# LEVEL

D D C
RECEIVED
JUL 13 1979
C

**PURDUE UNIVERSITY**

West Lafayette, Indiana

THE EFFECTS OF SUBSTRATE COMPOSITION
ON THICK FILM CIRCUIT RELIABILITY

R. W. Vest

1 May 1979

Quarterly Report No. 1

For the period 2/1/79-4/30/79

Contract No. N00019-79-C-0240

Prepared for

NAVAL AIR SYSTEMS COMMAND

# SCHOOL OF MATERIALS ENGINEERING

79 07 13 018

THE EFFECTS OF SUBSTRATE COMPOSITION
 ON THICK FILM CIRCUIT RELIABILITY

R. W. Vest

1 May 1979

Quarterly Report No. 1

For the period 2/1/79-4/30/79

Contract No. N00019-79-C-0240

Prepared for

NAVAL AIR SYSTEMS COMMAND

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|---|
| 1. REPORT NUMBER<br>1 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle)<br>THE EFFECTS OF SUBSTRATE COMPOSITION ON THICK FILM CIRCUIT RELIABILITY.<br>A001-051, A063 782 | | 5. TYPE OF REPORT & PERIOD COVERED<br>Quarterly Report<br>2/1/79-4/30/79 |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s)<br>R. W. Vest | | 8. CONTRACT OR GRANT NUMBER(s)<br>N00019-79-C-0240 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY<br>West Lafayette, Indiana 47907 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br>22 p. |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>NAVAL AIR SYSTEMS COMMAND, AIR 310B<br>Washington, D. C. 20361 | | 12. REPORT DATE<br>31 May 1979 |
| | | 13. NUMBER OF PAGES<br>19 |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) | | 15. SECURITY CLASS. (of this report) |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE:
DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Quarterly rept. 2, Jan - 30 Apr 79.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

| | |
|---|---|
| Thick Film Resistors | Temperature Coefficient Resistivity |
| Ceramic Substrates | Electronic Glass |
| Electrical Resistivity | Glass Sintering |

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The high temperature surface tensions and viscosities of thick film glasses were measured as a function of temperature and the amount of AlSiMag 614 substrate dissolved in the glasses. The magnitude of the surface tension was observed to increase and the temperature coefficient of surface tension to decrease as the amount of dissolved substrate was increased. The ripening of $RuO_2$ particles in thick film glasses was measured as a function of temperature and the amount of AlSiMag 614 substrate dissolved in the glasses.

DD FORM 1473 1 JAN 73     EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601 |

410 421

## ABSTRACT Continued

The ripening kinetics in all glass compositions were in agreement with a phase boundary reaction rate limiting step, and the rate constant was observed to decrease by a factor of 4 when the amount of dissolved substrate reached 10 weight percent.

FOREWORD

Research described in this report constitutes the first three months
of effort under Contract No. N00019-79-C-0240 with the Naval Air Systems
Command, Department of the Navy, under the technical cognizance of James
Willis. The research was conducted in the Turner Laboratory for Electro-
ceramics, School of Materials Engineering and School of Electrical
Engineering, Purdue University, West Lafayette, Indiana 47907, under the
direction of Professor R. W. Vest. Contributing to the project were
Messrs. J. M. Himelick, P. Palanisamy, R. L. Reed and C-T Tarn.

iii

## TABLE OF CONTENTS

# 1. INTRODUCTION

The print and fire processing of thick film cricuits ensures that there always will be some degree of chemical interaction between the film and the substrate, because all common substrate materials are soluble to some degree in the glasses used in thick film inks. This interaction is primarily responsible for the development of adhesion between the thick film and the substrate, but it also leads to changes in the composition of the glass with the net result that the physical properties of the glass will change. These changes in physical properties of the glass will result in modified kinetics for the various microstructure development processes and all electrical properties of the resistors are related to the micro-structure. The goal of this research program is to develop a sufficient level of understanding of the phenomena involved so that appropriate models can be developed. These models should lead to the writing of specifications for impurity limits and additive ranges for substrates, and to recommenda-tions concerning glass composition and processing conditions.

