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Research on oxidation characteristics of electrical contact melted mark in short circuited fire

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ABSTRACT

Electrical contact melted mark is a product of conductor to melt and deform when it fails during electrical contact. The short circuited fire is essentially caused by failure of electrical circuit at electrical contact to ignite surrounding combustible. It is extremely important to study the oxidation process of short circuited metal melted marks from the angle of electrical contact for improving the accuracy and scientificity of cause identification. This paper discusses the heating of electrical contact and high temperature oxidation of copper, analyzes and studies the element distribution at the surface and inside the primary short circuited melted marks and second short circuited melted marks. Melted mark samples with different type of electrical contact is prepared by stimulation experiment and structural feature parameters of samples, element content and element distribution map are obtained with scanning electron microscope, energy spectrometer and computer image processing software. In addition, after comparison and analysis of experimental results, SEM&EDS is used to qualitatively and quantitatively analyze the electrical contact melted mark in short-circuited fire.

KEYWORDS

Oxidation; The short circuited melted marks; SEM/EDS; Short circuited fire.

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INTRODUCTION

Short circuited fire is the most common electrical fire. Major fire due to electrical short circuit frequently occurs every year, which causes very bad social influence. Electrical failure during fire can be divided into first short circuit and second short circuit. First short circuit, namely short circuit before fire, is the short circuit occurs before the fire; second short circuit after fire is the short circuit occurs for reason of damaged insulation layer during fire; melted mark during electrical short circuit is important evidence used for fire investigation. There are two kinds of melted marks caused by electrical short circuit: Primary Short circuited melted Marks (PSMs) and Second Short circuited melted Marks (SSMs). PSMs and SSMs are of vital importance to cause analysis and confirmation of responsibility.

Electrical short circuit is actually the electrical contact failure caused by electrical insulation failure. Large amount of charged particles may breakdown the air insulation in between conductors and generate high temperature fire. The fire may melt the conductor in a flash and the melted conductor may rapidly solidify into melted marks. The formation environment of PSMs is quiet different from that of the SSMs, therefore, the internal metallographic structure of melted marks formed may be different. At present, the method used to determine PSMs and SSMs is primarily based on this theory and a standard titled *Technical Determination Method for Electrical Fire Cause. Part 4: Metallographic analysis method*. (GB/T 16840.4-1997) is formulated. Direct heat source of short circuited fire is joule heat of electrical contact which is generated by current heating effect. It releases heat subject to the I^2R law and it mainly consists of two electrical physical quantities, namely current and resistance. In short circuit accident, the current-carrying part may bears an instant heating effect of short-circuit current and electrodynamic impact much greater than that during normal operation. Short circuited accidents happen in the normal condition of handicraft protection of protection device. Low impedance short circuited lines have big electricity current, protection device also needs certain actuation time. Temperature of electric appliance or the contact segment between conductor and electricity can be heated to very high degree in the function of heat effect of short-circuit current before accidents are removed. If the protection device doesn’t install or actuate current and time by rule, set value are excessively big, and device failure can’t have the function of protection, the big current of low impedance short circuited lines will greatly threaten to every link of the electric circuit, big current will produce great heat in the contact segment of electricity so as to fire surrounding fuel and melt electric contact things. At present the scholar of electrical contact field study mainly at two respects: the first, arc strike and arc extinction problem is resulted in that breaker and other electrical elements in electric cabinet are with bad contact; the second, identifying problem for voltage current fluctuation law during failure of electrical contact; For the research on identification method for melted mark of short circuit fire, pay attention to measurement technique and representation way. The research on formation mechanism of melted mark is to be studied further. Cross between electrical contact theory and identification method of melted mark of short circuit is a new research direction. Process of high-temperature and vigorous oxidation is a very special physical and chemical process. Oxidation characteristic of melted mark need be studied further. Study representation problem of different kinds of melted mark oxide layer from point of view that electrical contact failure to enrich and improve identification method of PSMs and SSMs.

