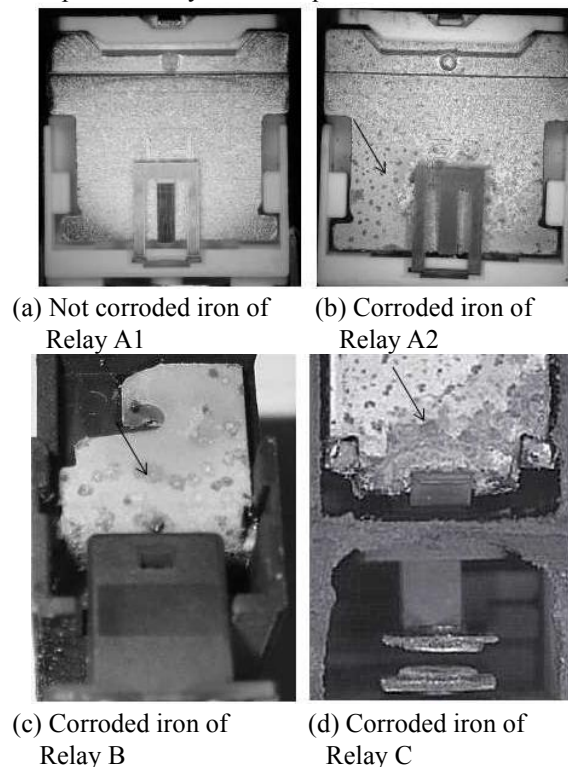


Fig.1 Different relay corrosion after electrical life test

In this paper, through the systematic analysis of the corrosion form and composition of the relay internal iron parts after the electrical life test, and

through the test, we confirmed that the nitrogen oxide compound produced by oxygen and nitrogen under the action of the arc reacts with the water to form the nitric acid compound, which is the basic cause of the corrosion of the iron parts, and the humidity is the most important external environmental factor affecting the corrosion of the iron parts. Combined with the corrosion mechanism of the iron parts, the internal micro-environment of the electric life test process of the relay is simulated, and the fast evaluation method of the corrosion resistance of the iron parts is explored.

2 Test method

After the electrical life test of relay samples from different sources of iron parts, the corrosion form, products and content were analyzed by stereomicroscope, metallographic microscope, SEM-EDS, FT-IR, ICP-OES, IC and other instruments. In order to further accelerate the corrosion resistance of different iron parts, the fast evaluation method of corrosion resistance of relay iron parts is discussed by using the combined tested environment of different temperatures and humidity.

2.1 Analysis of the components of corrosion products

2.1.1 SEM-EDS analysis of corrosion on relay iron surface

SEM-EDS detected higher content of N and O elements and lower content of Ni element in the corrosion area than in the normal area, as shown in Fig.2.

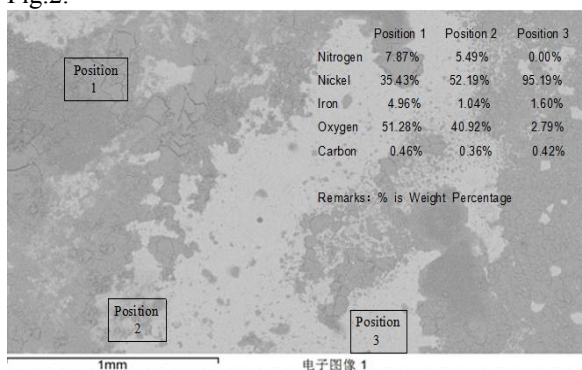


Fig.2 SEM-EDS detected higher content of N and O elements in the corrosion area than in the normal area.

2.1.2 FT-IR analysis of corrosion on relay iron surface

Four relays (A, B, C, D) were tested 100,000 operations under the same conditions. Among them, there were obvious peaks near the infrared spectrum 1350cm^{-1} on the surface of armature of three relays (A, B, C), it was hereafter that the corrosion location

contained nitrate. However, no obvious corrosion was found on the armature surface of relay D, and no obvious peak was found near the infrared spectrum 1350cm^{-1} . It is inferred that the armature surface contains very small amount of nitrate if not absent, as shown in Fig.3. The results of FT-IR analysis at the corrosion site of iron parts are consistent with the high content of N and O detected by SEM-EDS.