Previously reported studies [1-3] under this program have established the magnitude of the effects resulting from chemical interaction between a thick film resistor and a ceramic substrate, and have determined the specific influence on important properties of the resistor glass. The rates of dissolution of two substrates, 96% $Al_2O_3$ (AlSiMag 614) and 99.5% $Al_2O_3$ (AlSiMag 772), in two lead borosilicate glasses (63 w/o PbO-25 w/o $B_2O_3$-12 w/o $SiO_2$ and 70 w/o PbO-20 w/o $B_2O_3$-10 w/o $SiO_2$) were measured at various temperatures. The rate limiting steps for each substrate-glass system were determined in all appropriate temperature ranges, and analytical

equations were developed to predict the substrate recession as a function of time and temperature for thick film resistors. The saturation solubility of AlSiMag 614 (96% $Al_2O_3$) substrates in 63-25-12 glass was determined as a function of temperature, and these results were combined with the dissolution rate studies in order to test various kinetic models. Studies of the kinetics of initial stage sintering of glass particles were conducted in order to determine the ratio of surface tension to viscosity for the two standard glasses, and the standard glasses with additions of substrate ingredients. Both the magnitude and the activation energies of this ratio were found to be significantly different for the gasses, confirming the extreme sensitivity of this parameter to small changes in glass composition. The viscosity of the 63-25-12 glass was measured as a function of amount of dissolved AlSiMag 614 substrate from the softening point to the annealing point. The isothermal viscosity was found to increase by a factor of 20 with 10 w/o dissolved substrate relative to the standard lead borosilicate glass. The affects of the minor constituents (4%) in the AlSiMag 614 substrate composition on viscosity and surface tension of the glasses was determined to be small. The sheet resistance, temperature dependence of resistance, and the current noise were measured for thick film resistors as a function of the amount of substrate dissolved in the resistor for various firing temperatures at constant firing time, and for various firing times at 800°C. Large variations in these three properties were observed, and the changes were qualitatively correlated with changes in viscosity of the glass. The microstructure development and charge transport models used to correlate the results indicated a retardation of microstructure development in the resistors as the amount of dissolved

substrate increased which led to changing proportions of sintered and
nonsintered contacts in the $RuO_2$ networks within the body of the resistor.

## 2. MICROSTRUCTURE DEVELOPMENT

### 2.1 RuO$_2$ Ripening Studies

### 2.1.1 Theory

In order to develop an adequate model for the influence of the substrate on microstructure development and electrical properties of thick film resistors, it is necessary to know the influence of dissolved substrate on conductive ripening and sintering. Sintering and ripening of the conductive phase are the two final processes in microstructure development of thick film resistors. In the initial stages of the sintering process, necks develop between adjacent RuO$_2$ conductive particles; as the sintering process proceeds, the necks grow until adjacent particles coalesce to form larger particles. In the ripening process, the smaller particles preferentially dissolve and the material is transported through the liquid phase to precipitate on larger particles. The primary driving force for both sintering and ripening processes is the reduction in interfacial area between the conductive phase and the glass phase.

Earlier studies [4] have shown that the rate limiting step for the ripening of RuO$_2$ in 63-25-12 glass is the phase boundary reaction, that is, the rate of dissolution at the surface of the smaller particles or the rate of precipitation at the surface of the larger particles. The kinetics of the sintering process could not be measured directly, but rates consistent with experimental observations were calculated from the ripening results based on a solution-precipitation mechanism. It was also observed in the earlier study [4] that the presence of AlSiMag 614 substrate dissolved in the resistor glass decreased the rate of RuO$_2$ ripening. The decreased ripening kinetics could be due to a decrease in the equilibrium

solubility of $RuO_2$ in the glass, the interfacial energy between $RuO_2$ and the glass, or the transfer coefficient for the passage of material across the interface.