The main work of the text is to conduct the short circuit simulation experiment and to prepare primary and secondary short circuited melted mark sample. By applying electrical contact theory, high-temperature oxidation of cuprum theory, SEM&EDS method and computer image processing software, obtain the structure characteristic parameters of the sample, elementary composition content and element distribution map. By comparative analysis, make a qualitative and quantitative analysis on the electrical contact melted mark in shot circuited fire.

HIGH-TEMPERATURE OXIDATION PROCESS OF CUPRUM

When a short-circuit fault occurs in the electrical circuit, the temperature on the contact interface of the cuprum shall rise instantly (short circuit fire temperature 2000℃-3000℃) and the cuprum surface shall absorb the oxygen in the air due to current heating effect. After a series of physiochemical processes, the cuprum oxide is generated. Because the oxygen is absorbed on the surface, the concentration gradient make the oxygen diffuse into the metal. The metal oxide grows along the horizontal direction to form continuous oxide thin films. The oxide thin films perpendicular to surface direction grow continuously and the thickness of oxide films increases. Generally, cuprum high-temperature oxidation is divided into 3 stages: early oxidation stage: Cuprum participates in oxidation reaction; Medium oxidation stage: Both cooper and cuprum ions participate in oxidation reaction; Last oxidation stage: The oxide films are thick enough to prevent the cooper from contacting with the outside oxygen, at this moment, only the cuprum ions diffused shall participate in oxidation reaction or the oxygen shall be diffused in to oxidize the cuprum[4]. Under certain conditions, along with the increase of the thickness of oxide films, double oxide films may appear on the surface of cuprum.

The initial stage of oxidation——form oxide film

The first step in process of forming a surface oxide film, is oxygen physical adsorption (van der Waals force), its adsorption mainly depends on the surface area. The outer of oxygen atom with chemical adsorption obtains electron, and form O^{2-} which enters into the lattice structure of copper, so Cu atom loses electron and generates Cu^{+} ion. Cations and anions combine Cu_2O at high temperature. The speed of oxidation progress is determined by this step. Copper conductor with fastest response when the concentration of O^{2-} is largest, its surface grow crossly and form the oxide film.

Through verification of energy Spectrometer for component to oxidation kinetics experiment of fine copper, copper oxygen ions combined with the primary composition of oxide film is Cu_2O, and the speed of initial oxide film depends on the speed of combination speed of Cations and anions. Because of ionization reaction of oxide film layer on both sides, a certain electric field is formed on both sides of the membrane layer. Since electric field has a great impact on ion mobility speed, when the film layer is very thin the film layer grows rapidly. The growth rate of copper oxide film decrease sharply when film layer is about 50nm. At this time the growth rate of oxide film is proportional to tunneling effect probability.

The interstage of oxidation——growth of oxide film

The direct oxidation of copper and oxygen weakens after the formation of oxide film, which mainly depends on the longitudinal diffusion of Cu^{+} and O^{2-} to generate oxide film, that is O^{2-} anion of air/ oxide film interface transfer to copper oxide film through oxide film, while the Cu^{+} cations on the oxide film / Cu interface will transfer to air/ oxide film interface. Thus the longitudinal growth of oxide film thickens, when the surface oxidation rate of copper conductor is subjected to ion diffusion rate. When oxide film grows to a certain thickness, the electron field force restricting on ion may decrease. The concentration gradient of cations and anions become the main controlling factors to the continuous growth of oxide film, at this time the oxidation will occurs on the two interfaces, the both sides of oxide film.

Final stage of oxidation-oxide film changes into double membrane

As the thickness increase, Cu^{+} transfer to the side of air/ oxide film with increasing energy. When Cu^{+} can not transfer to Cu^{+}/O^{2-} interface, in no need of lots of energy or high temperature condition, original Cu_2O will be oxidized into CuO, which increases continuously by surplus O^{2-}. If it is fully oxidized, the generation of Cu_2O is restrained due to the low temperature and other factors. The growth rate of CuO layer will gradually become greater than Cu_2O layer, and finally it thicker than Cu_2O layer.

