Internal Oxidation Thermodynamics and Isothermal Oxidation Behavior of AgSnO_2 Electrical Contact Materials

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Abstract: The thermodynamics and isothermal oxidation behavior of the internal oxidation of Ag-Sn alloy were investigated. The thermodynamic calculation results show that Ag-Sn alloy internal oxidation is feasible in thermodynamics. The curves of isothermal oxidation behavior of Ag-Sn alloy were obtained by the oxidation experiment. The temperature range of the rapid internal oxidation of Ag-Sn alloy is from 550 °C to 800 °C, and internal oxidation will be more complete when the internal oxidation temperature increases. The SnO_2 particles are dispersed in Ag matrix, and no particles agglomerate in the matrix. With the oxidation continuing, the diffusion of oxygen causes the inner oxidation, resulting in forming many crystalline oxides with a mutually mixed reticular structure.

Key words: AgSnO_2 ; internal oxidation; thermodynamics; isothermal oxidation behavior; microstructure

Silver-tin oxide materials have acceptable arc resistance, sufficient safety with respect to contact welding, comparably low material migration with low contact resistance, good over temperature behavior, practical processing and jointing properties and a possibility to replace AgCdO ^[1-3]. AgSnO_2 has become a focus of investigations in contact materials in recent years, got a rapid development and gradually been applied to current contactors, power relays and low-voltage circuit breakers. At present the preparation techniques for AgSnO_2 contact materials mainly include powder metallurgical process and alloy internal oxidation process. Oxidation temperature and oxygen partial pressure are the main parameters of internal oxidation process^[4-7]. The accurate control of internal oxidation parameters can not be realized without the thermodynamic analysis^[8-12]. However, in the theoretical study, the thermodynamics and the oxidation behavior of internal oxidation have not been analyzed in detail yet. In the present study, a more detailed thermodynamic and isothermal oxidation behavior analysis of Ag-Sn alloy internal oxidation has been done. It is authors' attempt to provide a reference formulation for Ag-Sn alloy internal oxidation.

1 Experiment

Ag and Sn powders with purity of more than 99.5% were used as the starting materials in the experiment. Ag and Sn powders were mixed with a certain mass ratio of Ag/Sn=9/1. The mixed powder was oxidized in two different ways. In the first way Ag-Sn mixed powder was directly put into TG9110 thermogravimetric analyzer for oxidation experiments; in the second way, Ag-Sn mixed powder was pressed into blocks containing about 5% porosity under 150MPa and then sintered in the box-type furnace at 800 °C for 4 h. The oxidizing atmosphere was air. The microstructure analysis was carried out by SEM of Hitachi S-3400N.

2 Results and Discussion

2.1 Thermodynamic analysis of Ag-Sn alloy internal oxidation

Internal oxidation of the alloy means that oxygen diffuses into the interior of the alloy, and then a oxidation reaction occurs between oxygen and the alloying elements. From the thermodynamic point of view, internal oxidation is the preferred

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oxidation. Oxygen partial pressure of the working medium is the key parameter to control the preferred oxidation. Considering a spherical specimen of Ag-Sn alloys, a preferential oxidation includes two aspects that Ag is not oxidized and Sn is oxidized. The corresponding oxidation reaction is as follows:

$$\Delta G_1^\theta = -30540 + 66.13T$$

$$\Delta G_2^\theta = -68300 + 23.16T$$

$$\Delta G_3^\theta = -581900 + 207.7T$$

$$\Delta G_4^\theta = -498340 + 116.86T$$

According to Gibbs function: $\Delta G = \Delta G^\theta + 2.303RT \lg Q_p$, where R denotes the gas constant, $R=8.314 \text{ J} \cdot (\text{mol} \cdot \text{K})^{-1}$. Assuming that $\Delta G=0$, applying the related thermodynamic data^[13-15] into the Gibbs' function, the relationship between the temperature (T) and the critical oxygen partial pressure for forming SnO_2 can be obtained, as follows:

$$\lg P_{\text{O}_2}^{\text{Ag}} = -\frac{3190}{T} + 11.91 \quad (5)$$

$$\lg P_{\text{O}_2}^{\text{SnO}} = -\frac{3567}{T} + 1.21 \quad (6)$$

$$\lg P_{\text{O}_2}^{\text{SnO}_2} = -\frac{30405}{T} + 10.85 \quad (7)$$

$$\lg P_{\text{O}_2}^{[\text{O}]} = -\frac{26026}{T} + 11.10 \quad (8)$$

According to equation (5), (6), (7) and (8), we can calculate the thermodynamic condition of oxidation and reduction of Ag and Sn. The thermodynamic condition of the internal oxidation is as follows:

$$10^{-\frac{30405}{T} + 10.85} < P_{\text{O}_2}^{\text{SnO}_2} < P_{\text{O}_2}^{\text{SnO}} < 10^{-\frac{3190}{T} + 11.91} \quad (9)$$

where $P_{\text{O}_2}^{\text{SnO}_2}$ is the required oxygen partial pressure when Sn is oxidized to SnO_2 and $P_{\text{O}_2}^{\text{SnO}}$ is the oxygen partial pressure when Sn is oxidized to SnO that we do not respect. The internal oxidation (preferential oxidation) of Ag-Sn alloy is feasible from the viewpoint of thermodynamics under the oxidation temperature and oxygen partial pressure of preferential oxidation. But it should be careful to avoid the forming of SnO phase. The upper limit of oxygen partial pressure of internal oxidation is a function of temperature determined by equation (6). We can select the reasonable process of internal oxidation through equation (6) and (7). The area chart of internal oxidation thermodynamics (Fig.1) is drawn at the same time.

2.2 Behavior of Ag-Sn alloy internal oxidation

In addition to satisfying the thermodynamic conditions, kinetics conditions should be met. The oxidation of Ag-Sn alloy contains four basic steps including adsorption, decomposition, reaction and diffusion. The extent of the internal oxidation

depends on the dynamic conditions in a certain period of time. Therefore, the study of oxidation behavior analysis is necessary.

Fig.2 shows the mass-gain plot for Ag and Sn mixed powder at different oxidation temperatures for 2 h. It can be seen from Fig.2 that with the increase of temperature, the mass of Ag and Sn mixed powder increases obviously. The temperature range of Ag-Sn alloy rapid internal oxidation is from 550 °C to 800 °C, and internal oxidation will be more complete when the internal oxidation temperature increases.

Fig.3 shows the isothermal oxidation behavior of Ag-Sn alloy block via internal oxidation. As shown in Fig.3, at constant oxidation temperature, the oxidation rate of Ag-Sn alloy block increases when the oxidation time extends. The isothermal oxidation curves display a parabolic feature in the initial stage because the diffusion of oxygen atoms is the main obstructive factor.

2.3 Microstructure of AgSnO_2 material

SEM image of AgSnO_2 prepared by internal oxidation at 800 °C for 4 h is shown in Fig.4. The dark and gray parts are SnO_2 particles and Ag matrix, respectively. The SnO_2 particles are dispersed in Ag matrix. In the process of internal oxidation, oxidation occurs preferentially at the grain boundaries of particles. With continuing oxidation, oxygen diffuses into the particles through the micro-pores and then the spherical oxides distributed in the Ag matrix are formed. As can be seen from Fig.4, during the course of the internal oxidation reaction of the alloy powder, the oxidation of Ag-Sn alloy first occurs at the boundary of the alloy particles. With the oxidation continuing, the diffusion of oxygen causes the inner oxidation, and many crystalline oxides with a mutually mixed reticular structure

Fig.1 Area chart of internal oxidation thermodynamics for Ag-Sn alloy

Fig.2 Mass-gain plot for Ag and Sn mixed powder

Fig.3 Isothermal oxidation behavior of Ag-Sn alloy block

Fig.4 SEM image of AgSnO₂ material

are formed. The binding between Ag phase and SnO₂ phase is very strong.

3 Conclusions

1) The internal oxidation behavior of Ag-10Sn alloy is feasible from the viewpoint of thermodynamics.

2) The temperature range of the rapid internal oxidation for Ag-Sn alloy is from 550 °C to 800 °C. The isothermal oxidation curves display the parabolic feature in the initial stage.

3) The SnO₂ particles are dispersed in Ag matrix. With the oxidation continuing, the diffusion of oxygen causes the inner oxidation, and many crystalline oxides with a mutually mixed

reticular structure are formed.

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AgSnO₂ 电接触材料内氧化热力学与恒温氧化行为

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摘 要: 研究了Ag-Sn合金内氧化热力学与恒温氧化行为。热力学计算结果表明, Ag-Sn合金内氧化在热力学上是可行的, 并绘制了合金氧化热力学区位图。经氧化实验获得Ag-Sn合金恒温氧化行为曲线。Ag-Sn合金快速氧化的温度区间为550 °C至800 °C。随内氧化温度的升高, 合金的氧化更为彻底并逐步趋于平稳。实验所得AgSnO₂材料中, SnO₂颗粒弥散分布于Ag基体中。在内氧化过程中, 氧的扩散使合金内部发生氧化, 并生成呈网状排布的氧化物。

关键词: AgSnO₂; 内氧化; 热力学; 恒温氧化行为; 显微组织

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