Degradation behavior of heat-treatment silicate adhesive under special working conditions

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Abstract: Inorganic adhesive is widely used in the sealing and connection of electronic devices. Its insulation is highly important in the performance of installation. In this paper, the insulation resistance and tensile strength of different composite silicate samples were measured by test machines. The morphology and surface composition were analyzed by electronic microscope and energy spectrum analyzer. The results show that: In a humid environment, the resistance insulation of adhesive increases with the rising of heat treatment temperature, and decreases with the increment of wet environment. When the modulus ratio of colloidal liquid is in the range of 7.2~9.1 and the heat-treatment temperature is larger than 600℃, the effect of moisture resistant is remarkable. The tensile strength of adhesive deteriorates with the increasing of humidity. Furthermore, with ascending heat treatment temperature, the tensile strength rises when the modulus ratio of adhesive is less than 7.2, and declines when it is more than 9.1.

1. INTRODUCTION

Inorganic adhesive owns a poly-crystalline composite ceramic structure which is composed of colloidal solution with high modulus ratio and solid refractory powder. It has the characteristics of high temperature resistance (up to 1000 ~ 3000℃), oxidation resistance and large insulation resistance, and is widely used in the insulation sealing and connection of various metal and ceramic electronic devices[1-2]. However, due to the water absorption on the surface of silicate adhesive, the adhesive will attach a large number of water molecules when it is used in humid environment, resulting in the damage of insulation between bonded electronic devices and the decrease of bonding force. Although it has been reported that proper heat-treatment process and controlling the content of alkali metal ions in the colloid can improve service performances of the silicate adhesive under the humid working conditions, the specific optimization parameters and the impacts on the insulation and bonding properties of the colloid have not been deeply studied. It limits the application of adhesive in relevant fields[3-5].

In this experiment, The different modulus ratios of the adhesive samples were prepared by mixing proportion solution of potassium silicate and alkaline silica. Through heating treatment at different temperatures, the influencing factors of insulation and mechanical properties under the specified
humidity environment are discussed, and the causes of relevant phenomena are analyzed. The reasonable heat-treatment temperature and humidity range of adhesive with different alkali metal content are determined.

2. EXPERIMENT
The preparation methods of adhesive were as follows: mixing the potassium silicate solution (SiO2/K2O=4.0; concentration 33%) with alkaline silica sol solution (SiO2/Na2O=99; concentration 35%) in the constant temperature magnetic stirrer vessel according to the proportion in Table 1, and then raising the system to 45℃ for 1H of stirring. The above five liquid components were mixed with solid SiO2 Solid Powder (600 mesh: 400 mesh: 200 mesh = 1:1:1) according to the mass ratio of 1:2 [6].

| Table 1 The composition of liquid components |
| component | Mass March | Modulus ratio |
|------------|------------|---------------|
| 1 Potassium silicate sol | 4.2        |               |
| 2 Potassium silicate sol: Alkalinity silica sol | 3:1 | 6.1 |
| 3 Potassium silicate sol: Alkalinity silica sol | 2:1 | 7.2 |
| 4 Potassium silicate sol: Alkalinity silica sol | 1:1 | 9.1 |
| 5 Alkalinity silica sol | 99 |               |

Then the adhesive was filled into the stainless steel casing with inserting wires at the center of both ends of the casing as the electrode[7]. The five samples were put into ksl1400x muffle furnace with heat-treatment temperature of 0℃, 200℃, 400℃, 600℃, 800℃ for 30min~90min respectively, and the high temperature insulation resistance was measured with zc-7 insulation resistance meter. Then the heat-treatment samples were placed into lrhs-225-lh humidity test chamber respectively with humidity of 60%, 70%, 80% and saturated atmosphere for 6 hours, and the insulation resistance was measured.