In the certain In a certain external conditions, such as fire and metal evaporation splash bead and so on, oxide film will formed micro crack of penetration style, which results in oxide layer lost, and forms micro channel to make oxygen diffuses inwards, and change it into the inside hole. Some added effects make copper dendritic crystal and the underlying oxide film (especially Cu_2O layer) mixed together to form a mixed layer.

The difference of the process of the oxidation on the first and the second short circuited melted marks

In the case of the short circuit, the temperature can reach 2000 degrees centigrade, and it exceeds the melting point of the copper 1083 degrees centigrade. Therefore, the copper at present is in the liquid state. The combination of the copper and the oxygen in the state of liquid or the solubility of the oxygen in the copper will become large with the temperature's rising after the break. Thus it will influence the oxidation condition of the copper. Obliviously, when the temperature rises suddenly, the dissolved oxygen will increase and the thickness of the skin of the oxidation. After the first circuit, the speed of the lava cooled will become quick relatively, and the oxygen absorbed do not response completely and just kept inside. Therefore, the degree of the oxidation of the first shore circuit is relatively low. However, the secondary short circuit happen is happened under the circumstance of heating, the higher temperature can promote the reaction of the oxygen and the copper, therefore, the degree of the oxidation is higher. The contact points of second short circuit are more than the primary short circuit, while fire temperature is lower than the primary. Therefore, from the surface, secondary short circuit of free copper ions and oxygen is less than primary short circuit with high oxidation degree.

EXPERIMENT OF THE SIMULATION ON SHORT CIRCUIT

Experimental materials and instrument

Material: The sectional area that is 2.5 square millimeters, normal single core of Polyvinyl Chloride copper wire. According to the 6^{th} standard role in GB/T3952-2008 of Copper drawing stock for electrical purpose, the copper core of the copper conductor is T3 type.

Instrument: ZX7-630IGBT of the inverter DC argon arc welder; the box of the simulation experimental electrical fire; draught chamber; the field emission scanning electron microscope of the type JSM-6010LA (This kind of scanning electron microscope is the integrated equipment of SEM and EDS.).

The experimental process and the handling of the samples

(1) The experiment of simulation on the primary short circuited melted mark;

(a) Wiping off the both ends of the single core copper conductor;

(b) Open up the ventilation equipment, modulate the output current value of the electric welding machine to 200A, and then turn off the power source of the electric welding machine;

(c) The experimental group of touching needs two conductors and each conductor connect with the each segment of the electric welding machine;

(d) Open up the power source of the electric welding machine, and the people in the experimental group of touching need touch the two conductors with the stick. Turn off the power of the arc welding machine after the short circuit of the conductor. Collect the short circuited melted marks and put them into the sampling bag and mark them.

(2) The simulation experiment of the second short circuited melted mark

(a) Prepare the sample of the single core copper conductor, link one side of the electric welding machine, and wipe off the skin of the insulation;

(b) Open up the ventilation equipment; modulate the output current value of the electric welding machine to 200A, and then turn off the power of the electric welding machine;

(c) Connect two single core copper conductors with the each side of the electric welding machine separately, and after that, twine and link the two conductors and put the experimental brazier below the sub conductor. Ignite the alcohol in the brazier, light the skin of the insulation of the copper conductors and close the door of the experimental box.

(d) Turn on the power of the electric welding machine, and turn off the power after the short circuit of the conductors.

(3) The experiment on analysis of the field emission scanning electron microscope

Observe the samples of the melted marks of the copper conductor collected from the experiment of the simulation in the electric contact, and analyze SEM and EDS. Observe the microcosmic shapes of the samples, measure the components and the content of the oxide layer on the surface, and hereby confirm the material type of the oxide layer on the surface. On the basis of the elemental distribution of the oxide layer on the surface, it can ensure the degree of oxidation of the oxide layer on the surface

RESULTS AND DISCUSSION

The external morphology and composition for melted mark (The 3D scatter diagrams for topography, ingredient list, and oxygen)

(1) Topography

Use SEM to observe the sample of melted mark in experimental group, you could see the picture of microscopic appearance of melted mark surface in the condition of magnifying larger multiples. The accelerating voltage of electron beam sets to 20.0eV.

