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DESIGNING ALUMINUM SEALING GLASSES FOR MANUFACTURABILITY

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INTRODUCTION

Future generations of advanced electronic components will require new combinations of materials to ensure reliability and improve functionality in specialized applications calling for unique material characteristics. Device attributes like weight, hermeticity and durability will become more important as sensitive electronics or pyrotechnic materials are exposed to a variety of potentially corrosive environments. Materials that are currently the choice for many non-hermetic components, such as lightweight aluminum for shells and high-expansion Cu/Be or stainless steel for contacts, are not compatible with the silicate-based sealing glasses used in conventional hermetic packages. If these materials are to be adapted to hermetic electronic applications, new sealing glasses compatible with their particular characteristics must be developed.

Manufacturability issues involved in the development of new sealing glasses include tailoring glass compositions to meet material and component requirements and determining the optimum seal processing parameters. For each of these issues, statistical analysis can be used to shorten the time between concept and product in the development of what is essentially a new manufacturing technology. We will use the development of our new family of phosphate-based glasses for aluminum/stainless steel and aluminum/CuBe hermetic sealing, the ALSG family [1], to illustrate the statistical approach.

Figure 1 shows a schematic drawing of an 18-pin electrical connector used at Sandia. The connector body is machined from a structural aluminum alloy such as AL6061, AL5086,

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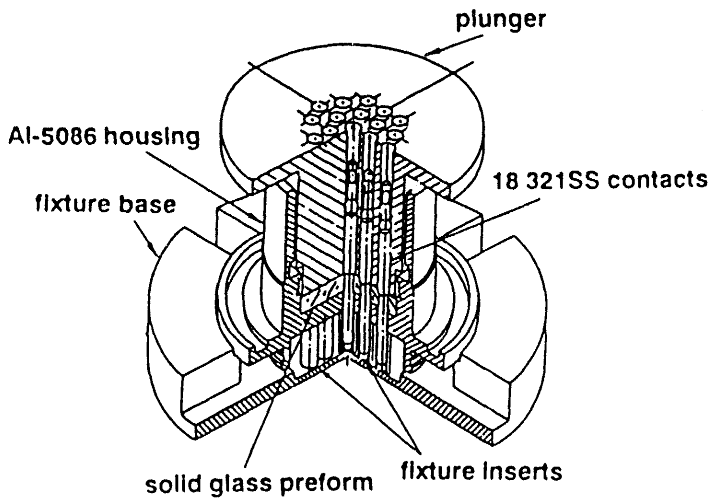
or AL5456, and the terminals are an austenitic stainless steel such as SS321 or SS304L. A glass seal electrically isolates the pins from each other and from the connector body while providing a hermetic barrier to protect air-sensitive materials. The requirements for the glass include a sealing temperature below ≈525°C to minimize sealing process degradation of the mechanical properties of the aluminum, a coefficient of thermal expansion (CTE) near 180 x 10^{-7}/°C to match the stainless steel terminals and avoid the development of tensile stresses during sealing, and good aqueous corrosion resistance to meet component shelf life requirements.

Figure 1. Aluminum LAC Fixture Assembly



This combination of material properties is not met by any commercially available sealing glass. Durable silicate-based glasses have sealing temperatures above the melting point of aluminum and have CTEs that are too low to be compatible with stainless steel. PbO-based solder glasses can be sealed at low temperatures, but they also have low CTEs. Previously developed phosphate glasses [2] have the requisite thermal properties, but their generally poor aqueous durabilities preclude widespread aluminum component application. The ALSG family of phosphate glasses meets the requirements for low temperature sealing, high thermal expansion, and good durability, and the statistical methods employed to tailor glass composition to material requirements have made the development process more efficient.

EXPERIMENTAL STRATEGY FOR OPTIMIZING GLASS COMPOSITION

The nominal composition of the ALSG glass family resulted from a recent study of the structure-property-composition relationships in the Na_2O - Al_2O_3 - P_2O_5 glass forming system [3]. That study showed that high expansion coefficients and low glass transition temperatures could be retained in a phosphate glass when Al_2O_3 is added if the nominal composition yields pyrophosphate structures. This is important because the addition of alumina (or B_2O_3) generally improves glass durability.

Table 1. Compositional Ranges for ALSG System

COMPONENT	RANGE (mole %)
Na_2O	10-20
K_2O	10-25
BaO	0-12
PbO	0-12
Al_2O_3	4-12
B_2O_3	0-10
P_2O_5	35-50

With this as the starting point, a variety of other oxides were included to form a seven-component system for study (see Table 1). The compositional ranges were kept as broad as possible, given the constraints of glass formation and the desire to retain a pyrophosphate-like network.