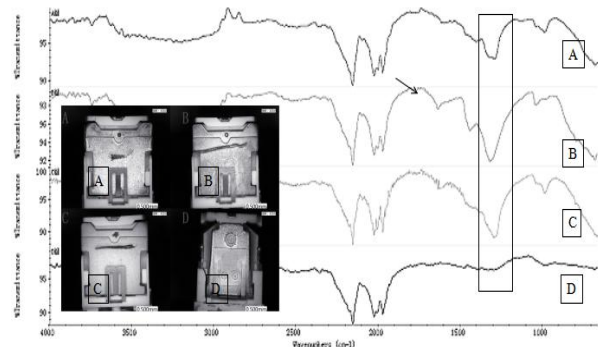
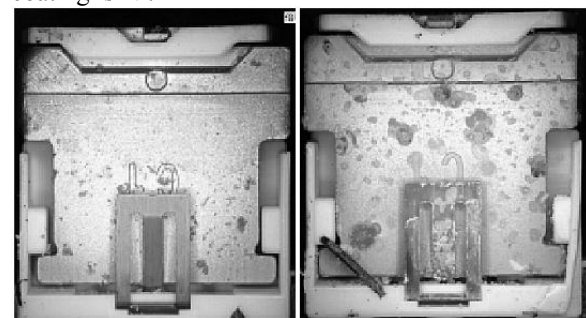


Fig.3 There are obvious peaks near 1350cm^{-1} in the corrosion site where may contains nitrate by the infrared spectrum

2.1.3 ICP-OES analysis of corrosion on relay iron surface

Put relay E (Fig.4. a) and F (Fig.4. b) armature after electrical life test into clean beaker. Add ultra pure water to a certain scale. Vibrate and clean the corrosion of armature surface by ultrasonic cleaning equipment. Transfer the corrosion solution to the volumetric flask and filter it. Analyze the content of Ni, Cu and Fe in the filtered corrosion solution by ICP-OES. There are more content of Ni, Cu and Fe in serious corrosion of iron parts. Note: the armature matrix of relay E and relay F is Fe, the sub-outer layer of armature coating is Cu, and the outer-most layer of coating is Ni.

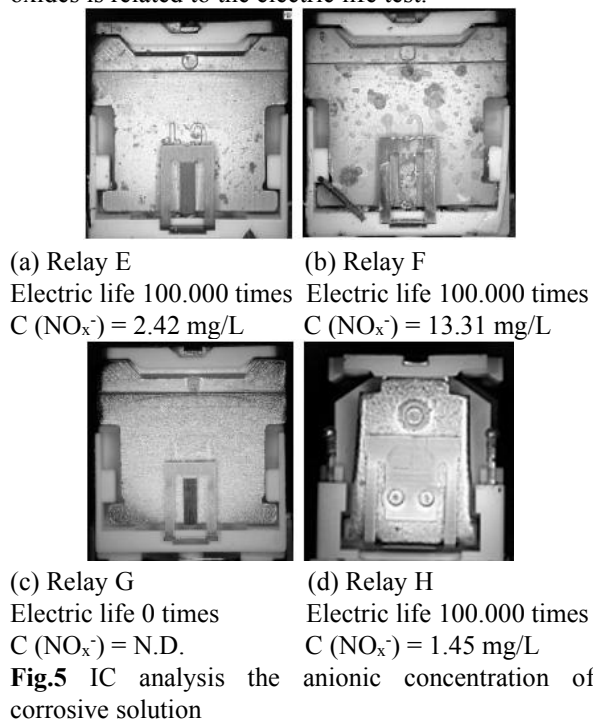


(a) Relay E Electric life 100,000 times Slight corrosion Ni:2.28 mg/L Cu:0.36 mg/L Fe:0.06 mg/L
 (b) Relay F Electric life 100,000 times Serious corrosion Ni:0.36 mg/L Cu:0.12 mg/L Fe:N.D.