The relationship governing the ripening by an interface controlled solution-precipitation mechanism is

$$(\bar{r}_t^2 - \bar{r}_o^2) = [(8/9)^2 \, C_o \, \gamma_{SL} \, V_o^2 \, K_T \, / \, RT] \, t$$

in which

$\bar{r}_t$ = average particle radius at time t

$\bar{r}_o$ = initial average particle radius

$C_o$ = equilibrium solubility of $RuO_2$ in glass

$\gamma_{SL}$ = $RuO_2$-glass interfacial energy

$V_o$ = molar volume of $RuO_2$

$K_T$ = transfer coefficient

The influence of dissolved substrate on the $RuO_2$ solubility was independently determined by atomic absorption measurements, and was presented in an earlier report [3]. The product $C_o \, \gamma_{SL} \, K_T$ can be obtained from the ripening results; knowing $C_o$ from the solubility measurements, and by using estimates [4] for $\gamma_{SL}$, $K_T$ can be calculated. From these results the initial stage neck growth can be computed from:

$$(x/r)^4 = (8K_1 C_o \gamma_{SL} \, V_o \, K_T \, / \, K_2 RT) \, r^{-2} t$$

in which x is the neck radius and $K_1$ and $K_2$ are constants.

### 2.1.2 Experimental

$RuO_2$-glass composites consisting of 20 w/o $RuO_2$ were prepared by blend-ing the powdered components in a jar placed on rollers. The $RuO_2$ powder was

prepared by drying the hydrate, and the glass compositions were fabricated by a procedure reported earlier [2]. The glass frit was reduced to -325 mesh in an agate ball mill prior to blending.

Approximately 1 gram of the composite was exposed to the given temperature for a known length of time and then quenched in deionized water. The quenched samples were decomposed by a HCl + HF treatment followed by a centrifugal separation of the $RuO_2$ solids from the solution. The $RuO_2$ is inert to HCl + HF mixtures. The $RuO_2$ particles were then washed with deionized water and dried at $125^{\circ}C$.

The average particle size of the $RuO_2$ was determined by measuring the surface area by the BET method utilizing a Monosorb* Surface Area Analyzer. The Monosorb, essentially a thermal conductivity detector, measures the quantity of adsorbate gas adsorbed on or desorbed from the sample surface by sensing the change in the thermal conductivity of an adsorbate-carrier gas mixture flowing over the solid. Selective adsorption or desorption of the adsorbate causes a momentary change in the gas composition and hence a change in the thermal conductivity of the mixture. The integrated signal due to the change in thermal conductivity is proportional to the amount of adsorbate adsorbed or desorbed. A 30 v/o nitrogen (adsorbate) in helium (carrier) was used in this work. The Monosorb was calibrated by injecting known amounts of nitrogen into the flowing gas mixture.

## 2.1.3 Results

The results of the preliminary ripening studies are presented in Figs. 1 and 2. The specific surface area of $RuO_2$ samples exposed to different