In order to optimize glass composition for specific glass properties, an efficient statistical approach to mixture development was applied. This approach involves defining an experimental region in terms of the range of levels of the various components in the mixture. Within this experimental region, various compositions are tested, and the resulting data are used to fit empirical models relating the component levels to the key response variables. These models approximate the true, unknown response surfaces and are used for optimization. The strategy used in the ALSG experiment consisted of the following steps:

1. Define the Experimental Region. This is determined by the constraints placed on the individual components in the mixture as well as any constraints involving multiple components. Typically, each component will have an upper and lower bound.

The components included in this mixtures experiment were:

$X_1=Na_2O$, $X_2=K_2O$, $X_3=BaO$, $X_4=PbO$, $X_5=Al_2O_3$, $X_6=B_2O_3$, and $X_7=P_2O_5$.

The constraints on the individual components used in the design were:

$10\% \leq X_1 \leq 20\%$, $10\% \leq X_2 \leq 25\%$, $0\% \leq X_3 \leq 12\%$, $0\% \leq X_4 \leq 12\%$,
$4\% \leq X_5 \leq 12\%$, $0\% \leq X_6 \leq 10\%$, $35\% \leq X_7 \leq 50\%$,

and the overall mixture constraint is:

$$X_1 + X_2 + X_3 + X_4 + X_5 + X_6 + X_7 = 100\%.$$

These constraints uniquely define the experimental region, from which test compositions were chosen.

2. Choose the Compositions to be Tested Experimentally. Candidate points for inclusion in the experimental design consist of the extreme vertices ("corner points"), center of mass centroids ("interior points"), and the overall center of the experimental region. The extreme vertices provide the most useful information because they spread the design out, and the interior points are helpful for detecting curvature in the response surface. Both extreme vertices and interior points were thus included in the design, as well as replications of the center point to estimate the experimental error variance.

The candidate points for the design, identified using Piepel's MIXSOFT™ program [4], were:

136 Extreme Vertices ("Corners" of the experimental region),

14 Five-Dimensional Center-of-Mass Centroids ("Centers" of 5-D Faces),

1 Overall Center-of-Mass Centroid (Center Point).

The design chosen consisted of the 14 five-dimensional center-of-mass centroids, the overall center-of-mass centroid (3 replicated melts), plus 8 of the extreme vertices, for a total of 25 experimental melts (see Table 2). The 14 five-dimensional center-of-mass centroids, the subset of 8 extreme vertices, and the overall center-of-mass centroid were identified using MIXSOFT™. The first 8 experimental melts listed in Table 2 are at extreme vertices of the experimental region, the next 14 are the 5-D center-of-mass centroids, and the final melt is at the overall center-of-mass centroid, to be replicated three times, for a total of 25 melts. The order of the melts was randomized, with the exception of the 3 melts at the center-of-mass centroid, which were performed at the beginning, middle, and end of the experiment to provide a check of stability in the results over the duration of the experiment. This design allows estimation of the full linear model:

$$\text{Response } Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_6 X_6 + \beta_7 X_7 + \varepsilon, \qquad (1)$$

where the β_i's are the coefficients to be estimated and ε represents a random experimental error term with expected value $E(\varepsilon) = 0$ and variance $Var(\varepsilon) = \sigma^2$. In addition, many of the possible quadratic terms that could be added to model (1) can be estimated, although a full quadratic model cannot be estimated with fewer than 28 distinct melts. Later experimental melts can be done if it is determined that additional parameters need to be estimated.

A useful criterion for evaluating a mixtures experimental design is the V-max criterion, where

V-max = max {Var(Y($\underline{x}$))}, over all $\underline{x} = (x_1, x_2, x_3, x_4, x_5, x_6, x_7)$

in the set of candidate mixture points. V-max is thus the maximum value of the prediction variance, Var(Y($\underline{x}$)), over all points in the candidate design space. Snee [5] comments that any design with V-max $\leq 1.0\sigma^2$ indicates a good design from a practical viewpoint because this emplies that the model predictions, Y($\underline{x}$), are as precise as the measured responses. The V-max criterion was checked for the design in Table 2, and resulted in V-max = $.78\sigma^2$, indicating a good design with respect to the linear model (1).

