CHEMICAL REACTION AND ELECTRICAL PROPERTIES OF AMORPHOUS RuO_2 -Ag-GLASS TERNARY SYSTEM

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The relationship between composition, electrical properties, and the chemical reaction during firing of amorphous RuO_2 -Ag-Glass ternary system are investigated. The results are as follows.

- 1) Iso-resistivity, iso-TCR and iso-noise index curves of the system are determined. They have a common feature with regard to their bending in the composition region containing less than about 10wt% Ag.
- 2) X-ray diffraction and thermal differential analysis reveals the solution of Ag into glass phase in addition to the crystallization of amorphous RuO_2 .
- 3) The triaxial diagram of isothermal section at 850 °C is given.
- 4) Electrical isograms in the system are discussed in relation to the solubility of Ag into glass phase.

1. INTRODUCTION

Electrical properties of thick film resistor systems containing crystalline RuO_2 have been investigated by many workers.^{1,2} It is known that none of the chemical reaction occurs during firing, unless lead rich Aluminoborosilicate glass is used as a binder with which crystalline RuO_2 reacts to form Lead Ruthenate. However, these properties of the system containing amorphous RuO_2 have not been reported. Consequently, we investigated the relationship between compositions and electrical properties, and the chemical reaction during firing of amorphous RuO_2 -Ag-Glass ternary systems.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Amorphous RuO_2 powder was obtained from Nippon Engelhard Co. It was identified as $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ by DTA, TGA and X-ray diffraction analysis.

Ag powder was prepared by reducing Ag_2O which was precipitated from AgNO_3 aq. solution by adding NaOH aq. solution.

Glass powder was prepared by melting the batch composition (SiO_2 :14.5wt%, B_2O_3 :22.9wt%, PbO :62.6wt%) in a Al_2O_3 crucible at 1200 °C for

1 hour, pouring it into water and wet milling for 24 hours.

2.2 Sample Preparation and Measurement

Pastes were prepared by mixing the base powders in the desired proportions with vehicle for 2 hours. Vehicle used was 3% α -terpineol solution of 45 cps ethyl cellulose. Thick film resistors were prepared by printing the pastes on 96% Al_2O_3 substrate and firing at 850 °C for 10 min. Electrode material used was Sumitomo Ag/Pd conductor C-4020.

Sample for X-ray diffraction and DTA were obtained by pressing the mixtures into disks, heating to selected temperatures and cooling to room temperature in air.

Temperature coefficient of resistance (TCR) was calculated from the resistance values at 25 °C and 125 °C. Noise indices were measured using a Quan-Teck resistor noise test instrument.

3. RESULTS AND DISCUSSION

3.1 Electrical Properties

Resistor compositions investigated and their electrical properties are given in Table I. The triaxial diagrams in Figure 1 summarize the variation of sheet resistivity, TCR and noise index with respect to composition.

(a) Composition investigated

(b) Resistivity

(c) TCR

(d) Noise index

FIGURE 1 Electrical properties of the compositions system $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ -Ag-Glass.

The resistivity of the ternary system exhibits a tendency to increase with increasing the content of Glass and the ratio of Ag to $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$. However, the prominent feature of the iso-resistance curves is the shape like a flat S in the compositions containing less than about 10wt% Ag. Therefore, the resistivity in

this composition region shows a complex variation with respect to the ratio of Ag to $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$.

The shape of iso-TCR curves closely resembles those of the iso-resistance curves shown in Figure 1(b). Since the zero TCR curve lies between the 10 k Ω /square curve and 1 k Ω /square curve, crossing