The Figures from 1 to 4 show the observed result of positive pole of SEM

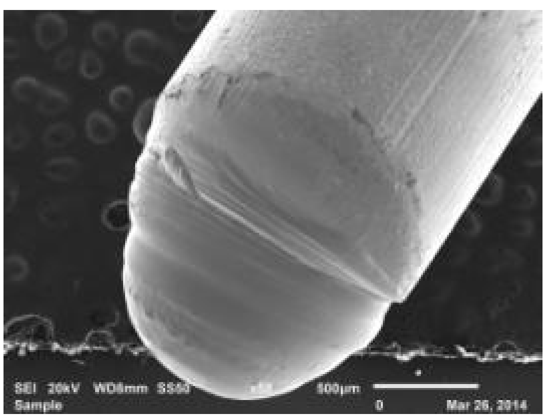

Figure 1 : The appearance for the primary short circuited melted marks, Positive pole, 50x

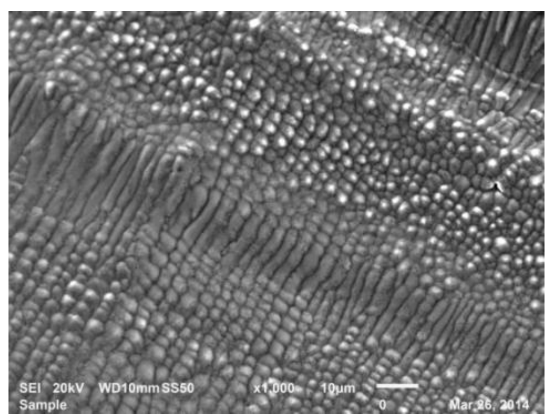

Figure 2 : The appearance for the primary short circuited melted marks, Positive pole, 1000x

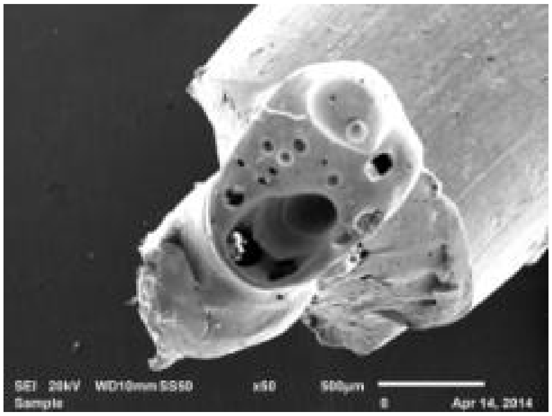

Figure 3 : The appearance for the second short circuited melted marks, Positive pole, 50x

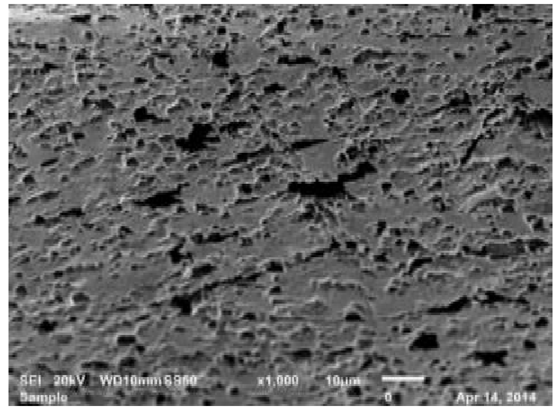

Figure 4 : The appearance for the second short circuited melted marks, Positive pole, 1000x

The Figures from 5 to 8 show the observed result of negative pole of SEM

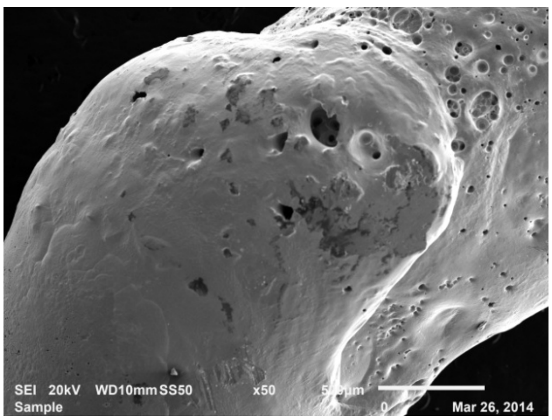

Figure 5 : The appearance for the primary short circuited melted marks, Negative pole, 50x