---
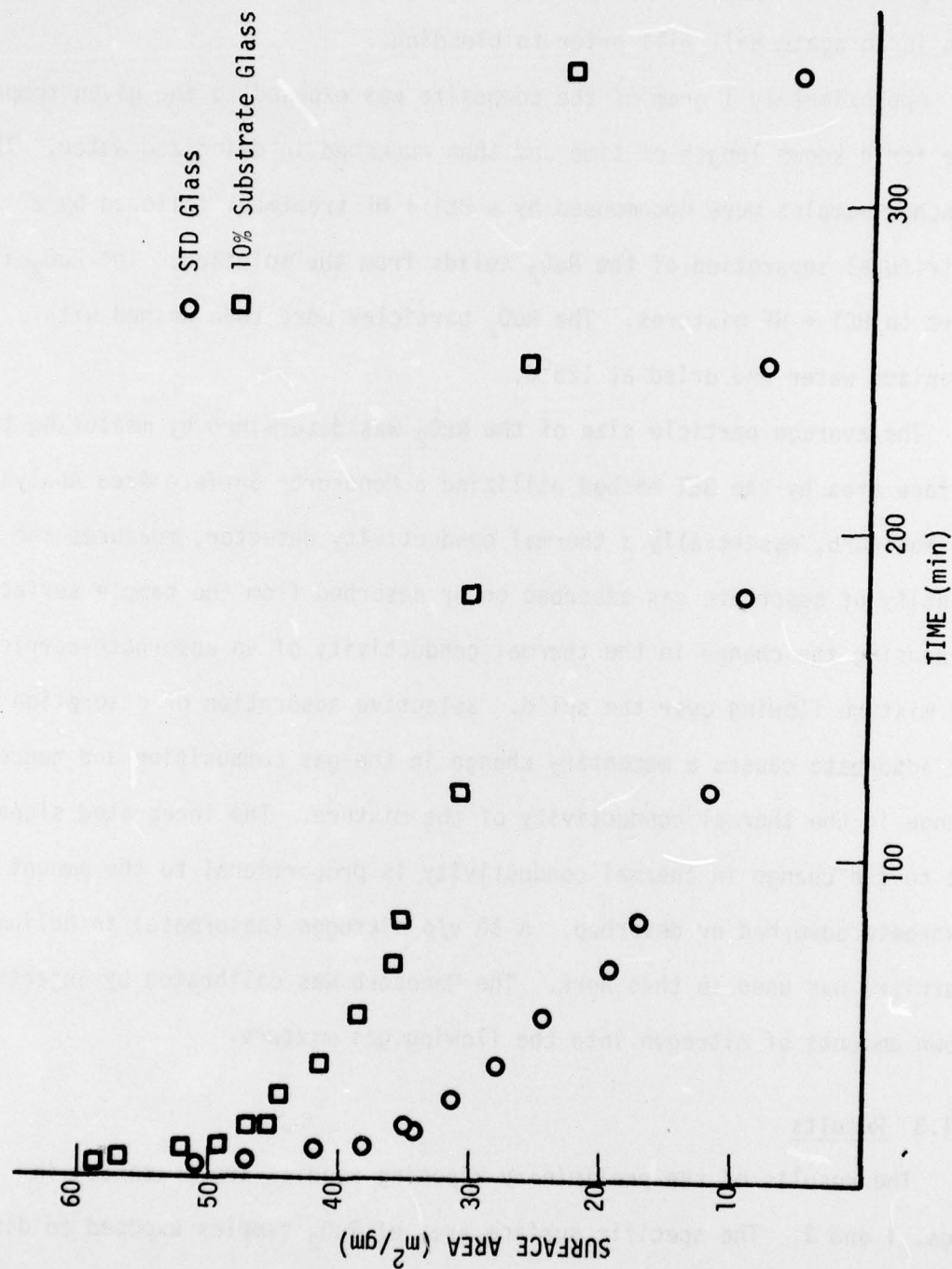
* Quantachrome Corp., Greenvale, NY.