TABLE I
Electrical properties of the compositions system RuO₂·2H₂O-Ag-Glass

No. ^a	Electrical properties			No.	Electrical properties		
	R ^b	TCR ^c	N ^d		R	TCR	N
1	38000	-608	-	28	12.8	-237	-20.8
2	500	-278	-	29	27.3	-323	-22.0
3	1130	-360	-	30	0.583	+465	-24.1
4	1650	-535	+10.0	31	3.30	-61.5	-16.3
5	312	-280	+5.3	32	6.03	+49.2	-16.4
6	583	-420	+4.1	33	19.4	-374	-13.3
7	39.8	-148	+3.6	34	144	-538	-7.4
8	119	-190	-0.7	35	1.71	+104	-24.1
9	157	-460	-10.3	36	5.63	-154	-23.1
10	1130	-635	+5.9	37	13.8	-247	-20.0
11	27.3	-104	-5.1	38	0.823	+293	-23.4
12	24.5	-215	-15	39	2.15	+142	-19.4
13	4.08	+177	0	40	6.33	-134	-16.9
14	6.8	+125	-1.4	41	18.8	-317	-16.4
15	8.63	+14	-12	42	75.8	-455	-4.6
16	8.65	-415	-3.6	43	3.00	-51.8	-24.1
17	555	-616	+1.6	44	0.137	+634	-23.2
18	3.38	+225	-5.9	45	1.20	+166	-22.2
19	5.25	-108	-16.5	46	4.36	-66.2	-18.3
20	41.8	-363	-16.1	47	8.00	-266	-13.8
21	0.89	+280	-8.9	48	1.23	+59.5	-27.3
22	0.85	+520	-13.6	49	0.460	+188	-30
23	1.76	+303	-17.7	50	0.778	+55.6	-25.9
24	12.5	-143	-15.5	51	4.38	-167	-18.6
25	61.0	-446	-12.4	52	0.300	+285	-27.5
26	244	-565	-9.2	53	0.975	+86.6	-21.6
27	1.33	+216	-21.0	54	2.35	-100	-16.8

^aComposition No. shown in Figure 1 (a)

^bResistivity (kΩ/square/10 μm).

^cTCR (ppm/deg).

^dNoise index (dB).

with the former near the RuO₂·2H₂O-Glass side and with the latter near the Ag-Glass side of the triangle, the resistivity of compositions with zero TCR ranges from 1 kΩ/square to 10 kΩ/square. It is obvious by similar consideration that the resistivity of compositions with TCR ± 200 ppm/deg, ranges from 0.1 to 100 kΩ/square.

The shape of the iso-noise index curves differ significantly from those of the iso-resistance curves and iso-TCR curves. However, it can be seen that there is a common feature with regard to their bending in the composition region containing less than 10wt% Ag.

3.2 X-ray Diffraction and DTA

Figure 2 shows the change of X-ray diffraction pattern of composition No 24. Relative intensity of

diffraction pattern of Ag decreases with increasing firing temperature and disappears completely above 500 °C. The diffraction pattern of RuO₂ appears from 500 °C and increases its relative intensity with increasing firing temperature.

Figure 3 compares the DTA curves of Glass used and the composition No 24 fired to 850 °C. It is recognized that the characteristic points of Glass are lowered about 50 deg. by firing with Ag and RuO₂·2H₂O. The changes of X-ray diffraction pattern and characteristic points of Glass indicate the solution of Ag into Glass.

Triaxial diagrams in Figure 4 show an iso-thermal section at 850 °C in the system RuO₂·2H₂O-Ag-Glass. The ternary system is divided into three areas: area I where RuO₂·2H₂O and Glass are present, area II characterized by coexistence of RuO₂ and Ag with Glass phase, and area III in which Ag and Glass

FIGURE 2 Variation of X-ray diffraction pattern of the composition No. 24 during firing.

FIGURE 3 DTA curves of Glass and of composition No. 24.

(a) Results of X-ray Diffraction analysis

○ : RuO_2 , ● : RuO_2 and Ag, ⊙ : RuO_2 and trace of Ag,
 △ : Ag

(a) Isothermal section at 850 °C
 in the system $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ -Ag-Glass

FIGURE 4 Results of X-ray diffraction analysis and phase relation in the system $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ -Ag-Glass.

coexist. The line dividing area I and II indicates the solubility of Ag into the Glass used and coincides with the composition from where the isograms shown in Figure 1 begin to bend. This fact should lead to further consideration that the complex change of isograms in the compositions containing less than about 10wt% Ag were caused by the change of electrical properties of Glass matrix due to the solution of Ag.

4. CONCLUSIONS

- 1) Iso-resistivity, iso-TCR and iso-noise index curves of the $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ -Ag-Glass ternary system were determined.
- 2) X-ray diffraction and differential thermal

analysis revealed the solution of Ag into glass phase in addition to the crystallization of $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$.

3) Triaxial diagram of isothermal section at 850°C in the system were given.

4) The electrical properties of the system are closely related to the solubility of Ag into Glass.

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