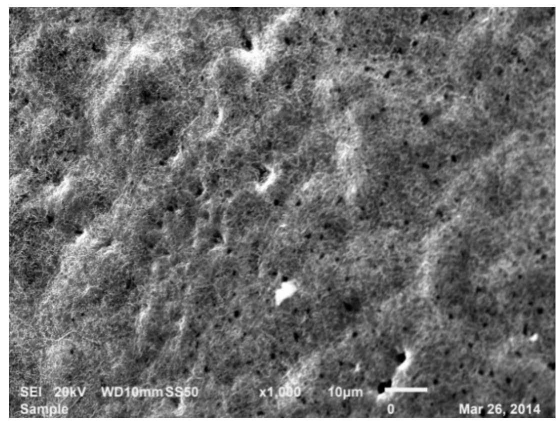

Figure 6 : The appearance for the primary short circuited melted marks, Negative pole, 1000x

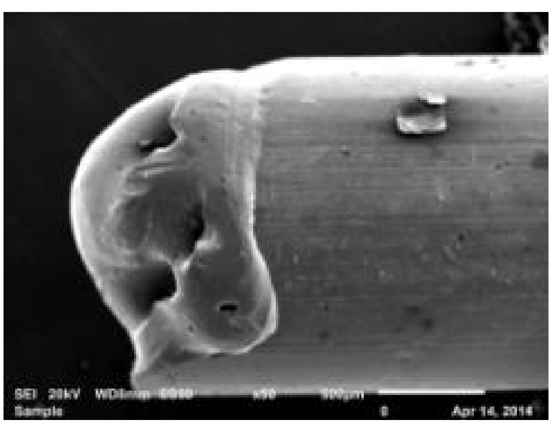

Figure 7 : The appearance for the second short circuited melted marks, Negative pole, 50x

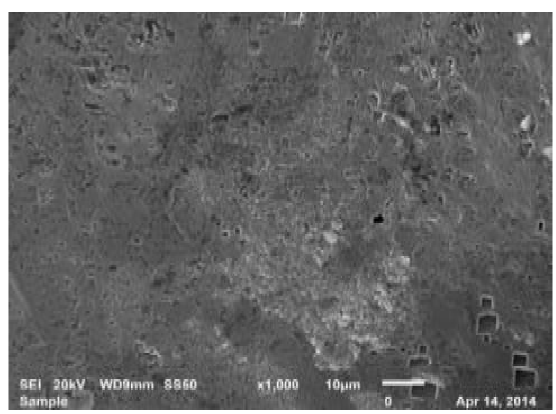

Figure 8 : The appearance for the second short circuited melted marks, Negative pole, 1000x

Seen from appearance, there is Level 1 exist porosity in both first and second short circuit. The second ones are large size and quantity; Beads are less, and surface is rougher. Compared with second short circuit, the first one is smaller size and less numbers; you could find neat surface in the beads and regular columnar crystal structure.

Parsing from the electrical contact theory, due to less time from high temperature fire to rapid solidification of first short circuit, the crystal structure and porosity grow up too late, so it is less and small. The formation process of secondary short circuit with alcohol heating, fast air flow, porosity grows up easily and further develops.

(2) Ingredient list

Use EDS matched by SEM to analyze melted marks component in surface and section respectively, you could get component distribution for the primary short circuited melted marks and the second short circuited melted marks, so that you could judge the forming reason for it. Tests revealed that the main components of melted marks are Cu, O and C, but others could be negligible for their molar fraction all under 0.5%. Besides, as a result of the limitation of EDS itself, those molecular mass is smaller than Na could not be tested. (Such as H)

Cu is raw material for wire, and through high temperature and electric current in electrical simulation, Cu exists in sample as CuO and Cu_2O.