Fig.4 Analysis of metal element concentration of corrosives by ICP-OES

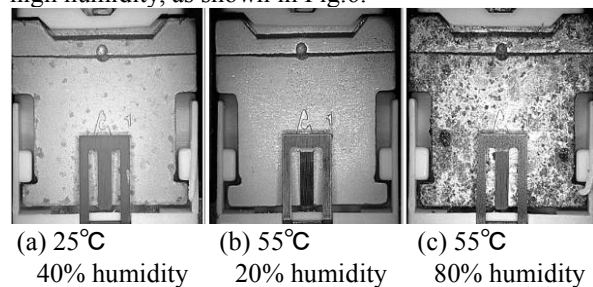
2.1.4 IC analysis of anionic concentration of corrosive solution

Obvious NO_3^- and NO_2^- were detected in relay E (Fig.5. a) with slight corrosion and relay F (Fig.5. b) with severe corrosion, and higher concentration of anion NO_x^- (total NO_3^- and NO_2^-) was detected in relay F with severe iron corrosion. No anions of NO_3^- , NO_2^- and Cl^- were detected in the corrosive solution of relay G (Fig.5. c) without electrical life test after vibration cleaning by ultrasonic cleaning equipment. After 100.000 operations electric life tests of relay H (Fig.5. d) of competitor, although there is no obvious corrosion on the surface of iron parts, 1.45mg/L NO_x^- is also detected in the corrosive solution, as shown in Fig.5. The results show that the production of nitrogen oxides is related to the electric life test.



2.2 Electrical life test of different temperatures and humidity

The same batch of relays were put into three different temperatures and humidity for electrical life test to 100.000 times. The results show that the corrosion degree of iron parts is the most serious in high humidity, as shown in Fig.6.



3 Results and discussion

3.1 Discussion on the form of corrosion products of iron

3.1.1 Iron corrosion is divided into five periods according to the severity

Observe the relay after electrical life test according to the corrosion degree of iron surface from light to heavy (Fig.7). Corrosion can be divided into five periods according to severity, as follows: no corrosion (Fig.7.a) → corrosion induction (Fig.7.b) → early stage of corrosion (Fig.7.c) → corrosion period (Fig.7.d) → later stage of corrosion (Fig.7.e).

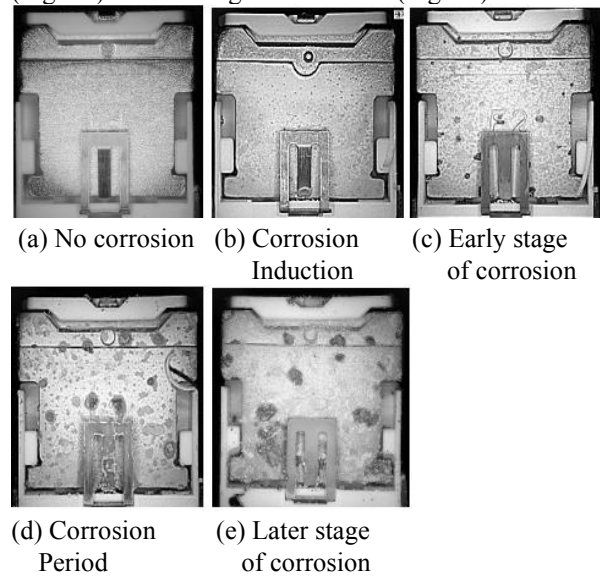
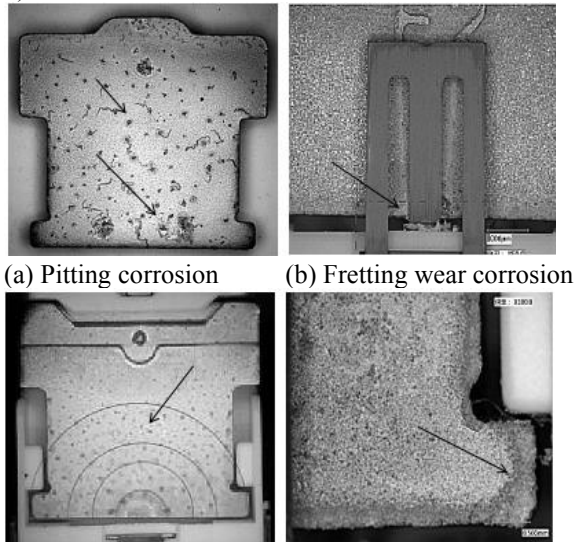


