Study on corrosion mechanism of shielding line of copper clad aluminum cable in substation terminal box

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Abstract. By means of scanning electron microscope, energy spectrometer and X-ray diffraction method, the chemical element analysis and phase analysis of the cross section, corrosion products, fire resistance mud and shielding line of the copper clad aluminum cable under the special service environment in the terminal box of the substation were analyzed and the corrosion mechanism was studied. Salt Mist corrosion test was carried out on the shielding line with dilute HCl solution, NaCl solution and NaOH solution. The results showed that there are Cl elements and AlCl3, CuCl and other substances in the corrosive products, and a large number of Cl elements are found in the corrosion resistance mud and shielding line outsourcing materials. The salt mist test showed that the dilute HCl solution makes the corrosion rate of copper clad aluminum wire the fastest, and the cause of corrosion fracture of copper clad aluminum wire is the result of chemical corrosion of acidic atmosphere, corrosion of primary battery and corrosion of electrolytic pool.

1. Introduction
In order to save precious copper resources, copper-clad aluminium wires have been widely used in shielding cables. However, in the terminal box of substations, this shielding net woven from finer copper clad aluminum wire is exposed in the air environment when it is grounded by peeling off the outer plastic cladding layer, often broken by rapid corrosion, it causes the electromagnetic interference signal to interfere with the normal signal and affect the correct transmission of the control signal, which poses a serious threat to the security of the power grid[1]. In this paper, the corrosion products and surrounding environment of copper-clad aluminium wire collected from a substation site are analyzed, and the causes and mechanism of corrosion of copper-clad aluminium wire are found out.

2. Experimental
X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to analyze the corrosion products and copper-clad aluminium wires retrieved from the site. Combined with three kinds of analysis results, the corrosion mechanism was deduced according to the corrosion products, and the corrosion speed was compared with HCl, NaCl and NaOH solution with the concentration of 0.85mol/L in the laboratory conditions.

3. Results and discussion
3.1. Cross-sectional analysis of corroded copper clad aluminum wire
SEM observation and energy spectrum analysis were carried out after polishing the cross section of the ground copper clad aluminum line, which has been seriously corroded in the field, and the results are
shown in Figure 1.

Figure 1. SEM Analysis and EDS analysis of corroded copper clad aluminum wire section

The darker part of the center of the SEM image is the Al monomer core, and the brighter section of the lower right is the copper layer. SEM image there is no copper layer in the upper right, Al single wire core exposed, indicating that copper clad aluminum wire in the corrosion process, the outer copper has a certain degree of corrosion or even stripping. On the left side of the SEM image, you can see that there is also a black corrosion product between the remaining copper layer and the aluminum core, indicating that the copper layer is protected by aluminum after the aluminum core is exposed, and the aluminum core is given priority corrosion.  

3.2. Determination of corrosion Products

3.2.1. Elemental Analysis of corrosion products

Through field observation, it was found that there were two kinds of corrosion products, white and blue, which fell below the serious corrosion site of the shielding line. The results of its energy spectrum analysis are shown in Figure 2.

Figure 2. (a) SEM Analysis and EDS analysis of white corrosion products
(b) SEM Analysis and EDS analysis of blue corrosion products
The elemental mass fraction of the corrosive product is shown in table 1, because EDS is difficult to accurately determine the content of light elements, and by Figure 2, the O element is the main existing light element, so table 1 lists the content of O element after subtracting the other main elements with 100%.

Table 1. Mass fraction of elements contained in corrosive products

| Chemical          | Na  | Mg  | Al   | Cu   | Cl   | O       |
|-------------------|-----|-----|------|------|------|---------|
| White Corrosion Products | 0.43% | 0.88% | 35.7% | 1.71% | 2.39% | 58.89%  |
| Blue Corrosion Products | 0.48% | 0.91% | 26.4% | 11.75% | 2.06% | 58.40%  |

3.2.2. Phase Analysis of corrosion products
After shredding the two corrosion products into fine powders, the XRD phase analysis is made, and the final calibration results are as shown in Figure 3:

Because EDS analysis is difficult to detect elements with a lower atomic number, H, C, N three elements are added to the phase calibration, and these elements are present in the air.

3.2.3. Comprehensive analysis of corrosion products
From the analysis of the elements of the corrosion products, it can be seen that the main elements of the sample after corrosion are: O, Al, Cu, Cl, and the quality of the content of the score decreased in turn. Combined with the results of XRD phase analysis, it is determined that the content of Al$_2$O$_3$, Al(OH)$_3$ in corrosion products is the highest, followed by AlCl$_3$, CuCl, Cu$_2$(NO$_3$)(OH)$_3$. Due to the poor crystallization of the corrosion products retrieved at the site, the dorsal bottom of the XRD test is very high, and there may be other corrosion products that cannot be identified due to the extremely low content.