C is raw material for wire, too. And its molar fraction is about 17%. The quantity of C is invariant after electrical simulation, but there is mixed with impurities inevitably during making the melt mark profile, which includes vast C. So molar fraction of C is added, and it regarded as system error.

O is produced in the reaction process. The content of Cu and C is an important indicator to analyze the component for melted marks. The molecular mass ratio of Cu and O is close to 2:1, and it shows the main component of melted marks is Cu_2O; However, if it is close to 1:1, its main component to be CuO.

TABLE 1 : Primary and Second Short Circuited Melted Marks Surface Copper Oxidation

Element	Serial No.	Y-Z-1	Y-Z-2	Y-Z-3	Y-F-1	Y-F-2	Y-F-3	Mean alue
	Cu	55.33	42.58	52.62	44.89	55.64	47.28	49.72
Primary short circuit mole fraction	O	15.89	27.33	26.49	27.26	10.94	26.87	27.46
	Cu: O	2.1:1	1.6:1	2.0:1	1.6:1	1.8:1	1.8:1	1.8:1
Element	Serial No.	E-Z-1	E-Z-2	E-Z-3	E-F-1	E-F-2	E-F-3	Mean value
	Cu	28.20	38.69	33.78	47.20	45.87	38.94	38.78
second short circuit mole fraction	O	8.58	8.52	10.27	8.33	10.03	8.73	9.08
	Cu: O	3.3:1	4.5:1	3.3:1	5.7:1	4.6:1	4.5:1	4.3:1

Melted marks surface copper oxidation ratio of different electrical contact types and the C content mole fraction mean value can be concluded from above.

TABLE 2 : Comparison of the melted marks surface copper oxidation of different electrical contact types

	Copper oxidation ratio			C content mean value
	Mean value	Maximum value	Minimum value	
Primary short circuit	1.8	2.1	2.0	22.82
Second short circuit	4.3	5.7	3.3	52.14

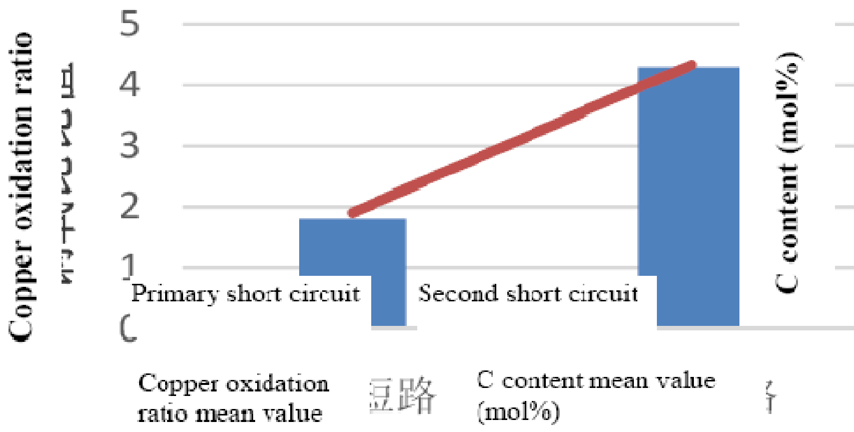

Figure 9 : Surface Elements Analysis

To speak of the short circuit under the same current, after fire melts the metallic conductor, the surface of liquid metal will adsorb a large quantity of oxygen molecules during its solidification process. But the second short circuited melt marks will further solidify under heating condition, the diffusion speed towards the melted marks interior of oxygen atoms is faster than the primary short circuited melt marks, so the oxygen content left on their surface will be less than the oxygen content left on primary short circuited melt marks, and the contact points of second short circuited melt marks are more than those of primary short circuited melt marks, the temperature of fire is relatively low; the Cu^{+} ion dissociating on the surface of second short circuit are less than those dissociating on the surface of first short circuit. Therefore, second short circuit absorbs less oxygen, and it has higher copper oxidation ratio.

