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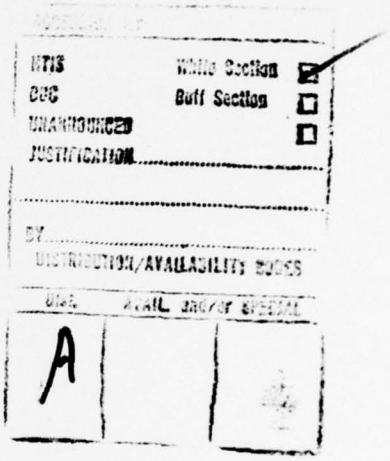

THE EFFECTS OF SUBSTRATE COMPOSITION ON THICK FILM CIRCUIT RELIABILITY

R. W. Vest

31 May 1977

First Quarterly Report

For the period 2/1/77 - 4/30/77

Contract No. N00019-77-C-0327

Prepared for

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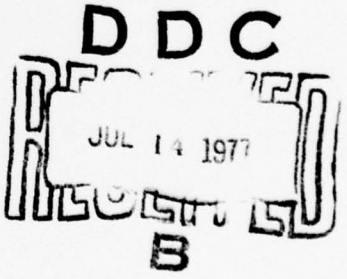

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The initial stage sintering kinetics for lead borosilicate glass spheres of two compositions were studied in order to determine the effects of glass composition on the surface tension to viscosity ratio. The glass with the higher PbO content had a surface tension to viscosity ratio higher by a factor of 100 and an activation energy higher by a factor of two. Techniques have been developed for fabricating thick film resistors without changes in glass composition due to resistor-substrate interactions in processing.

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FORWARD

Research described in this report constitutes the first three months of effort under Contract No. N00019-77-C-0327 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 Electroceramics, 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 Assistant Professor G. L. Fuller, and Messrs. J. M. Himelick, P. Palanisamy and R. L. Reed.

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I. INTRODUCTION

The print and fire processing of thick film circuits ensures that there will always be some degree of chemical interaction between the film and the substrate because all common substrate materials are soluble to some degree in the glass used in the thick film inks. This interaction is primarily responsible for the development of adhesion between the thick film resistor and the substrate. By virtue of the substrate-resistor interaction, the composition of the glass is changed, and as a consequence all of the physical properties of the glass will change to some extent. These changes in physical properties of the glass will result in modified kinetics for the various microstructure development processes in thick film resistors and all electrical properties of the resistors are related to the microstructure. This research program is directed toward the determination of the effects of the major constituent, common additives, and impurities in alumina substrates on the kinetics of microstructure development, electrical characteristics and the adhesion of thick film resistors.

Research under a previous contract [1] showed that the rate of dissolution of 96% Al_2O_3 substrates (AlSiMag 614) in a model glass was determined by the phase boundary reaction at times important to thick film resistor processing, and rate equations were developed to allow the prediction of the total quantity of substrate dissolved in the resistor glass under any processing conditions. Standard processing (800°C, 10 min) will result in a fired resistor volume containing up to

20% of ingredients derived from the substrate. Studies of the distribution of the substrate ingredients throughout the resistor glass at 800°C produced results consistent with a step change in concentration at the substrate-resistor interface. Dissolution rate studies with 99.5% Al_2O_3 substrates (AlSiMag 772) showed similar results and were consistent with the proposed rate limiting step. The presence of substrate constituents dissolved in the glass were shown to have a significant effect of the temperature coefficient of resistance (TCR). A low TCR characteristic of reliable thick film resistors cannot be achieved with the model system unless an appreciable amount of substrate material is dissolved in the resistor glass.

2. GLASS SINTERING STUDIES

The surface tension and viscosity of the glass used in thick film resistors are two properties which strongly influence the kinetics of microstructure development and hence the final electrical behavior. In order to predict the influence of resistor-substrate interactions on the electrical parameters critical in reliability considerations, it is necessary to know how the surface tension and viscosity of the resistor glass vary with composition as more substrate is dissolved. Studies of the kinetics of initial stage sintering will yield the ratio of surface tension to viscosity, and this was the initial experimental technique utilized with two lead borosilicate glasses of different compositions. The change in the surface tension to viscosity ratio with additions of substrate ingredients to these glasses will be the subject of subsequent experimental studies.