3.3. Corrosion mechanism and Salt mist experiment
The corrosion product contains Cl elements with a mass fraction of about 2%, which is analyzed and concluded that the shielded cable and the flame retardant mud in the terminal box are released in the form of HCl after being heated and decomposed\cite{4}. Moreover, a large number of AlCl$_3$ have been found in the corrosion products, which further proves the existence of the HCl atmosphere in the terminal box, because the AlCl$_3$ evaporates from the solution and is produced to remain in the HCl atmosphere, otherwise a double hydrolysis reaction will occur: Al$^{3+}$+3Cl$^-$+3H$_2$O→Al(OH)$_3$↓+3HCl↑. The HCl atmosphere causes the HCl pressure of this reaction to reach saturated vapor pressure, thus inhibiting the formation of Al(OH)$_3$, and finally crystallization the AlCl$_3$ crystal. In rainy weather, the air in the terminal box is moist, HCl gas in the air in the small water droplets to form an acid solution.
adsorbed on the surface of the shielding line copper layer, under this acidic conditions, the corrosion rate of copper accelerated, when the surface of copper has a layer of oxidation products for Cu₂O and a small number of CuO[5]. These two oxidizing products form a dense oxide film leading to the passivation of copper, but in a non-oxidizing dilute acid solution, the following reactions occur: 2HCl+Cu₂O→2CuCl+H₂O; 2HCl+CuO→CuCl₂+H₂O. This is exactly the CuCl of the generation in XRD phase analysis. After the oxide film is dissolved by an acidic solution, the fresh Cu atoms are exposed and the oxidation continues to occur, so the circulation, corrosion is increasing. Because of the small radius of the atom, the Cl element is an electrolyte element that can easily cause the corrosion of small holes, which accelerates the corrosion perforation process of the copper layer. In combination with two points, HCl released from the aging of fire-resistant mud and cable-coated plastic in the terminal box is the main reason for the rapid corrosion and perforation of the external copper layer of the copper clad aluminum shielding line in the terminal box of the substation.

In order to further verify that the rapid corrosion fracture behavior of the shielding line in the terminal box is related to the acidic HCl atmosphere in the box, the salt mist experiments at room temperature of 24, 48, 72 and 96 hours were carried out with the same concentration of HCl, NaCl and NaOH solution as salt mist mother liquor, and the same copper-clad aluminum wire the corrosion rate of copper clad aluminum wire was measured by SEM observation (Fig. 1) to reduce the thickness of copper cladding by the cross section of the shielding line before and after corrosion. The final result, as shown in Figure 4, shows that over time, the thinning rate of copper in acidic environment is about 3 times that of the other two conditions, and the corrosion rate of the shielding line in the terminal box is greatly accelerated in the acidic environment.

As can be seen from Figure 1, the copper layer is no longer continuous, the upper right corner of the Al core has been completely exposed. The above inference is confirmed by the appearance of the copper layer similar to a sinkhole or hole in the lower right corner. On the basis of the above corrosion, the electrolyte solution is produced, the Cu, Al monomer is in contact, the original battery reaction occurred, resulting in the electrical coupling corrosion.

Because the shielding line is used to shield the external interference electromagnetic wave signal, so according to faraday electromagnetic induction law, the shielding line circle will produce induction EMF, shielding line grounding, the production of inductive current, the current density is mainly concentrated in the surface of the wire, will be in the contact surface of copper and aluminum electrolytic cell corrosion, according to the direction of the inductive EMF different, the electrode reaction formula can be an anode. The resulting Al(OH)₃ flocculate is loose and precipitated, and
most of the drying is converted to $\text{Al}_2\text{O}_3$ after stripping falls on the ground. The corrosion of electrolytic pool mainly occurs in the late stage of corrosion after corrosion thinning and even stripping of copper layer.

4. Conclusion

1. There are three corrosion mechanisms in the copper clad aluminum wire in the terminal box of substation: chemical corrosion of acidic atmosphere, corrosion of primary battery and corrosion of electrolytic pool. The corrosion process is divided into the initial copper is corroded by acidic atmosphere and electrochemical corrosion in the middle and late stage. When the outer layer of copper is corroded and perforated, electrochemical corrosion will begin, and the shielding line quickly breaks due to corrosion.

2. The reason why the shielding line in the terminal box of substation is very easy to corrode is that the terminal box of substation is installed in the outdoor near surface, the wet atmosphere and the acidic atmosphere caused by aging decomposition such as fire-resistant mud, shielding line cladding plastic layer, etc., in acidic atmosphere, the copper outer layer, which was already corrosion-resistant in the air, was also quickly corroded and perforated, resulting in an electrical coupling, and the use of copper clad aluminum wire as the conductor of the inductive current, which was mainly concentrated on the surface of the wire, was prone to the corrosion of the electrolytic pool and accelerated the corrosion rate.

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