**SURFACE AREA (m²/gm)**

○ STD Glass
□ 10% Substrate Glass

60
50
40
30
20
10

100　　200　　300

**TIME (min)**

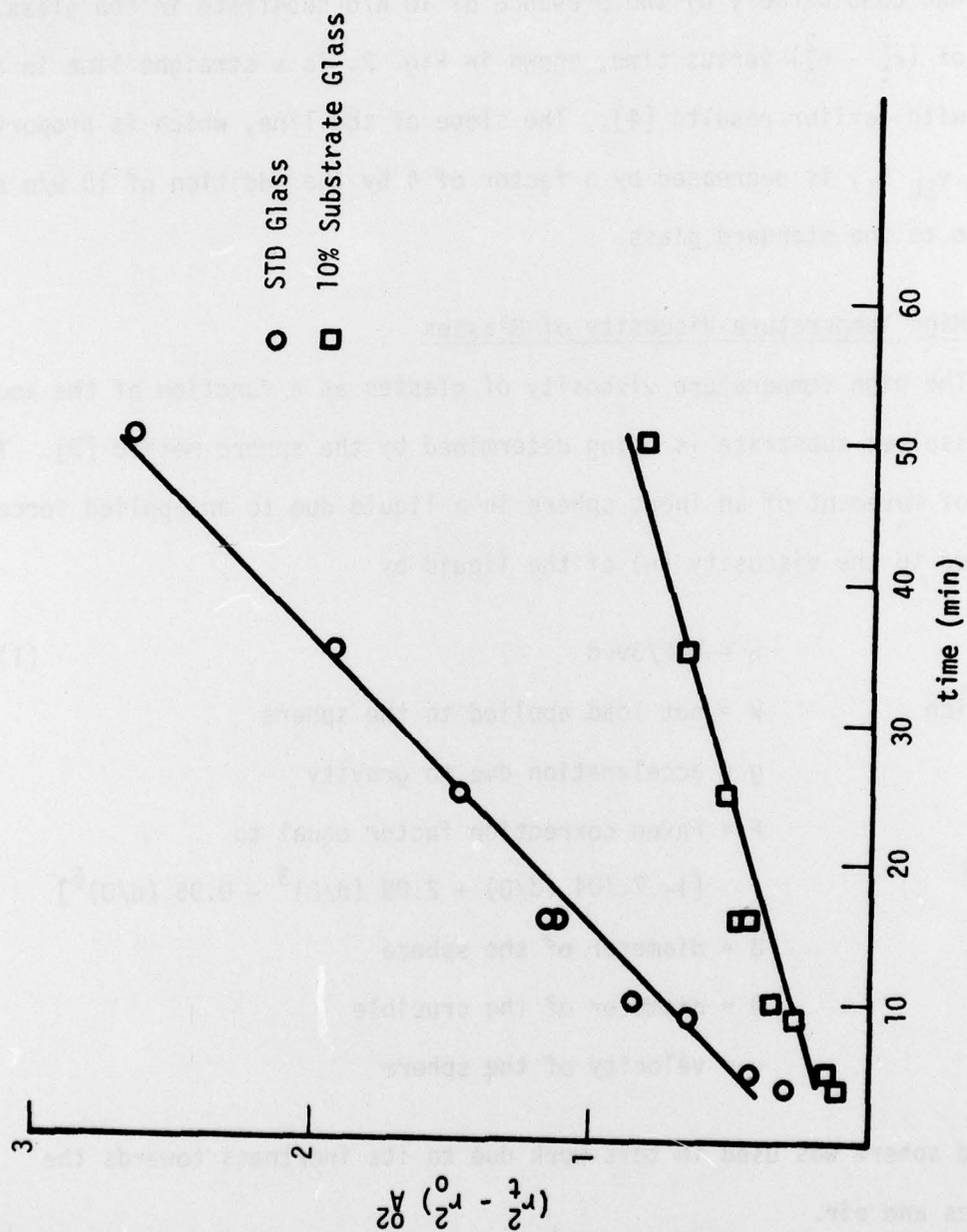Figure 1. RuO₂ Ripening in 63-25-12 Glass at 950°C.

Figure 2. Fit of RuO$_2$ Ripening Data to the Phase Boundary Reaction Rate Limiting Step.

times at 950°C for two glass compositions are given in Fig. 1. After a rapid decrease, the specific surface area nearly levels off at longer times for both compositions. It is apparent that the ripening process is retarded considerably by the presence of 10 w/o substrate in the glass. A plot of $(r_t^2 - r_0^2)$ versus time, shown in Fig. 2, is a straight line in agreement with earlier results [4]. The slope of the line, which is proportional to $C_0 \gamma_{SL} K_T$, is decreased by a factor of 4 by the addition of 10 w/o substrate to the standard glass.

## 2.2 High Temperature Viscosity of Glasses

The high temperature viscosity of glasses as a function of the amount of dissolved substrate is being determined by the sphere method [5]. The rate of movement of an inert sphere in a liquid due to an applied force is related to the viscosity ($\eta$) of the liquid by

$$\eta = WgF/3v\pi d \tag{1}$$

in which
W = net load applied to the sphere

g = acceleration due to gravity

F = Faxen correction factor equal to
$[1- 2.104 \ (d/D) + 2.09 \ (d/D)^3 - 0.95 \ (d/D)^5]$

d = diameter of the sphere

D = diameter of the crucible

v = velocity of the sphere

A gold sphere was used in this work due to its inertness towards the glasses and air.