2.1 Experimental

2.1.1 Sample preparation

Two lead borosilicate glasses of compositions 63 wt % PbO, 25 wt % B_2O_3, 12 wt % SiO_2, and 70 wt % PbO, 20 wt % B_2O_3, 10 wt % SiO_2 were fabricated using Pb_3O_4, H_3BO_3, and SiO_2 as starting materials. The appropriate quantities of starting materials were mixed in a rolling jar for 1 hour and then heated to 900°C in a platinum crucible and held for 2 to 3 hours until a clear, single phase liquid was obtained. The glass was fritted in deionized water, ground in an agate mill, and separated into particle size fractions utilizing standard sieves. The sieved fraction between 175 and 230 μm was used for making spheres in a two section vertical tube furnace with the lower section maintained at 800°C and the upper section at 1200°C. The glass particles were fed into the top of the furance utilizing a vibrating sieve, and they became spherical in order to minimize their surface energy as they travelled through the furnace. The spheres were collected in vacuum pump oil at the bottom of the furnace and cleaned with trichloroethylene and acetone.

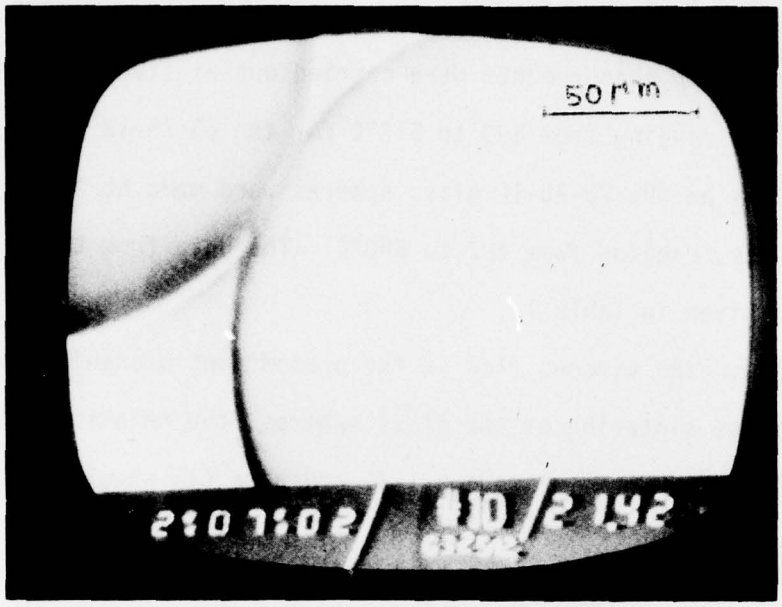
2.1.2 Apparatus

Neck growth measurements were conducted utilizing a modified hot stage metallograph with the regular camera system removed and replaced by a Sony AVC-3200 video camera. A second video camera was used to monitor a digital clock and a digital voltmeter that measured the sample thermocouple emf. A Sony SEG-1 special effects generator was used to combine the two video signals so that the time, the glass composition, and the thermocouple emf were positioned at the bottom of the image on the TV monitor screen. All information thus obtained was recorded on a