Fig.7 Corrosion photographs of iron during different periods

3.1.2 Classification of iron corrosion according to micro mechanism

According to the micro mechanism, the corrosion of materials can be divided into pitting corrosion, fretting wear corrosion, galvanic corrosion, crevice corrosion and other types. The pitting corrosion, also called keyhole corrosion, is a kind of pitting corrosion form that focuses on a small area of metal surface and penetrates into the metal interior^[1]. When pitting corrosion occurs, it usually starts from the defective part of the material, from the loss of metallic luster → pitting local corrosion → pitting corrosion gradually spread → comprehensive corrosion. Fig.8(a) shows the common pitting corrosion morphology characteristics. Fretting wear corrosion is the result of the synergistic effect of fretting wear and corrosion. Fretting refers to the relatively sliding state with periodic small amplitude. As a result, micro-pores or pits appear on the surface of metal coating. In addition, the corrosion of corrosive substances makes the fretting wear position susceptible to produce corrosion (Fig.8 b). Galvanic

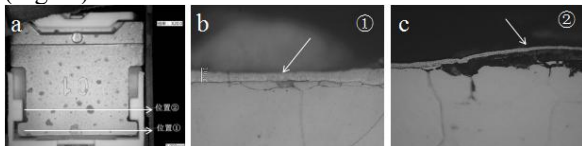
corrosion is also known as contact corrosion or dissimilar metal corrosion. When two different metals or alloys are in contact, the corrosion rate of the metal with a negative potential in the solution increases (armature plated with Ni, anode), while the metal with a positive potential is protected as cathode in compression spring (Fig.8 c). Crevice corrosion is a form of localized corrosion, which may occur at the joint of metal and metal or metal and nonmetal (Fig.8 d).



(a) Pitting corrosion (b) Fretting wear corrosion
(c) Galvanic corrosion (d) Crevice corrosion
Fig.8 Main forms of iron corrosion in relay

3.1.3 Pitting corrosion is the main form of local corrosion of relay iron parts

The iron corrosion form of 44 relays was pitting corrosion, accounting for 88%, which indicated that pitting corrosion was the most important corrosion form. The Ni plating layer under the armature corrosion position of the relay with pitting corrosion becomes thinner (Fig.9b), and the matrix Fe is corroded (Fig.9c). The corrosion extends along the metal grain boundary to the depth of the iron base, (Fig.9c).



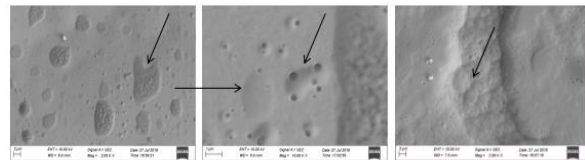
(a) Corrosion morphology of armature surface of Relay I after electrical life test.
(b) The Ni coating at green corrosion (position 1) becomes thinner.
(c) The Ni coating at yellow corrosion (position 2) becomes thinner and bulged.
Fig.9 Corrosion form of iron section

3.1.4 Discussion on the condition of pitting corrosion of relay iron parts

Pitting corrosion usually occurs on the metal with cathode coating on the surface (Ni coating on the surface of iron parts), when these coatings are damaged due to defects (Fig.10). The metal matrix in the failure area and the undamaged area of the coating form activated passive corrosion cell. The passivated surface (coating) is a cathode, and the area is much larger than the activated area. The corrosion develops to the deep iron matrix and forms small holes.

Pitting corrosion also occurs in the medium with special ions, uneven adsorption of NO_3^- and NO_2^- compounds on the surface of iron parts, and uneven damage of coating caused by corrosion^[1].

Pitting corrosion also occurs above a critical potential, which is called pitting potential. When the metal parts are in corrosion solution and the corrosion potential exceeds the pitting potential, uniform pitting corrosion will occur.

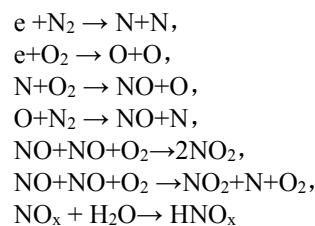


(a) Corrosion on iron surface (b) Surface holes of iron parts (c) Surface pits of iron parts
Fig.10 Corrosion and defects on the surface of iron

3.2 Discussion on the composition of corrosion products of iron parts

3.2.1 The mechanism of HNO_x produced by lightning

HNO_x is one of the main sources of acid rain^[5]. A large number of scholars at home and abroad have done a lot of analysis and research on the mechanism of NO_x produced by lightning^[6]. The main chemical reaction theories are as below^[7]:



3.2.2 Discussion on the mechanism of HNO_x in relay

For the relay, its arc is similar to the lightning in the atmospheric environment, but different from the atmospheric environment, the relay cavity is relatively small, and the concentration of NO_x and HNO_x generated inside may be relatively large.

