Thermochimica Acta, 85 (1985) 103–106
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL DECOMPOSITION OF AgO to Ag_2O

P. TISSOT and B. PERRENOT
Department of Mineral, Analytical and Applied Chemistry, University of Geneva, 1211 Geneva 4, Switzerland.

ABSTRACT

The mechanism of the reaction 2 AgO = Ag_2O + 1/2 O_2 is determined by isothermal thermogravimetry for three different samples of AgO. The influence on the mechanism of the presence of Ag_2O produced by several methods is studied. The kinetic parameters of the rate-determining step are determined by use of DTA and TG. The results obtained by these dynamic methods are compared with those obtained by the classical isothermal procedure.

INTRODUCTION

The structure and the morphology of AgO is largely dependent on the method of preparation used (ref. 1). Two of the samples studied have the usual monoclinic structure; the type OSK, obtained by oxidation of metallic silver with ozone, is constituted by large flakes of 20 to 30μm of length, while the type Msp, obtained by oxidation of Ag^+ by persulfate, is constituted by small grains of 1 to 2μm of diameter. The third sample, named type OS, is also obtained by oxidation of metallic silver with ozone; it presents a tetragonal structure and is formed by particles of 2 to 3μm of diameter.

EXPERIMENTAL METHODS

All the experiments were performed in static dry air, with a sample weight of ca. 50 mg. A balance (Setaram B70) equipped with a movable furnace was used for isothermal thermogravimetry; the sample reached the chosen temperature after less than 5 minutes; this non-steady state period was neglected with regard to the much longer duration of the experiment (> 120 minutes). TG and DTA were made with a Mettler TA 1, and a Mettler TA 2000 apparatus, respectively. All the data were transferred to a microcomputer (Tektronix 4051) and treated with different programmes developed in our laboratory.

0040-6031/85/$03.30

RESULTS AND DISCUSSION

In figure 1 an example of the fractional decomposition vs. the reduced time for the sample OSK is shown (ref. 2). The curve fitting with the A_2 mechanism random nucleation determining step, (ref. 3) is good up to $\alpha = 0.5$. The behaviour of the two other samples is the same, except that a better curve fitting with a $A_{1.5}$ mechanism is obtained for the Msp type.

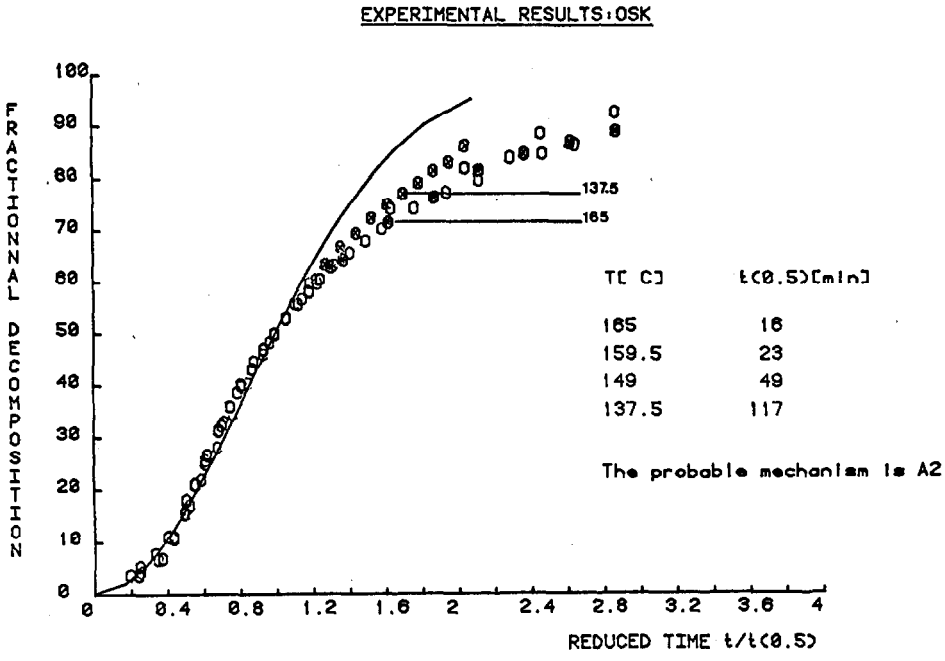

Fig. 1 Reduced time plots for the decomposition of OSK

The differential form of the kinetic expression corresponding to the A_2 mechanism is