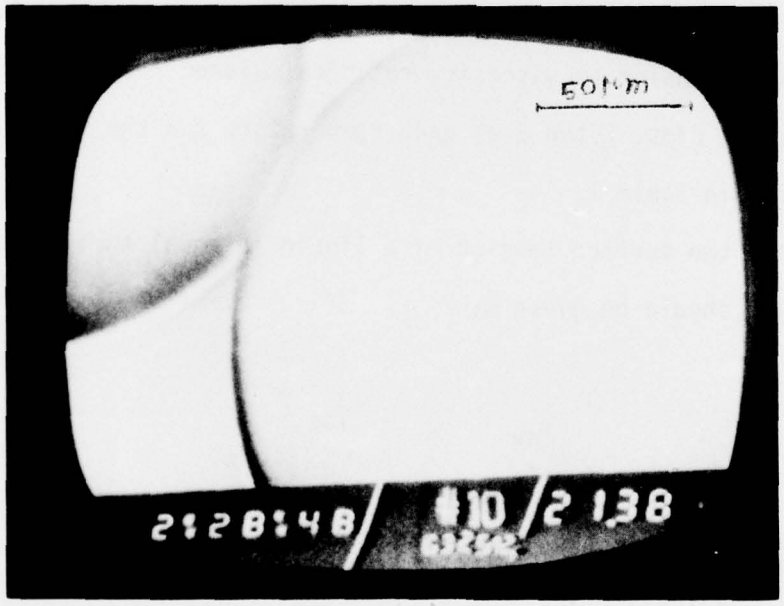
Sony AV-3600 video recorder with stop frame capability, and observed on a Conrac SMA television monitor.

The hot stage unit was a modified Unitron HHS vacuum stage with the tungsten ribbon electric heater replaced by a cylindrical heater made of platinum-30% rhodium wire wound on a boron nitride core. The sample holder was a small platinum pan positioned at the top of the boron nitride core. Two thermocouples, one to control the furnace temperature and the other to measure the sample temperature, were installed. Because of the high temperatures employed, several heat shields were required inside the hot stage, and a water cooled infra red filter was installed between the quartz viewing window of the hot stage and the objective lens. The objective lens used was a special focal length (Vickers M-028041) with a working distance of 14mm at 20X. A high intensity projector lamp with intensity control was used as the reflected light source.

The experimental procedure consisted of placing a few glass spheres of similar size in the platinum pan of the hot stage unit and locating two particles touching each other for neck growth study. The furance was heated to the required temperature and the neck growth data, including time and thermocouple emf, were recorded continuously on video tape during the sintering process. Figure 1 shows two successive steps during the sintering of glass particles as recorded at one temperature. This method of recording data was useful because it created a virtually continuous and complete record of the sintering process and all data for a particular temperature could be taken on the same pair of glass spheres.



a. Relative time 0 min



b. Relative time 20 min, 46 seconds

Figure 1. Initial Stage Sintering Study of 63-25-12 Glass Spheres at 503°C

2.2 Results

Neck growth measurements were carried out at five different temperatures ranging from 499 to 517°C for the 63-25-12 glass spheres. Measurements on the 70-20-10 glass spheres were made at four different temperatures, ranging from 487 to 550°C. The data from these measurements are given in Table 1.

If Newtonian viscous flow is the predominant mechanism for the initial stage sintering of the glass spheres, the relationship between neck radius (x), particle radius (r), and time (t) should follow,

$$\left(\frac{x}{r}\right)^2 = \frac{3}{2}\left(\frac{\gamma_{sv}}{\eta}\right) r^{-1} t \qquad (2.1)$$

where γ_{sv} is the solid-vapor interfacial energy (surface tension), and η is the viscosity. If Equation 2.1 applies, a plot of $(x/r)^2$ vs time should give a straight line, and this was the observed behavior at all measurement temperatures for both glasses as shown in Figs. 2 and 3. The surface tension to viscosity ratio calculated from the slopes of the lines in Figs. 2 and 3 at each temperature for the two glasses are also given in Table 1.

