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By: N.L. Boling, L. Spanoudis, and P.R. Wengert

DAMAGE THRESHOLD STUDIES OF GLASS LASER MATERIALS

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OWENS-ILLINOIS, INC.
TOLEDO, OHIO
PHONE: (419) 242-6543, EXTENSION 3300

FORWORD

The work outlined in this semi-annual report was performed under Contract DAHC15-69-C-0303, ARPA Order 1441, and Program Code P9D10. The work was performed within the Consumer and Technical Products Division of Owens-Illinois, Inc., Toledo, Ohio and covers the time period from 1 July 1970 through 31 December 1970.

The principal investigator for the program is N. L. Boling and the program manager is H. A. Lee. The thermodynamics of the melting of laser glass in platinum is being conducted by L. Spanoudis under the direction of P R. Wengert. This contract is administered by the Chief, Defense Contract Administration Services Office, Toledo, Ohio Dr. Maurice J Sinnott, Director for Materials Sciences, ARPA, is the Contracting Officer's Technical Representative

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ABSTRACT

DAMAGE THRESHOLD STUDIES OF GLASS LASER MATERIALS

This report discusses work performed under ARPA contract no. DAHC15-70-C-0303 during the period 1 July 1970 to 31 December 1970.

This work has two aspects: an investigation of elimination of damaging platinum particles from laser glass melted in platinum crucibles, and a study of the causes and prevention of surface damage to laser glass exposed to high intensity laser pulses.

Work performed on the former aspect in the specified period has involved a theoretical investigation -- based upon a literature search -- of activity coefficients. The goal of this is determination of partial pressures of oxygen in the melting environment which will prevent formation of damaging platinum particles and at the same time prevent crucible attack.

The surface damage study involves a search for causes of damage through high speed holography. Further, chemical treatments of glass surfaces are being explored as a means of increasing the damage threshold. Work on this surface damage phase has primarily involved design and modification of experimental equipment which will be used.

1 SUMMARY

The problem addressed by the work described in this report is the damage of laser glass by high power laser pulses. This damage is generally considered to take one of three forms. In order of increasing damage threshold these are: particulate damage, surface damage, and self focusing damage. This work concerns itself primarily with the first two of these.

Damage, due to platinum particles, of laser glass melted in platinum crucibles has been characterized by previous work under this contract. One of the goals of the present effort is the prevention of the formation of these particles during the melting of the glass, at least to the extent that they are no longer of appreciable concern as damaging agents.

Our study is predicated on the assumption, which has much supporting evidence, that oxygen in the melting environment is necessarily involved in producing platinum in the finished glass. The oxygen level cannot, however, be reduced arbitrarily since attack of the platinum crucible by elements of the melted glass occurs below a certain partial pressure of oxygen. Consequently, the first phase of our approach to this problem consists of a theoretical study of the thermodynamics of melting laser glass in platinum crucibles. By determining the activity coefficients of the several oxides present during the melting process and the corresponding activity coefficients in platinum, the minimum partial pressure of oxygen that must be maintained to prevent crucible attack can be determined.

Subsequent phases of the particulate damage study will consist of reducing to practice the theoretical results obtained in the thermodynamics study. Although various methods of detection have been and are being investigated, the most reliable test to date is subjection of the glass to a high power laser pulse. In view of this, a laser testing facility, previously constructed using equipment furnished by Redstone Arsenal, is being adapted to this end.

Work accomplished in the particulate damage phase of this contract is briefly as follows:

1.) A literature search for activity coefficients of oxides in laser glasses and corresponding activities in platinum has been completed and data obtained have been evaluated.

2.) Samples of laser glass have been sent to Battelle Memorial Institute of Columbus, Ohio, for experimental determination of some activity coefficients. The purpose of this is verification of the theoretical approach taken.

3.) The high power Q-switched laser alluded to above is in the final stages of modification.

Surface damage, the second form of damage studied under this contract, is being approached from two complementary directions. The first of these involves the plasma created by the laser pulse at the damage site. Evidence obtained by various investigators implies that this plasma is a cause of damage. In view of this, one phase of our surface damage program involves chemical treatments of glass surfaces. These treatments are designed either to strengthen the surface against the damaging plasma or to eliminate the plasma.

The second of our two approaches to surface damage takes the form of an investigation of its causes. This investigation looks not only at the plasma aspect of damage mentioned above, but also explores other proposed damage mechanisms involving creation of shock waves inside the glass. High speed holography is being used to detect any shock waves created by the passage of a laser beam through a glass sample.

Work on the surface damage study has been directed thus far toward equipment modification and study of experiments which will be conducted. Consequently, no numerical data have yet been obtained. Work completed is as follows:

1.) A ruby laser has been received, assembled, and checked out. This is the laser which is being used to construct high speed holograms.

2.) Modification of the Nd glass laser to be used for damaging glass samples has been completed. This modification involved replacement by a Kerr cell of the rotating mirror previously used for Q-switching.