Table 2. Set of Melts for Mixtures Experiment (percent of composition)

Trial #	Na_2O	K_2O	BaO	PbO	Al_2O_3	B_2O_3	P_2O_5
1	10.0	25.0	11.0	0.0	4.0	0.0	50.0
2	10.0	10.0	12.0	12.0	12.0	0.0	44.0
3	20.0	25.0	0.0	12.0	4.0	0.0	39.0
4	20.0	21.0	12.0	0.0	12.0	0.0	35.0
5	10.0	25.0	12.0	0.0	4.0	10.0	39.0
6	10.0	21.0	0.0	12.0	12.0	10.0	35.0
7	20.0	10.0	9.0	12.0	4.0	10.0	35.0
8	20.0	10.0	0.0	0.0	12.0	10.0	48.0
9	10.0	18.8	6.7	6.7	8.3	5.5	43.7
10	20.0	16.2	5.2	5.2	7.6	4.4	41.2
11	15.9	10.0	7.3	7.3	8.5	5.9	44.7
12	14.0	25.0	4.6	4.6	7.4	4.0	40.2
13	15.6	19.1	0.0	6.9	8.4	5.6	44.1
14	14.3	15.8	12.0	5.0	7.5	4.3	40.8
15	15.6	19.1	6.9	0.0	8.4	5.6	44.1
16	14.3	15.8	5.0	12.0	7.5	4.3	40.8
17	15.4	18.5	6.5	6.5	4.0	5.4	43.4
18	14.6	16.5	5.4	5.4	12.0	4.5	41.5
19	15.5	18.8	6.7	6.7	8.3	0.0	43.7
20	14.4	16.2	5.2	5.2	7.6	10.0	41.2
21	15.9	19.8	7.3	7.3	8.5	5.9	34.9
22	14.0	15.2	4.6	4.6	7.4	4.0	50.0
23	15.0	17.5	6.0	6.0	8.0	5.0	42.5

3. <u>Perform the Experimental Melts and Measure Glass Properties.</u> At this stage, experimental procedures must be carefully followed, and measurements must be made according to well-defined procedures to minimize experimental error. In this experiment the key measured responses were:

Coefficient of Thermal Expansion (CTE),

Glass Transition Temperature (T_g),

Delta Temperature (ΔT), a measure of working range,

Dissolution Rate (DR), a measure of aqueous durability.

4. <u>Fit the Empirical Models.</u> For each of the above response variables, empirical polynomial models were constructed consisting of all the linear terms of model (1) above, as well as the important second-order terms determined from the statistical treatment of the data. The following models were fit to the experimental data:

$$CTE \approx 8.08*Na_2O + 8.01*K_2O + [0.24*BaO] + 2.88*PbO - 2.73*Al_2O_3 - 1.18*B_2O_3$$
(1.37) (1.10) (1.67) (0.57) (0.49) (0.57)

$$- [.015*P_2O_5] - .284*Na_2O*K_2O + .155*Na_2O*BaO - .357*BaO*PbO$$
(0.33) (0.082) (0.096) (0.093)

$$T_g \approx 2.87*Na_2O - [0.16*K_2O] + 3.73*BaO + 1.64*PbO + 8.19*Al_2O_3$$
(1.04) (0.74) (1.04) (0.98) (1.41)

$$+ 10.1*B_2O_3 + 4.27*P_2O_5$$
(1.14) (0.53)

$$\Delta T \approx 18.7*Na_2O - 19.5*K_2O + [30.2*BaO] - 10.3*PbO - 49.3*Al_2O_3 + [0.01*B_2O_3]$$
(11.6) (14.8) (30.5) (4.77) (31.8) (2.53)

$$+ 5.05*P_2O_5 - 2.89*Na_2O*BaO + 3.50*K_2O*Al_2O_3 + 2.18*BaO*PbO$$
(2.08) (1.84) (1.96) (0.78)

$$Log(DR) \approx 1.14*Na_2O + 1.61*K_2O - 0.60*BaO - 0.67*PbO - 0.79*Al_2O_3$$
(0.34) (0.27) (0.11) (0.10) (0.11)

$$- 1.51*B_2O_3 + 0.78*P_2O_5 + 0.057*Na_2O*B_2O_3 - 0.049*Na_2O*P_2O_5$$
(0.23) (0.16) (0.012) (0.010)

$$- 0.05 * K_2O * P_2O_5$$
$$(0.008)$$

Standard errors of the estimates are in parentheses. Statistical tests were performed to determine which terms should be included in the models. The brackets [ ] denote the linear terms in the models that were not statistically significant.