Since the surface tension of a liquid is equal to its surface free energy γ_{sv}, should be given by

$$\gamma_{sv} = U_s - TS_s \qquad (2.2)$$

where U_s and S_s are the energy and entropy change associated with the formation of the surface. To a first approximation, if U_s and S_s are

TABLE 1. Neck Growth Data

Glass Sample	r Particle Radius (μm)	Temperature (°C)	Relative Time (min)	x neck radius (μm)	γ_{sv}/η (m/sec)
63-25-12	110	499	0	11.3	2.83×10^{-10}
			10.0	12.4	
			24.8	14.1	
			44.0	15.8	
63-25-12	124	503	0	12.4	6.01×10^{-10}
			9.5	15.2	
			19.6	17.4	
			29.6	19.1	
			41.4	20.8	
63-25-12	110	506.5	0	11.2	8.25×10^{-10}
			8.0	13.5	
			20.9	16.9	
			29.2	19.1	
63-25-12	108	510	0	12.4	1.45×10^{-9}
			3.9	14.6	
			10.0	17.4	
			19.7	20.8	
63-25-12	117	516.7	0	11.8	3.58×10^{-9}
			2.0	14.6	
			4.0	17.4	
			6.7	19.7	
70-20-10	101	487	0	12.4	2.66×10^{-10}
			8.0	13.5	
			31.9	15.2	
			52.5	16.9	
70-20-10	112	490	0	14.0	5.63×10^{-10}
			12.5	16.3	
			27.7	18.5	
			41.8	20.8	
70-20-10	112	493.4	0	12.4	1.79×10^{-9}
			4.3	14.6	
			8.1	16.9	
			13.1	19.7	
70-20-10	108	497	0	13.5	5.82×10^{-9}
			.78	15.2	
			1.53	16.3	
			4.4	20.8	