The high temperature viscometer assembly is shown in Fig. 3. The gold sphere, 0.9 cm is diameter, is suspended from the sample pan of an
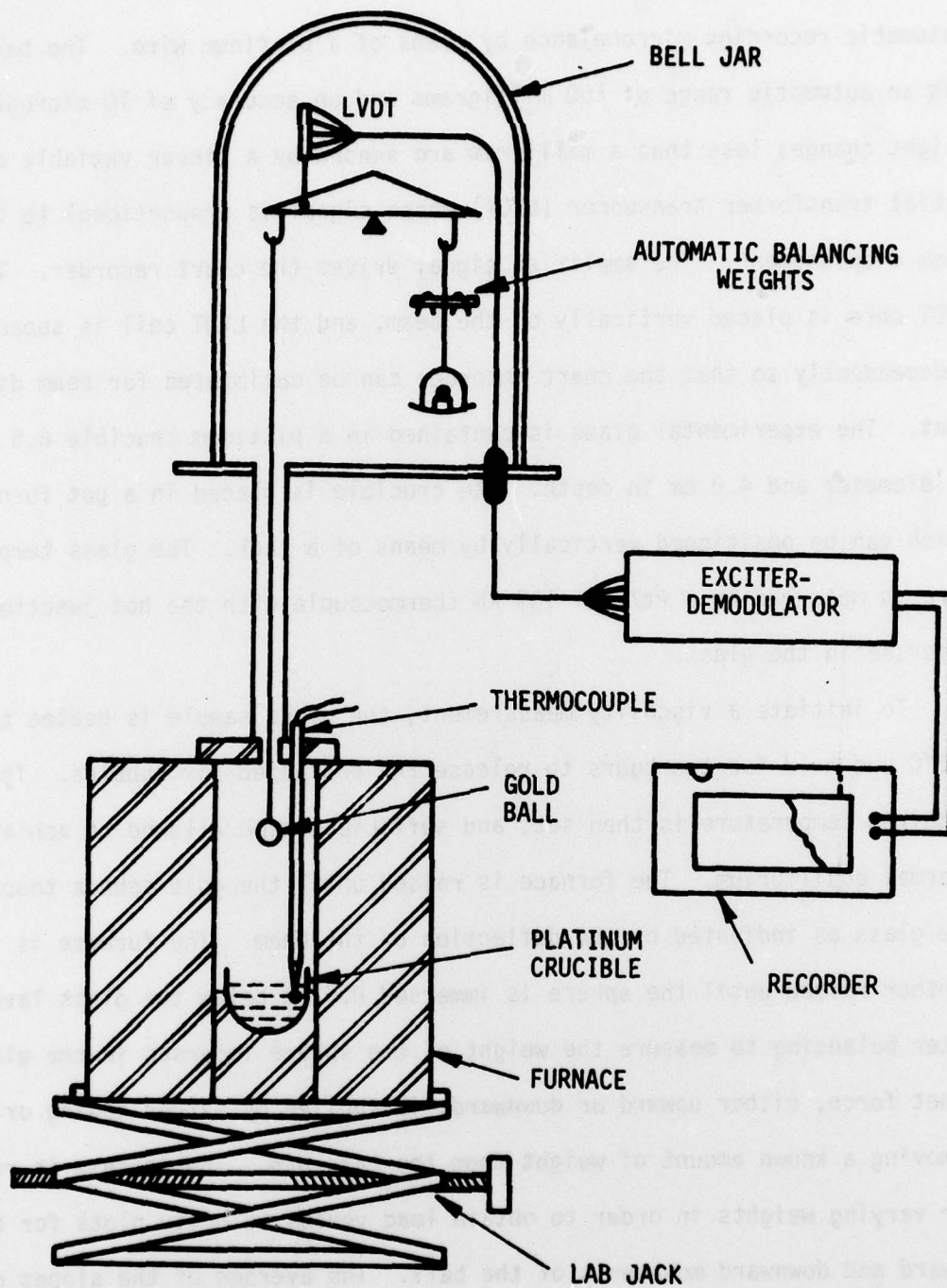
Figure 3. Viscosity Apparatus.

automatic recording microbalance by means of a platinum wire. The balance
has an automatic range of 100 milligrams and an accuracy of 10 micrograms.
Weight changes less than a milligram are sensed by a linear variable differ-
ential transformer transudcer (LVDT) whose signal is proportional to the
beam displacement. The amplified signal drives the chart recorder. The
LVDT core is placed vertically on the beam, and the LVDT coil is supported
independently so that the chart recorder can be calibrated for beam displace-
ment. The experimental glass is contained in a platinum crucible 6.5 cm
in diameter and 4.0 cm in depth. The crucible is placed in a pot furnace
which can be positioned vertically by means of a jack. The glass tempera-
ture is measured by a Pt/Pt + 10% Rh thermocouple with the hot junction
immersed in the glass.