(3) The Oxygen elements 3D scatter diagrams

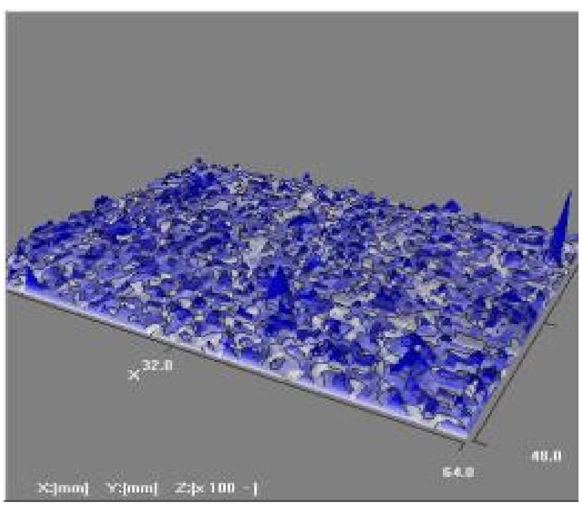

Figure 10 : The Oxygen Elements 3D Diagram of Primary Short Circuit Melted Marks Profile

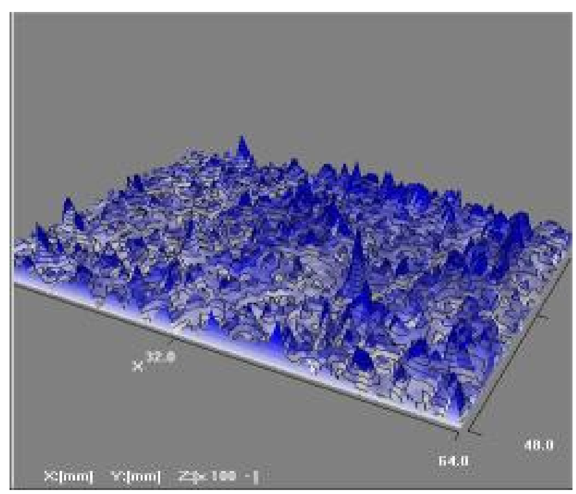

Figure 11 : The Oxygen Elements 3D Diagram of Second Short Circuit Melted Marks Profile

Zone oxidation analysis (melted marks area, transition zone, wire zone)

Concluded form the melted marks analysis bases on EDS:

TABLE 3 : Comparison of different zone oxidation of different melted mark types

Copper oxidation ratio	Melted mark zone	Transition zone	Wire zone

Primary short circuit	9.1	23.1	16.1
Second short circuit	9.2	19.4	10.4

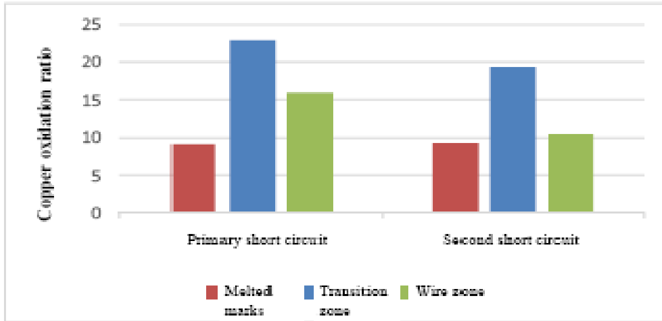

Figure 12 : Copper Oxidation Ratio of Different Zone Oxidation of Different Melted Mark Types

Ignore the affections of impurities, copper oxidation ratio depends on the oxidation degree of conductor. The oxidation ratio depends on the temperature and heating time.

Short circuit generates high temperature, this phenomenon of second short circuit is the same as that of the first short circuit. Because the second short circuit experiment in lab is conducted by the method of positive and negative winding, there are many contact points; the temperature is lower than the temperature in the first short circuit experiment. But the second short circuit has longer heating time. Considering the temperature and time, it's hard to judge the oxidation degree. Seeing from the experimental data, the oxidation ratio is higher if the copper oxidation ratio of second short circuit is lower than that of the primary short circuit.