The results of SEM-EDS, FT-IR, ICP-OES and IC instruments comprehensive analysis of the components of corrosives further confirmed that: under the action of arc, the internal N_2 and O_2 of relay will produce NO_x , and generate HNO_x with the

internal environment moisture, while the main corrosion of relay iron parts after the electrical life is the electrochemical corrosion reaction between the coating Ni and HNO_x .

The causes of iron corrosion are external environmental factors and internal material factors. The following is a brief discussion.

3.3 Discussion on the environmental factors affecting corrosion of iron

3.3.1 The relationship between corrosion rate of iron and the thickness of water film on the surface

Water can react with NO_x to produce HNO_x , but also provide medium for iron corrosion. When the relay works and the surrounding humidity is high, the water film is easy to form on the surface of the iron parts because the temperature difference inside the relay will change. The relationship between the corrosion rate of iron parts and the thickness of water film formed on the surface is shown in Fig.11^[8]

In zone I, there are several molecular layers of adsorbed water film on the metal surface, the thickness of which is less than 10nm, no continuous electrolyte is formed, and the corrosion rate of metal is very small.

In zone II, when the humidity exceeds the critical relative humidity, the thickness of the water film on the metal surface is between 10nm and 1 μm , due to the rapid diffusion of oxygen, the corrosion rate of the metal is multiplied.

In zone III, with the further increase of water film thickness, a visible liquid film will be formed. At this time, due to the barrier of the liquid film, the diffusion of oxygen becomes difficult, so the corrosion rate of the metal is correspondingly reduced.

In zone IV, when the thickness of water film increases gradually to form water drop, the thickness of water film is more than 1 mm, and the corrosion rate is similar to that of metal immersed in liquid.

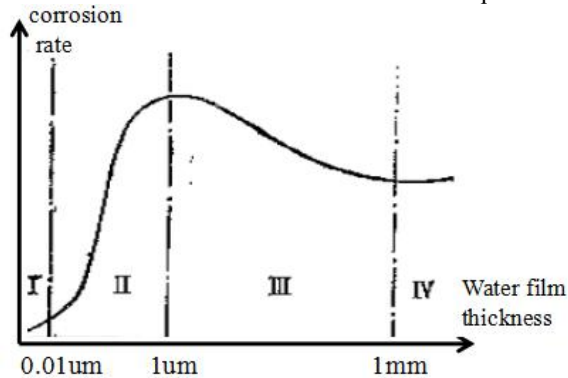


Fig.11 Relationship between thickness of water layer on metal surface and corrosion rate

When the thickness of the water film on the surface of the iron parts inside the relay is in the area II and III, the iron parts are prone to corrosion. At this

time, the corrosion speed is related to the thickness of the water film. Therefore, the analysis of its environment can further promote understanding of corrosion of relay iron parts.

3.3.2 Discussion on the mechanism of increasing iron corrosion in high humidity environment

When water molecules are adsorbed on the surface of relay iron, they can react with water chemically. At this time, the condensation of water on the surface of iron is called chemical condensation. When the relative humidity is between 70% and 80%, HNO_x will agglomerate on the surface of iron and react with Ni coating. The formation of electrolyte nickel nitrate aggravates the corrosion of iron.

When the relative humidity of metal storage environment is lower than its critical value, the temperature has little effect on the corrosion rate. However high the temperature is, because the environment is dry, the metal is not easy to rust. When the relative humidity reaches the critical relative humidity of metal corrosion, the influence of temperature plays a significant role. At this time, when the temperature increases by 10 °C, the corrosion rate increases by about two times^[3].

The main effect of temperature is that when the temperature is greatly reduced, it will cause condensation on the metal surface and accelerate the corrosion. Large temperature difference between day-night and in-outdoor temperature difference will make condensation happen. If condensation happens periodically, iron parts will rust seriously.

3.4 Discussion on material factors affecting corrosion of relay iron

3.4.1 Discussion on pitting corrosion resistance of iron coating

Pitting corrosion occurs above a critical potential, which is called pitting potential. Metal parts are in corrosion solution. when the corrosion potential exceeds the pitting potential, uniform pitting corrosion will occur. When two different metals contact, the corrosion rate of the metal with negative potential increases, while the metal with positive potential is protected.