To initiate a viscosity measurement, the glass sample is heated to
900°C and held for two hours to release the entrapped air bubbles. The
required temperature is then set, and sufficient time allowed to achieve
thermal equilibrium. The furnace is raised until the gold sphere touches
the glass as indicated by the deflection of the beam. The furnace is
further raised until the sphere is immersed 0.5 cm below the glass level.
After balancing to measure the weight of the sphere immersed in the glass,
a net force, either upward or downward, is applied by either adding or
removing a known amount of weight from the tare pan. The process is repeated
for varying weights in order to obtain load versus velocity plots for both
upward and downward movements of the ball. The average of the slopes of
these lines is utilized in the viscosity calculations using Eq. 1. The
viscosity results will be presented in the next report.

## 2.3 Surface Tension of Glasses

The high temperature surface tension of glasses as a function of the amount of dissolved substrate is being determined by the modified dipping cylinder method [6]. A hollow platinum cylinder, 1.3 cm in diameter and 1.3 cm in height with a wall thickness of 0.013 cm, is being used in this study. The apparatus for the surface tension measurement is similar to the viscometer assembly shown in Fig. 3. The platinum cylinder is suspended by a platinum wire from the sample pan of the microbalance. The glass is thermally equilibrated, and the furnace raised until the bottom of the cylinder is 0.2 cm below the glass level. The furnace is then slowly lowered and the maximum pull exerted by the glass on the cylinder determined by adding weights until the breakaway is indicated by the deflection of the beam. The surface tension is calculated using the following equation:

$$\gamma = \frac{gW}{4\pi R} \left[ 1 - \frac{2.8284\delta}{\sqrt{hR}} - \frac{0.6095\delta}{R} + \frac{3\delta^2}{hR} + \frac{2.585\delta^2}{\sqrt{hR}} + \frac{0.371\delta^2}{R^2} \right] \qquad (2)$$

in which

$\gamma$ = surface tension

g = acceleration due to gravity

W = maximum pull exerted on the cylinder

R = mean radius of the cylinder

$\delta$ = half thickness of the cylinder

h = $W/\pi R^2 \rho_g$, $\rho_g$ = density of glass

The surface tension results for three glass compositions are presented in Fig. 4. Addition of AlSiMag 614 substrate to the standard 63-25-12 glass increases the surface tension and decreases the temperature coefficient of surface tension.
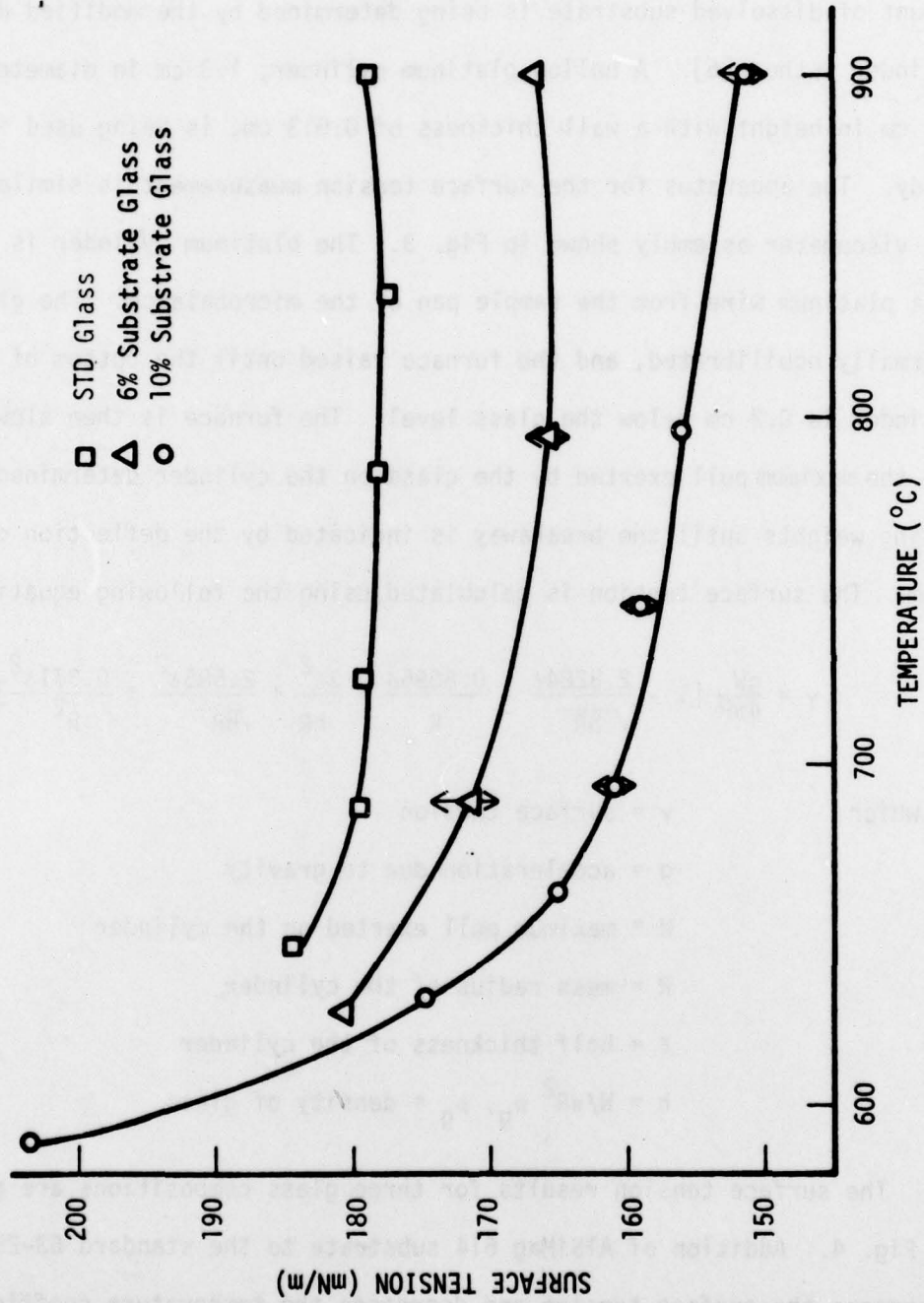
Figure 4. Surface Tension of 63-25-12 Glass With and Without Dissolved Substrate.