Considering the analysis based on EDS, the copper oxidation ratio of sample will be changed if impurities mixed in it, and it will cause error to the experimental data. In fact, it can be found from the survey data of each time. No matter first short circuit or second short circuit, there are big changes in copper oxidation ratio, so system errors in experiment should be reduced.

Infiltration oxidation analysis (infiltrate from melted marks pathway to oxidation)

	Cooper oxidation ratio mean ratio		**C content mean value**	
	Surface	**Melted marks interior**	**Surface**	**Melted marks interior**
Primary short circuit	1.8	9.1	22.82	49
Second short circuit	4.3	9.2	52.14	46

TABLE 4 : Different Melted Marks Pathways' Change to Copper Oxidation Ratio

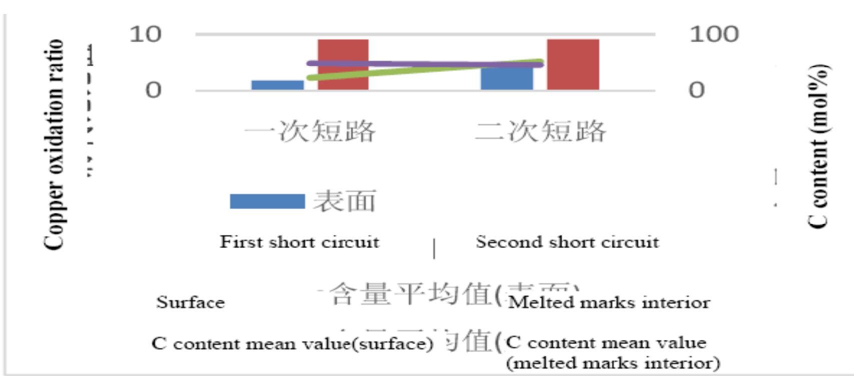

Figure 13 : Melted Marks Zone Pathways Oxidation Analysis

It can be seen that the melted marks interior copper oxidation ratio is generally higher than that of the melted marks surface, that’s to say the surface oxidation degree is high, and the primary short circuit cooper oxidation ratio and interior cooper oxidation ratio are higher than those of the second short circuit. The carbon content of the second short circuited melted marks surface is the highest, whereas the carbon content of the melted marks interior is lower than that of the first short circuit.

CONCLUSION

This paper studies the appearance and element distribution of and the primary short circuited melted marks and the second short circuited melted marks through the analysis of Scanning Electron Microscopy and Energy Disperse Spectroscopy (EDS) elemental analysis. We conclude that:

(1) Appearance analysis: less and small porosity in first short circuit, structured surface with obvious columnar crystal structure; more and big porosity in second short circuit, rough surface.

From the analysis of the electrical contact theory, the time from high temperature fire to rapid solidification is short and the crystal structure and porosity has no time to grow up, so the porosity is less and small. There is alcohol heating before producing fire and solidification n the second short circuit, so the porosity develops completely.

(2) Component analysis: cooper oxidation ratio is high in first short circuit and the integral oxidation degree is low; the oxidation degree is high in the second short circuit. The cooper oxidation ratio of the second short circuited melted marks is lower than that of the primary short circuited melted marks according to the experimental data, because the first short circuit is the same as the second short circuit. The temperature is high in short circuit, but the second short circuit experiment in lab is conducted by the method of positive and negative winding, there are many contact points. And the heating time in second short circuit is longer, at the same time continuous heating promotes the oxygen to diffuse towards the internal melted marks, which can be proved according to the oxygen distribution of the melted mark profile.

The cooper oxidation ratio in melted marks is lower than that in transition region and in wire rod region among all kinds of the electrical contact melted marks, which can prove that the oxidation degree of melted marks near the highest temperature and reaction core is the highest. From the analysis of the electrical contact theory, the fire in the first shot circuit and the second short circuit is produced in contact points surface. The electron moves from the surface to the wire rod region, so the surface is firstly oxidized.

(3) This paper also concludes the SEM&EDS map of the first short circuit and the second short circuits, providing basis for identifying two kinds of different melted marks.

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