5. Optimize a Glass Composition for Model Verification. The models identified in this experiment were used to predict optimal ALSG family compositions with respect to aqueous durability (DR, dissolution rate) and coefficient of thermal expansion (CTE). A glass batch was melted using composition percentages predicted by the models, and CTE and DR were measured to check the model predictions. The optimization problem was:

Minimize: Log (DR) $(x_1, x_2, x_3, x_4, x_5, x_6, x_7)$, and

Subject to: $x_4 = 0$ (for a lead-free glass), and

$175 \leq$ CTE $(x_1, x_2, x_3, x_4, x_5, x_6, x_7) \leq 190 \times 10^{-7}/°C$ (required CTE range).

The IMSL subroutine DNCONF (for non linear constrained optimization) was used to numerically solve this problem. The solution within the experimental region was at:

$(x_1, x_2, x_3, x_4, x_5, x_6, x_7) = (15, 22, 2.8, 0, 11.2, 4, 45)$

with Log(DR) ≈ -8.1 ($\pm$ 0.8) and CTE $\approx 175 \times 10^{-7}/°C$ ($\pm$ 2).

The measured property values of the glass batch were:

Log(DR) = -9.0 and CTE = $180 \times 10^{-7}/°C$. (see Table 3)

The material properties measured from the confirmatory glass batch indicated that the models fit the data well.

Table 3. Predicted and Measured Values

	CTE	Log(DR)
Predicted Value	175	-8.1
Measured Value	180	-9.0

EXPERIMENTAL STRATEGY FOR OPTIMIZING PROCESS PARAMETERS

In order to optimize processing parameters for sealing the newly developed glass compositions, an efficient statistical approach can be applied. This procedure is currently being investigated at Sandia, and while final results are not available for presentation at this time, preliminary strategy and set-up information can be reported. The approach involves defining an experimental region in terms of the controllable factors (process parameters) that will be manipulated. Within the defined experimental region, various combinations of the factors are tested, and the resulting data are used to fit empirical models relating the factors to the key response variables. These models approximate the true, unknown response surfaces and are used to optimize the sealing process. The strategy used in the sealing process experiment consists of the following steps:

1. Select the Response Variables. Clearly define the objective of the experiment. A list of potential response variables is prepared by asking "what could I measure that would determine whether I reach my objective?" It is also important to consider what measurements can be made precisely and without great expense. The objective for this experiment: Determine process parameters that will result in a "robust" glass-to-metal seal. The response variables identified were:

Visual Quality (per standard inspection procedures),

Hermeticity (leak rate, standard requirement),

Load (pin-pull testing, bond strength requirement).

The visual quality measurement is comprised of subjective ratings of the glass seal in various areas, such as glass wetting, bubbles, and cracking, which are quantified for statistical manipulation.

2. Select Factors That Will Be Investigated in the Experiment. For each response variable, list all factors that may have an impact on the outcome of that variable. Determine which factors are controllable by asking for each whether it is procedurally possible and economically feasible to control the factor in a manufacturing environment. For each of the factors that is procedurally controllable, consider the feasibility of controlling the factor experimentally, the precision with which the factor can be controlled, and the potential impact (high, medium, low) on the response variables. These considerations are used to decide which of the controllable factors will be included in the experiment. (For example: High and medium impact factors should almost always be included, low impact factors are included if time and money allow.) In this experiment, the factors chosen for optimizing the glass sealing process are:

Maximum furnace temperature (sealing temperature), Hold time at maximum temperature,

Cool down rate after sealing (including anneal hold),

Weight on sealing fixture (pressure on glass during sealing),

Furnace atmosphere flow rate.

3. Choose Factor Levels and the Experimental Design Pattern. Determine whether the purpose of the experiment is to identify the most important factors, estimate main effects and interactions only, or develop detailed empirical models and maps that can be used for optimization. The purpose of this experiment is to develop the models and maps to optimize the glass sealing process. The next step is to determine high and low levels for each factor to be controlled. Use any known relationships between response variables and factors to set reasonable levels.