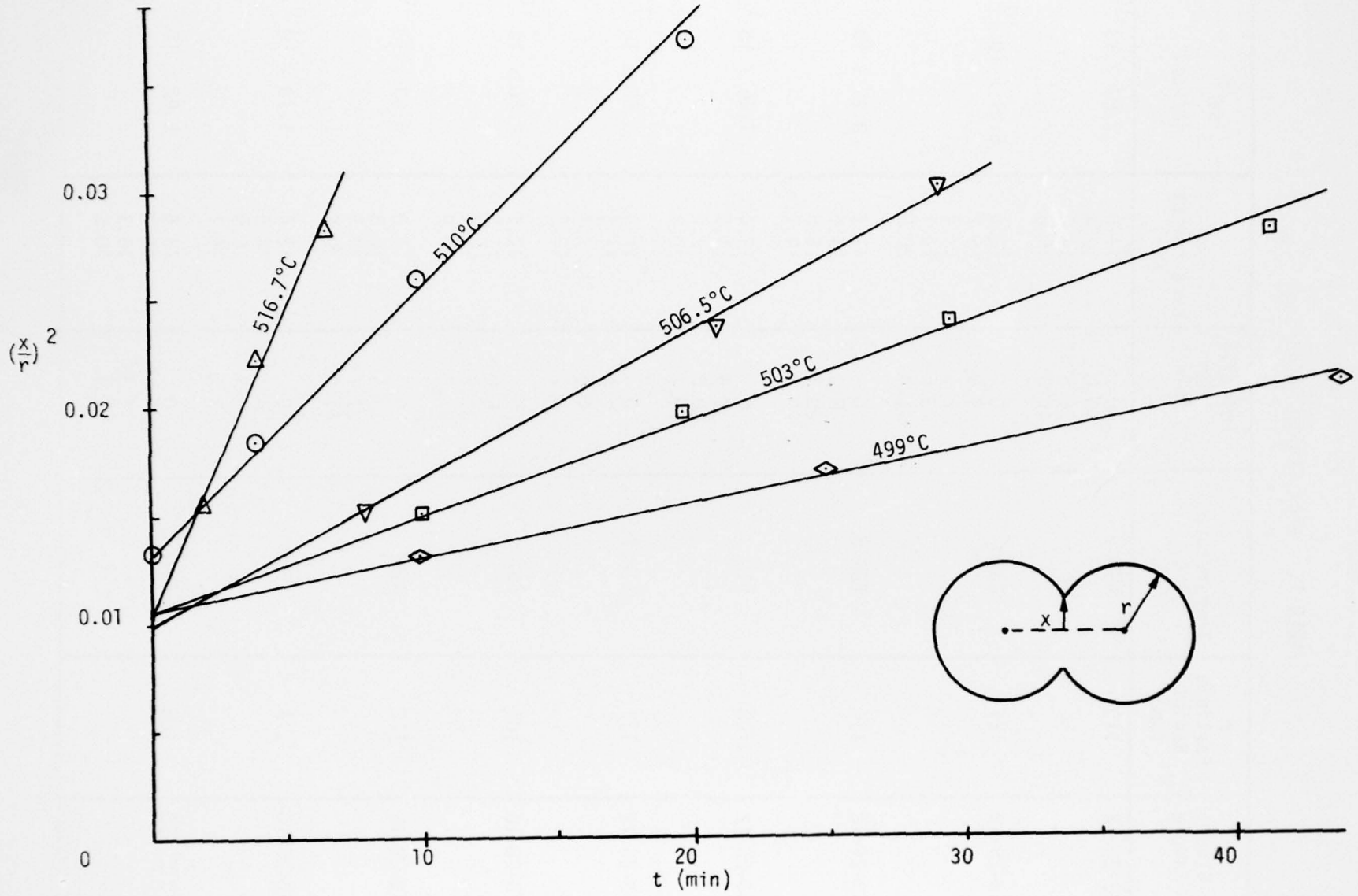


Figure 2. Initial Stage Sintering Kinetics for (63-25-12) Glass Spheres

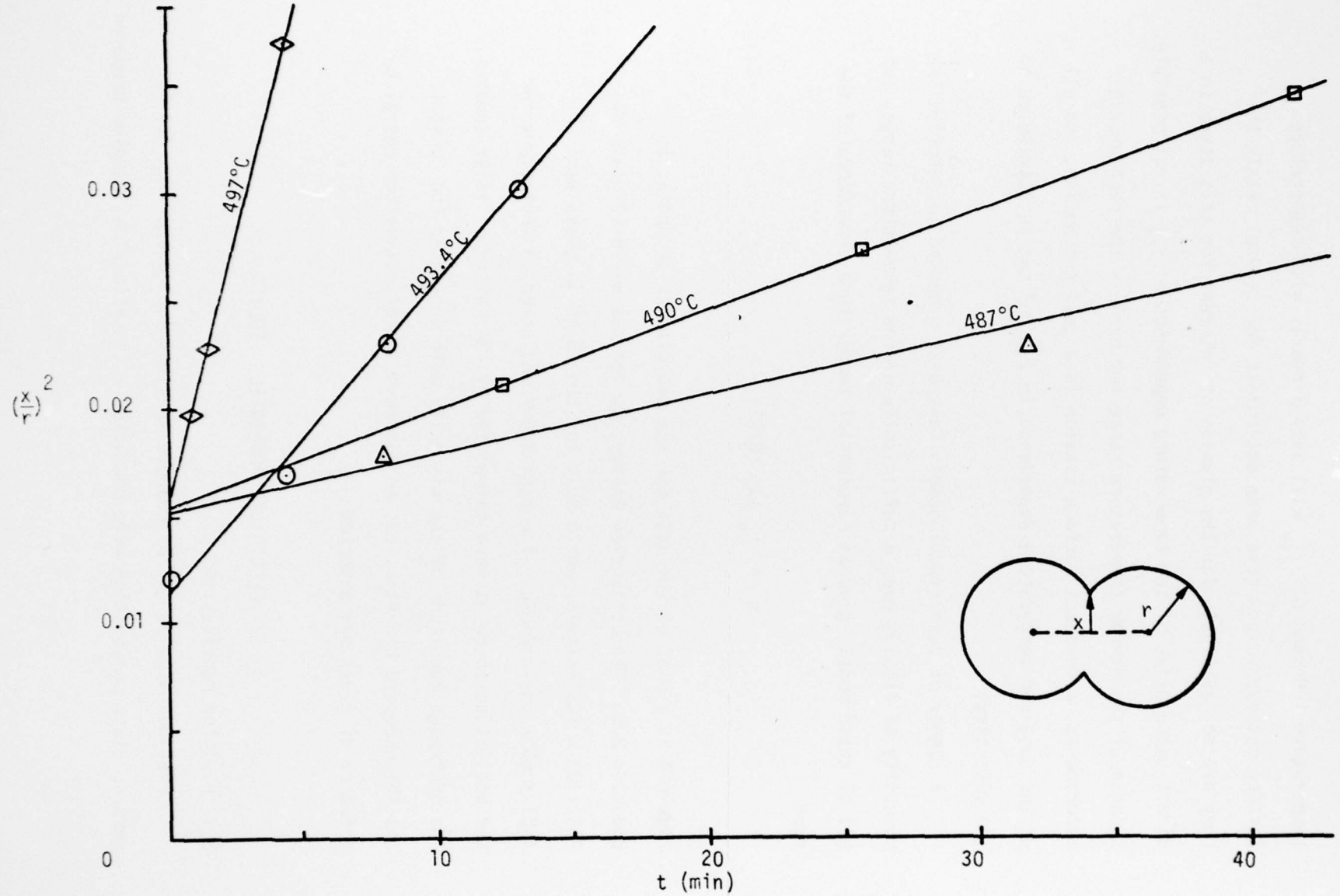


Figure 3. Initial Stage Sintering Kinetics for (70-20-10) Glass Spheres

temperature independent γ_{sv} will vary linearly with temperature. Surface entropy values have been determined for several metals but they are not available for the glasses of interest for this study so a direct calculation of the temperature dependence of γ_{sv} is not possible. Because of the narrow temperature range employed in the neck growth experiments, a constant surface tension is a good assumption, and all of the observed temperature dependence in (γ_{sv}/η) can be attributed to the viscosity.

A number of theoretical models have been proposed to describe the viscosity of liquids over a sufficiently narrow temperature range, but all of these models give an exponential temperature dependence of the type

$$\eta = \eta_0 \exp (Q/RT) \qquad (2.3)$$

Figure 4 is a plot of the data for the two glasses according to Equation 2.3. The activation energy, Q, for the 63-25-12 glass was 713 ± 32 K joules/mole, while that for the 70-20-10 glass was 1521 ± 69 K joules/mole. The magnitudes and standard deviations for the activation energies were calculated by the method of least squares. The decreased magnitude of the viscosity with increased PbO content was the expected behavior, but an increase in the activation energy by a factor of 2 was not expected.

3. ELECTRICAL PROPERTIES STUDIES

3.1 Resistor Fabrication

Previous studies [1] of changes in electrical properties due to varying glass composition were conducted with cylindrical samples prepared