## 3. FUTURE WORK

Viscosity and surface tension measurements as a function of glass composition and temperature at higher temperatures will be completed. Studies of the kinetics of ripening of $RuO_2$ in the glass as a function of glass composition will be completed, and the kinetics of the initial stage of liquid phase sintering of $RuO_2$ will be calculated from the ripening data and the solubility data. These results will then be correlated utilizing the previously developed models for microstructure development, and the influence of glass composition established. The effects of substrate dissolution on charge transport processes in nonsintered contacts will be modeled, and the dependence of both the glass properties and the electrical properties of the nonsintered contacts on glass composition will be incorporated into a revised charge transport model for thick film resistors.

## 4. REFERENCES

1. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Final Technical Report on Contract No. N00019-76-C-0354, 28 February 1977.

2. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Final Technical Report on Contract No. N00019-77-C-0327, 28 February 1978.

3. R. W. Vest, "The Effects of Substrate Composition on Thick Film Circuit Reliability," Final Technical Report on Contract No. N00019-78-C-0236, 28 February 1979.

4. A. N. Prabhu and R. W. Vest, "Investigation of Microstructure Development in $RuO_2$-Lead Borosilicate Glass Thick Films," Mat. Sci. Res., 10, 399-408 (1975).

5. L. Shartis and S. Spinner, "Viscosity and Density of Molten Optical Glasses," J. Res. Nat. Bur. Std., 46, 176 (1951).

6. L. Shartis, S. Spinner, and A. W. Smock, "Surface Tension of Compositions in the System $PbO-B_2O_3$ and $PbO-SiO_2$," J. Am. Cer. Soc., 31, 23 (1948).

## 5. STATEMENT OF ESTIMATE COSTS

Contract No.   N00019-79-C-0240

February 1, 1979 - January 31, 1980

| | |
|---|---|
| Beginning Fund Balance | $ 40,000.00 |
| Funds Expended Through 4/30/79 | 10,508.19 |
| Funds Remaining | $ 29,491.81 |

Planned Expenditures (Approximate)

| | |
|---|---|
| May | $ 3275 |
| June | 3275 |
| July | 3275 |
| August | 3275 |
| September | 3275 |
| October | 3275 |
| November | 3275 |
| December | 3275 |
| January | 3300 |