Table 4. Experiment for Optimizing ALSG Sealing Process

Run	Max Temp °C	Hold Time min	Cool Rate °C/min	Weight grams	Flow Rate cfm	Visual	Leak Rate	Load
1	425.0	15.0	20	2.0	12.5			
2	550.0	15.0	20	2.0	2.5			
3	425.0	60.0	20	2.0	2.5			
4	550.0	60.0	20	2.0	12.5			
5	425.0	15.0	100	2.0	2.5			
6	550.0	15.0	100	2.0	12.5			
7	425.0	60.0	100	2.0	12.5			
8	550.0	60.0	100	2.0	2.5			
9	425.0	15.0	20	5.0	2.5			
10	550.0	15.0	20	5.0	12.5			
11	425.0	60.0	20	5.0	12.5			
12	550.0	60.0	20	5.0	2.5			
13	425.0	15.0	100	5.0	12.5			
14	550.0	15.0	100	5.0	2.5			
15	425.0	60.0	100	5.0	2.5			
16	550.0	60.0	100	5.0	12.5			
17	425.0	37.5	60	3.5	7.5			
18	550.0	37.5	60	3.5	7.5			
19	487.5	15.0	60	3.5	7.5			
20	487.5	60.0	60	3.5	7.5			
21	487.5	37.5	20	3.5	7.5			
22	487.5	37.5	100	3.5	7.5			
23	487.5	37.5	60	2.0	7.5			
24	487.5	37.5	60	5.0	7.5			
25	487.5	37.5	60	3.5	2.5			
26	487.5	37.5	60	3.5	12.5			
27	487.5	37.5	60	3.5	7.5			
28	487.5	37.5	60	3.5	7.5			
29	487.5	37.5	60	3.5	7.5			
30	487.5	37.5	60	3.5	7.5			
31	487.5	37.5	60	3.5	7.5			
32	487.3	37.5	60	3.5	7.5			

Choose levels that are "bold" yet meaningful to the process or product. For any factor that is qualitative rather than quantitative (ie. visual quality), arbitrarily assign levels to the different categories for that factor.

The type of experimental design used depends on the purpose of the experiment. To develop a detailed empirical model that can be used for optimization, a response surface design should be used. The particular response surface design chosen for this experiment is a 5-factor face-centered cube design. This design contains factorial points (corner points of a 5-dimensional "cube"), points in the center of each face of the 5-dimensional cube, and points in the overall center of the experimental region. Table 4 lists the points (factor levels) chosen for each sealing run in this experiment. Data from the experimental runs at these points can be used to estimate main effects, interactions, and curvature.

4. Calibrate Equipment and Conduct a Precision Study. Be sure that the precision and accuracy of the measurements that will be made during the experiment are known. Calibrate equipment if necessary and take care to conduct the experimental runs in a manner that simulates the eventual production environment. This will ensure that the data collected are valid for the intended application and will be useful for modeling the responses.

5. Conduct the Experiment, Analyze the Data, Document Results. Conduct the experiment using established procedures for the given operation and record and verify the data. For this experiment, standard operating procedures are used for piece-part preparation, fixture design, assembly, furnace operation, disassembly, and post-seal inspection. Fit the desired models (equation) to the responses and analyze the results. The models will be empirical polynomial models with linear terms, interaction terms, and (possibly) quadratic terms. In this experiment, the models will be used to optimize the ALSG glass sealing process with respect to visual quality, leak rate, and load. When the experimental runs are completed and the models have been used to optimize the process, document the results.

ALSG FAMILY OF ALUMINUM SEALING GLASSES

As mentioned at the outset, the ALSG family of phosphate glasses for aluminum sealing was developed for specific applications through the use of statistical methods of optimization. The statistical models allow specific material properties to be predicted and achieved with much fewer glass melts than would otherwise be required. For example, robust glass compositions afford the manufacturer wide constituent composition ranges, making the glass easier to make in large batches and affording a wide window for processing. Statistical modeling can be used to predict robust compositions, after the initial set of experimental melts is made to determine the models, before any glass melts are required for material property measurement.

ALSG compositions were optimized for sealing to Aluminum shells (6061, 5086, and 5456) and 304SS pins in this manner. Previous work indicated that a melting temperature of ≤ 525°C could be virtually assumed from this glass family, and therefore the modelling was needed to predict the other two requirements: coefficient of thermal expansion (CTE) ≈ 180 x 10^{-7}/°C and good aqueous durability (log(DR) < -8). The confirmatory glass batch melted to check the initial model predictions in this experiment was also a glass composition designed to meet these specific requirements. As discussed earlier (see Table 3), the models predicted the measured properties well, and the result was ALSG-32, a durable phosphate glass suitable for sealing to Aluminum shells and 304SS pins.

During the ALSG composition optimization experiment, many furnace runs were made to determine the sealability of various sample glasses. A large body of processing data was accummulated, and therefore the statistical processing optimization strategy was not employed for the ALSG-32 glass. That strategy is currently being defined and tested, as discussed in this paper, for other ALSG compositions with material properties suitable for sealing to Cu/Be pins and other potential shell materials.

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