3.) The two lasers alluded to in (1) and (2) have been interconnected to allow timing of the ruby pulse relative to the Nd pulse to within ± 3 ns.

4.) Holograms of fringe patterns in a transparent plastic block under stress have been made.

5.) Construction of the laser to be used in the chemical treatment phase of surface damage has been completed. This laser is in the final stages of beam characterization.

6.) A study of several chemical treatments to which glass surfaces under investigation will be subjected has been completed.

Work during the second half of this fiscal year will involve further modification of the Nd glass laser to be used in the holographic studies. The reasons for this are twofold. First, the Kerr cell used for Q-switching exhibits a tendency to damage and will have to be replaced by a Pockels cell. Second, if reliable results are to be obtained, the damaging laser beam must be well characterized. Because of this the glass laser will be modified so that it emits a diffraction limited beam. This beam will be used not only in the holographic study, but also in the later stages of the chemical treatment investigation.

2. PARTICULATE DAMAGE STUDY

2A. PRACTICAL APPLICATION OF THERMODYNAMICS TO LASER GLASS MELTING

1. INTRODUCTION

The goal of this phase is to determine the thermodynamic activities of oxides in laser glass melts of practical importance and of the corresponding metals in platinum. Table 1 lists the laser glasses of practical importance being melted throughout the world. During the first half of the 1971 fiscal year, a literature search has been conducted covering the following main areas:

1. activities of oxides in binary and ternary systems;
2. activities of metals in platinum;
3. general data on similar systems and methods of estimating thermodynamic activities, free energies of formation, and heats of formation.

This is the first attempt of gathering and consolidating activities of oxides and of platinum alloys to appear in the literature. The empirical studies to be carried out at Battelle have been started but no results have been obtained to date. Because only one glass system is being studied empirically, substantial effort has been devoted to estimating the thermodynamic activities in the other laser glass compositions. Determination of the thermodynamic activities is divided into the following categories: direct empirical measurement of activities; estimations based upon experimental observations; and estimations based upon more theoretical properties such as electronegativity.

TABLE 1
LASER GLASS COMPOSITIONS OF COMMERCIAL INTEREST

Glass No.	Component	Mole Fraction
1	SiO_2	0.785
	BaO	0.014
	Na_2O	0.080
	K_2O	0.112
	Nd_2O_3	0.010
2	SiO_2	0.719
	Al_2O_3	0.014
	Sb_2O_3	0.002
	BaO	0.014
	ZnO	0.017
	Li_2O	0.023
	Na_2O	0.068
	K_2O	0.113
	Nd_2O_3	0.010
3	SiO_2	0.791
	TiO_2	0.004
	Sb_2O_3	0.005
	BaO	0.018
	PbO	0.006
	Na_2O	0.045
	K_2O	0.126
	Nd_2O_3	0.006
4	SiO_2	0.480
	B_2O_3	0.174
	Al_2O_3	0.073
	As_2O_3	0.073
	BaO	0.255
	Nd_2O_3	0.013

TABLE 1
LASER GLASS COMPOSITIONS OF COMMERCIAL INTEREST (cont'd)

Glass No.	Component	Mole Fraction
5	SiO_2	0.593
	Al_2O_3	0.025
	K_2O	2.12×10^{-7}
	CeO_2	1.6×10^{-3}
	Fe_2O_3	9.4×10^{-8}
	Na_2O	9.42×10^{-7}
	Li_2O	0.275
	Nd_2O_3	0.005
	CaO	0.100
6	SiO_2	0.762
	Al_2O_3	0.017
	Sb_2O_3	0.002
	BaO	0.023
	ZnO	0.017
	Li_2O	0.023
	Na_2O	0.077
	K_2O	0.080
	Nd_2O_3	0.010
7	SiO_2	0.792
	Al_2O_3	0.010
	BaO	0.022
	ZnO	0.012
	Li_2O	0.022
	Na_2O	0.080
	K_2O	0.053
	Nd_2O_3	0.007
8	SiO_2	0.773
	Sb_2O_3	0.002
	BaO	0.113
	Na_2O	[illegible]
	K_2O	[illegible]

II. LITERATURE SEARCH

A literature search is summarized in the bibliography attached as Appendix I.

The melts of interest as listed in Table 1, are basically ternary oxides with two to six additional oxides added in small quantities, from 1.5 to 9 weight percent. The relative abundance of binary oxide data is caused by the steel industry's interest in slags as well as glass industry's interest in immiscible glass systems.

Data on the activities of metals in platinum is not very abundant. The main user of platinum is the oil refining industry where it is used as a catalyst. In this low temperature application, information on the thermodynamics of platinum-metal systems is not critical. The amount of glass melted in platinum containers or in contact with platinum within the glass industry is small in both volume and dollar value of glass sold. Although it is highly critical in optical glass applications, this sole application cannot support the magnitude of research which has been given to oxide systems or to other metal systems. Several of the references listed in this section of Appendix I are empirical observations which assist in estimating the activity of metals in dilute solutions in platinum.