Also, the adhesive was painted onto the self-designed tensile samples (as shown in Fig.1) for curing process after pressing and butting[7]. The tensile samples were put into muffle furnace with temperature of 20℃, 200℃, 400℃, 600℃, 800℃ for 30min respectively. Then the samples were placed into humidity test chamber with humidity of 60, 70, 80 and saturated atmosphere for 6 hours, and the mechanical properties were tested on the Instron 5982 tensile testing machine. The morphology and surface composition were analyzed by Hitachis-3400n scanning electron microscope and escalab250 XPS electron spectrometer.

3. RESULTS AND DISCUSSION

3.1 Insulation performance in humid environment
Figure 2 shows that the insulation resistance of adhesive samples increase with the raising heat-treatment temperature in the humid environment. The resistance of samples treated with temperature of 0℃, 200℃ and 400℃ are below 50MΩ at the conditions of humidity 60% and 70% (as shown in Fig. 2a and Fig. 2b). When the heat-treatment temperatures are 600℃ and 800℃, the resistance of samples are between 150~500MΩ, in which the samples 3, 4 and 5 are all 500MΩ at 800℃.

At the same time, the insulation resistance of samples decrease with the increasing of ambient
humidity. The insulation resistances of samples are descend inordinately when the humidity is 80% (as shown in Fig. 2c). In saturated water vapor environment (as shown in Fig. 2d), the insulation resistance of samples 3 and 4 are only 8 and 11MΩ. From the above all, we can see that the ideal moisture resistance conditions are that the humidity is below 80, the modulus ratio of liquid colloid is 7.2~9.1 (samples 3 and 4) and the heat treatment temperature is greater than 600°C.

3.2 Insulation performance in high temperature

Figure 3 shows the numerical values of insulation resistance decrease with the increasing temperature and holding time. At the certain critical temperature, the insulation resistance decreases significantly, even dropping from 200MΩ to less than 10MΩ. According to the resistance formula (1) of solid dielectric materials [8,9]:

$$\rho = \frac{6KT}{nvq^2\delta^2 e^{\frac{W}{kT}}}$$

(1)

$\rho$ - resistance; $T$ - absolute temperature; $K$ - Boltzmann constant; $V$ - ion vibration frequency; $N$ - ion concentration; $\delta$ - Distance between ion and adjacent position; $Q$ - charge of ion; $W$ - ion activation energy.

Fig. 2 The insulation resistance of adhesive samples in different humidity and heat treatment
a) humidity 60% b) humidity 70% c) humidity 80% d) saturated aqueous atmosphere

Fig. 3 The variation of insulation resistance of several samples with different temperature holding a) for 30 min b) for 60 min c) for 90 min
From the formula we can see the resistance of silicate adhesive is affected by absolute temperature, ion concentration and ion vibration frequency. As shown in Fig. 3a), for the same holding time, the insulation resistance of the samples decrease successively with the increasing K+ content, which is related to the incremental concentration of free alkali metal ions in the adhesive. When the temperature is higher than 500℃, the intensifying molecular thermal motion in the colloid and the increasing ion vibration frequency in the dielectric lead to the probability of increasing ion activation energy and mobility, which means that the resistivity has dropped exponentially.

3.3 Mechanical performance in humid environment

Fig. 4 shows that the tensile strengths of samples 1, 2 and 3 with high alkali metal ion content (modulus ratio≤7.2) deteriorate with the increasing environmental humidity and improve with the heat-treatment temperature (as shown in Fig. 4a, 4b and 4c). After heat treatment of 400℃ and 600℃, the tensile strength of samples generally increases greatly. It is a turning point that when the heat-treatment temperature is 600℃ and the humidity is greater than 80, the tensile strength of the sample increases slowly (sample 1 and 3) and decreases (sample 2).

Also, that the tensile strengths of samples 4 and 5 with low alkali metal ion content (modulus ratio ≥ 9.1) decrease with the increase of environmental humidity and with the increasing heat treatment temperature, the samples 4 shows the trend is increasing at first, then decreasing and the samples 5 continuously decreases (as shown in Fig. 4d and 4e). In addition, when the temperature of the heat treatment is further than 400℃, the tensile test cannot be carried out because of the bonding surfaces of sample 4 and 5 falling off.