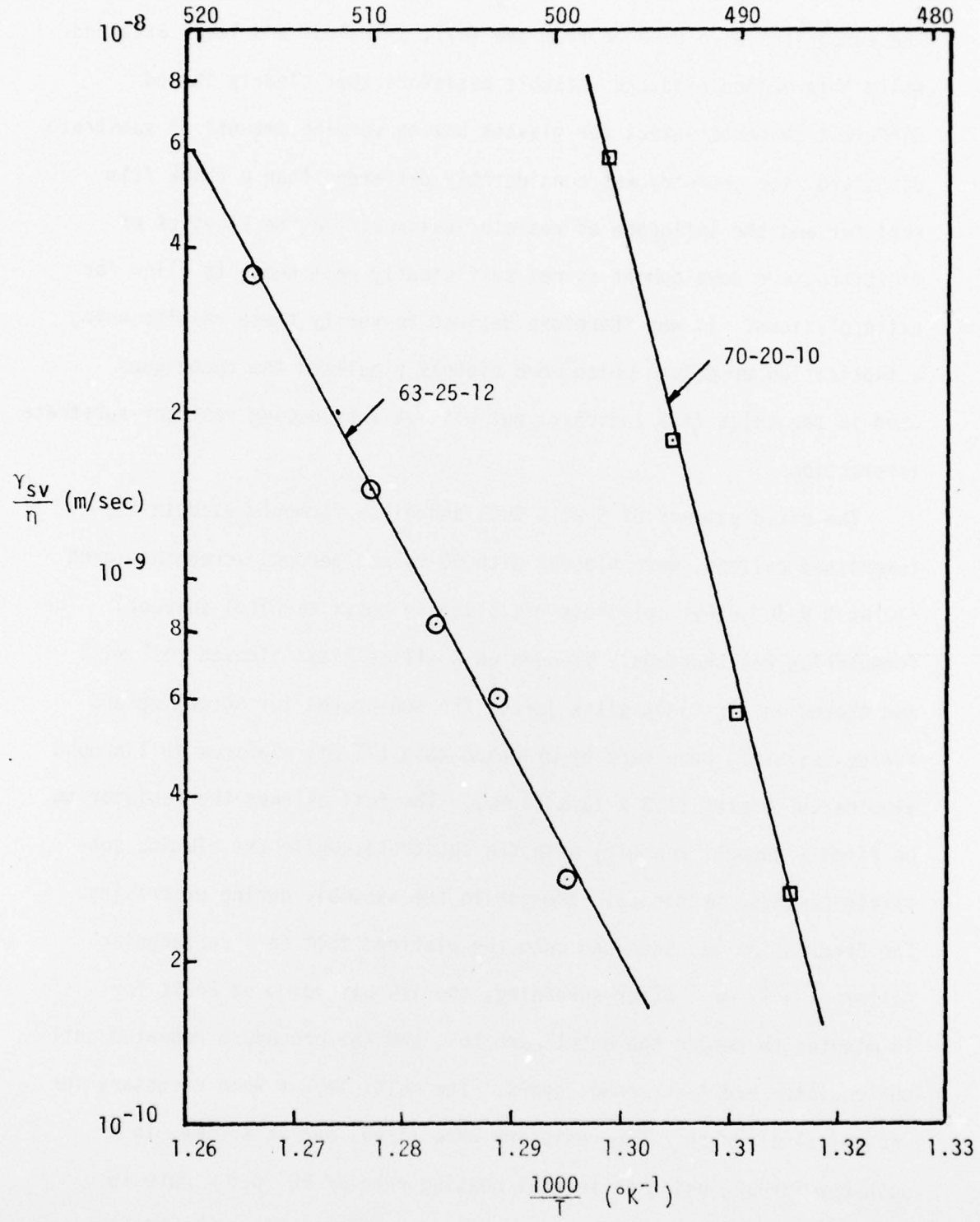


Figure 4. Temperature Dependence of Surface Tension to Viscosity Ratio for Two Glasses

by firing compressed pellets of RuO_2-glass mixtures in platinum boats. The composites were removed from the foil, annealed, and leads attached. While this method produced workable resistors that clearly showed different characteristics for glasses having varying amounts of substrate dissolved, the geometry was considerably different than a thick film resistor and the influence of resistor thickness on the kinetics of microstructure development is not sufficiently well known to allow for extrapolations. It was therefore desired to verify these results using a fabrication procedure which more closely simulated the techniques used in the thick film industry, but without introducing resistor-substrate interactions.

The mixed powders of 5 wt % RuO_2 and glass formerly used in the compressed pellets, were blended with 60 volume percent screening agent (10 wt % N-300 ethyl cellulose dissolved in butyl carbitol solvent). The formulation was thoroughly blended on a silica glass sleeved roll mill and stored in air tight glass jars. The substrates for screening and firing resistors were made by wrapping thin (76 μm) platinum foil around alumina substrates (1.3 x 13 x 13 mm). The foil allowed the resistor to be fired withought reacting with the substrate, while the alumina substrate provided mechanical strength to the assembly during processing. The formulation was screened onto the platinum foil in a rectangular pattern 4 x 12 mm. After screening, the ink was dried at 240°C for 15 minutes to remove the butyl carbitol, and the procedure repeated until the resistor had 4 screened layers. The multi layers were necessary for mechanical strength. The resistors were fired, one at a time, in a push-rod furnace using an initial heating rate of 50° per minute to 500°C, a 10 minute hold at 500°C, a heat at 60° per minute to 800°C