For the common coating of relay iron parts, the potential of Cu electrode is +0.337, Sn is +0.007, Ni is -0.25, Fe is -0.44, Cu is relatively the most positive, and the corrosion resistance is the strongest, followed by Sn, Ni, and finally Fe. Therefore, generally, the outer layer of Cu plated iron parts has strong corrosion resistance.

3.4.2 Discussion on the influence of defects of iron coating on corrosion

There are quality defects on the surface and inside of the coating of some iron parts (Fig. 12). These defects will weaken the protection ability of the coating and cannot effectively prevent the oxygen and water in the air from being immersed. For example, the high humidity environment discussed in the previous will accelerate the corrosion of iron parts. In addition, the nitric acid compound produced during the operation of the relay will agglomerate on the surface of the iron parts, and the corrosion will occur first at the defective part of the coating.

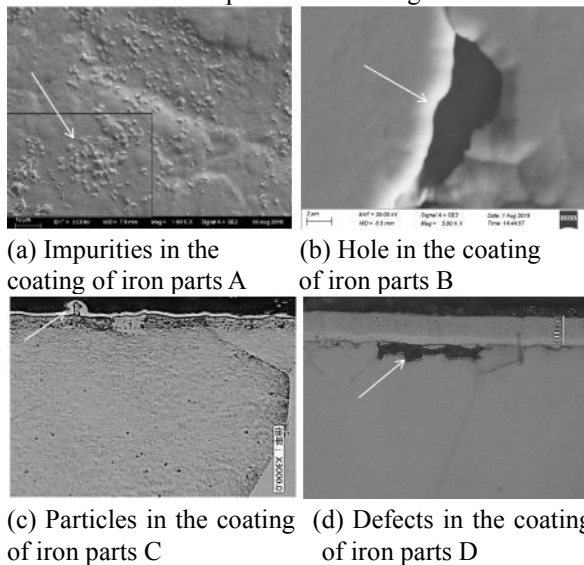


Fig.12 Defects in the coating quality of iron parts

3.5 Discussion on evaluation method of coating quality of iron parts

The internal micro-environment of relay is complex, so a constant test environment is needed to evaluate the corrosion resistance of iron coating.

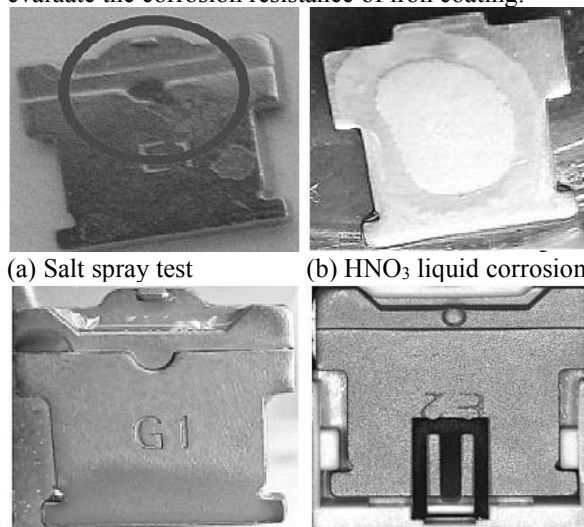


Fig.13 Comparison of evaluation methods for coating quality of iron

Salt spray test method, in which the mechanism of Cl ion corrosion of iron parts is completely different from that of HNO_x corrosion of iron parts; the speed of nitric acid liquid corrosion of iron parts is fast, but the method belongs to comprehensive corrosion, and there is no small difference in corrosion; The speed of HNO₃ vapour is fast, but the temperature and humidity are uncontrollable, and the edge of iron parts surface is prone to condense; Gas corrosion test box method is fast, the temperature, humidity and the concentration of NO_x can be effectively controlled, and the surface of iron parts is uniformly corroded, as shown in Fig.13 d.

4 Conclusion

(1) The observation of corrosion form shows that pitting corrosion is the most important form of iron corrosion, and pitting corrosion often occurs on the surface or internal defects of iron coating.

(2) The analysis of corrosion products shows that the corrosion of iron parts after electrical life of relay is mainly the electrochemical corrosion of Ni metal and HNO_x electrolytic medium. N₂ and O₂ in the relay generate NO_x under the action of arc and generate HNO_x in combination with water vapor.

(3) The combination test of different temperature and humidity shows that high humidity environment is the most important environmental factor affecting the corrosion of iron parts inside the relay.

(4) The method of gas corrosion test chamber to evaluate the quality of iron coating is fast and effective.

5 Reference

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