Fig. 4 The tensile strength of adhesive samples in different humidity and heat treatment
a) Sample1 b) Sample2 c) Sample3 d) Sample4 e) Sample5
3.4 Micro-morphology analysis for insulation and mechanics

Fig. 5 a) Model for circuit in humidity atmosphere of Sample and b) micro-structure morphology room temperature c) micro-structure morphology heat treatment 800°C

The insulation behavior of the adhesive sample in humid environment is that: according to the curing principle of silicate adhesive [10,11], there are a large number of active SiO2 particles in the cured adhesive, which can make the water molecules in the environment deposit on the colloidal surface. With the increase of humidity, the gradually formed water molecular layer forms a path between the stainless steel casing and electrode (as shown in Fig. 5a). Therefore, the insulation resistance of the samples decreases with the raising of ambient humidity. When there are a large number of cubic alkali metal salt crystals on the cured silicate surface (as shown in Fig. 5b), these alkali metal ion salts will dissolve into the water molecular layer, increasing the conductivity of the water molecular layer and accelerating the decline of insulation. After the colloid is in heat treatment, the activity of SiO2 colloidal particles decrease, reducing the adsorption of water molecules [12,13]. At the same time, due to softening behavior and the changing of colloidal surface structure, the crystalline alkali metal salt on colloidal surface disappears (as shown in Fig. 5c), which greatly reduces the conductivity of water molecular layer. Therefore, the insulation resistance of adhesive samples will improve with the increase of heat treatment temperature.

The mechanical behavior of the adhesive samples after heat treatment are affected by improving and reducing factors. The improvement factor of mechanical properties can be seen from Fig. 6a that more adhesive substances remain on the stainless steel bonding surface ② (800°C heat treatment) than substances on surface ① (without heat treatment) after the tensile test. The reason is that the adhesive produces shrinkage cracks during curing (as shown in Fig. 7a and 7b), and in the heat treatment, the cracks happen with self-healing effect in the adhesive because of soften and viscous flowing behavior of the active SiO2 (as shown in Fig. 7c), which will reduce the fracture failure caused by crack growth. In addition, it can be seen that the bonding surface of the colloid contains a trace of Fe, Ti and other alloy elements according to the energy spectrum in Fig. 6b, indicating that a small amount of bonding penetration occurs between the stainless steel and the adhesive under high temperature condition, which strengthens the bonding force between the interfaces.
The reducing factor of mechanical property is that when the adhesive solidifies on the adhered substrate, according to the bonding principle of silicate adhesive, the solid powder are wrapped by high active SiO2 particles with the reinforcing role of the alkali metal ions distributed in colloid, forming high bonding strength network structure. In this experiment, with the increase of humidity, the water molecular layer adsorbed by active SiO2 will gradually dissolve the alkali metal ions in the colloid, resulting in the descend of the strength of the adhesive. In addition, due to the different thermal expansion coefficient between silicate adhesive and stainless steel, the internal stress of adhesive is aggrandized by the increase of temperature [16], which reduces the tensile strength of the sample.

4. CONCLUSIONS
In this paper, the overall trend of humid resistance of adhesive insulation samples is to increase with the raising of heat-treatment temperature and deteriorate with the incremental environmental humidity. When the modulus ratio of colloidal liquid is in the range of 7.2~9.1 and the heat-treatment temperature is larger than 600°C, the sample has obvious moisture resistance. In mechanical property, the tensile strength of adhesive deteriorates with the increasing of humidity. Furthermore, with ascending heat-treatment temperature, the tensile strength rises when the modulus ratio of adhesive is less than 7.2, and declines when it is more than 9.1. In short, this article reveals the factors of reduction and enhancement of the service performances of the silicate adhesive in humid environment, and lays the foundation for further research of related work.
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