a 10 minute hold, and a cool to room temperature at 160° per minute. The 500°C constant temperature region was necessary in order to completely remove the ethyl cellulose. The difference in coefficient of thermal expansion between the glass in the resistor and platinum was such that appreciable thermal stresses were developed, but these were not sufficient to cause fracture in the resistor films. The platinum foil was removed from the fired resistor by first gluing the top of the resistor to a microscope slide with wax. The platinum foil was straightened, the alumina substrate lifted out, and the platinum foil gently peeled off to leave the resistor enbedded in the wax. To remove the wax, the glass slide was placed in trichlorethylene until the resistor released from the slide. It was then rinsed at least 10 times in trichloroethylene to remove all traces of wax. The cleaned resistors were very fragile ($\sim$ 125 μm thick); therefore, to provide mechanical strength, and to remove residual stresses, they were sintered onto AlSiMag 614 substrates and simultaneously annealed. Since sintering occurs below the softening point of glass and considerably below normal processing temperatures, there was negligible composition variation during bonding with substrate. For the resistors made with a lead borosilicate glass, an annealing temperature of 450°C for 1 hour provided good bonding between the resistor and the substrate. A somewhat higher temperature was needed for resistors using glass with dissolved substrate because of the increased softening point of the glass composition. Electrical leads were then attached to the resistor by one of two methods; platinum wires were attached using silver epoxy or appropriate metal electrodes were deposited by vacuum evaporation or sputtering.

3.2 MIM Device Fabrication

Branches of the conducting chains of RuO_2 in thick film resistors are sometimes separated by a thin layer of glass. In order to determine the effects of the composition of this glass on the electrical properties of the resistors, it is first necessary to characterize the electrical properties (bulk resistivity, dielectric constant, and dielectric strength) of the glass itself as a function of composition (amount of dissolved substrate). Most of these properties, in addition to the tunneling and emission characteristics, can be measured using a standard metal-oxide-metal (MIM) structure; therefore, the device for initial experiments will be a platinum-glass-platinum capacitor. This MIM device will be fabricated by first sputtering platinum on to a Corning 7059 glass substrate. The lead borosilicate glass of appropriate composition will be sputtered on top of the platinum, and a metal mask with round holes, approximately 0.5 mm, will be used to sputter platinum counter-electrodes.

The initial efforts at fabricating the MIM device have been centered on the development of techniques for sputtering the glass without changing its chemical composition. Preliminary results indicated an apparent reduction of the glass, presumably due to the formation of elemental lead. This was observed as a color change in the glass target from white to black. Subsequent experiments using a 20% O_2, 80% Ar atmosphere showed improvement, but still some darkening of the glass target. Variation of all parameters including input power, O_2 partial pressure, source to substrate spacing, and substrate temperature are currently underway in order to optimize sputtering procedures. If the reduction problem persists, a post-sputtering anneal will be employed to re-oxidize the glass.

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.

5. FUTURE PLANS

The kinetics of initial stage sintering of glass spheres will be determined as a function of glass composition (amount of dissolved substrate). Studies of the dissolution of AlSiMag 614 and AlSiMag 772 alumina substrates as a function of time and temperature and the distribution of the dissolved species will be conducted utilizing the second glass. The qualitative effects of glass composition on the kinetics of bubble motion and the development of macronetworks of conductive particles in thick film resistors will be determined utilizing hot stage microscopy.

6. STATEMENT OF ESTIMATED COSTS

Contract No. N00019-77-C-0327

February 1, 1977 - January 31, 1978

Beginning Fund Balance	$60,000.00
Funds Expended Through 4/30/77	13,031.64
Funds Remaining	$46,968.36

Planned Expenditures (Approximate)

May	$5200
June	5200
July	5200
August	5200
September	5200
October	5200
November	5200
December	5200
January	5200