$$\frac{d\alpha}{dT} = k(1-\alpha)\ [(-\ln(1-\alpha)]^{1/2}$$

Assuming that the Arrhenius equation can be applied, one can write the following logarithmic equation

$$\ln \frac{d\alpha}{dt} - \ln(1-\alpha) - 1/2 \ln(-\ln(1-\alpha)) = \ln A - \frac{Ea}{RT}$$

This equation is solved to determine the Arrhenius parameter E_A and lnA. The same procedure can be applied to any other mechanism determined by isothermal measurements. The results are summarized in the table 1.

TABLE 1

Kinetic parameters obtained by isothermal thermogravimetry. (ITG)

	Ea[kJ/mole]	lnA[min^{-1}]
OSK	113 ± 2	29 ± 0.7
OS	120 ± 8	32 ± 2
Msp	100 ± 7	24 ± 2

The dynamic results are presently under active study.

We have also tested the influence of the presence of Ag_2O in AgO on the kinetics of the decomposition. Ag_2O was formed either by partial thermolysis, or by partial reduction by H_2 at 30°C. We have also tested a sample not completely oxidized by O_3. All three samples contained ca. 25% of Ag_2O. The results are shown in the figure 2; only the Ag_2O formed by thermal decomposition modifies the mechanism of the decomposition; the rate determining step is than a phase boundary reaction with a spherical symmetry (mechanism R3).

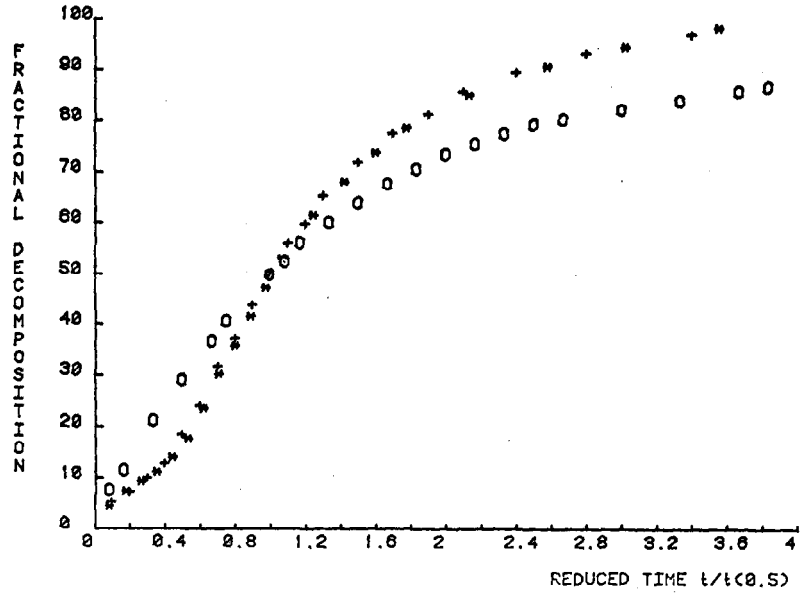

Fig. 2 Reduced time plots for OSK containing 25% of Ag_2O : Germs of Ag_2O obtained by reduction (*), by partial oxidation (+), and by thermal decomposition (o).

REFERENCES

1 R. Dallenbach, J. Painot and P. Tissot, Polyhedron 1 (1982) 183-186.
2 J. Sharp, G.W. Brindley and B.N. Narahari Achar, J.Am.Ceram.Soc. 49 (1966) 379-382.
3 M. Avrami, J.Chem.Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.