In order to use the information within the literature, and the data which will be generated within the empirical measurement of activities within one glass-platinum system, several methods of estimation have been examined in order to proceed from the level of information presented

directly in the literature to the level of information which would assist in the understanding of melting laser glasses in platinum crucibles. When attempting to estimate the activity of one metal within platinum, it is at times useful to know the activity of other metals in platinum or in metals similar to platinum. As a result, general data on activities and energies of formation are relevant to this study. Because some of the general data sources are texts which also include methods of estimating thermodynamic functions, the two categories have been placed together in the bibliography.

III. DETERMINATION OF ACTIVITIES

A. Activities of Oxides in Laser Glasses

1. Method used for Estimating Activities in Oxides

Although a substantial amount of data is available in the literature for oxide systems, the work is generally limited to simple binary alkali silicates or complex glasses and slags whose compositions do not approach that of the common laser glasses.

In estimating the activities, a complex glass composition of interest has been approached as a series of several binary systems. Each binary system consists of a network modifier and a network former. The calculated activities are tabulated in Table 2. Appendix II presents a sample calculation.

Activities of oxides were also calculated in binary silicates from free energy of formation data (Ref. 3.1.28). Table 3 shows the systems studied. Table 4 shows a summary of the calculated activities and activity coefficients. A sample calculation is given in Appendix III. These calculated values agree well with the activities presented in the literature. Free energy of binary silicate compounds have no doubt been used to calculate some of the values of activities across the binary system reported by Charles (Refs. 1.1.3, 4, 5, and 6) and others.

2. Estimating Activities of Oxides from Ternary Phase Diagrams

When the phase diagrams of a ternary system is known together with the activities of species at various points within the phase diagram, the isoactivity lines can then be estimated. Sufficient

TABLE 2

ACTIVITY OF METAL OXIDES IN SILICA AT 1533°K

Glass No.	Component	X_{MeO_x}	γ_{MeO_x}	a_{MeO_x}	Ref.
1	SiO_2	0.785	0.79	0.62	1.1.3.
	BaO	0.014			
	Na_2O	0.080	$1.6X10^{-7}$	$1.3X10^{-8}$	1.1.3.
	K_2O	0.112	$2.0X10^{-11}$	$2.2.X10^{-12}$	1.1.3.
	Nd_2O_3	0.010			
2	SiO_2	0.719	0.45	0.32	1.1.3.
	Al_2O_3	0.014			
	Sb_2O_3	0.002			
	BaO	0.014			
	ZnO	0.017			
	Li_2O	0.023	$1.6X10^{-5}$	$3.7X10^{-6}$	1.1.3.
	Na_2O	0.068	$1X10^{-7}$	$6.8X10^{-9}$	1.1.3.
	K_2O	0.113	$6.3X10^{-11}$	$7.1X10^{-12}$	1.1.3.
	Nd_2O_3	0.010			
3	SiO_2	0.791	0.87	0.62	1.1.3.
	TiO_2	0.004			
	Sb_2O_3	0.005			
	BaO	0.018			
	PbO	0.006			
	Na_2O	0.045	$6.3X10^{-8}$	$2.8X10^{-9}$	1.1.3.
	K_2O	0.126	$1X10^{-11}$	$1.26X10^{-12}$	1.1.3
	Nd_2O_3	0.006			
4	SiO_2*	0.480	1.1	0.53	1.1.17.
	B_2O_3	0.174			
	Al_2O_3	0.073			
	As_2O_3	0.005			
	BaO*	0.255	.15	$9.4X10^{-2}$	1.1.17.
	Nd_2O_3	0.013			

TABLE 2 (cont'd)

Glass No.	Component	X_{MeO_x}	γ_{MeO_x}	a_{MeO_x}	Ref.
5	SiO^2	0.593	0.63	0.37	1.1.3.
	Al_2O_3	0.025			
	K_2O	$2.12X10^{-7}$	$6.3X10^{-9}$	$1.3X10^{-}$	1.1.3.
	CeO	$1.6X10^{-3}$			
	Fe_2O_3	$9.4X10^{-8}$			
	Na_2O	$2.42X10^{-7}$	$6.3X10^{-7}$	$1.5X10^{-15}$	1.1.3.
	Li_2O	0.275	$2.0X10^{-5}$	$5.5.X10^{-6}$	1.1.3.
	Nd_2O_3	0.005			
	CaO*	0.100	$7.6X10^{-2}$	$7.6X10^{-3}$	1.1.17.
6	SiO_2	0.762	0.40	0.30	1.1.3.
	Al_2O_3	0.017			
	Sb_2O_3	0.002			
	BaO	0.023			
	ZnO	0.017			
	Li_2O	0.023	$3.68X10^{-5}$	$3.7X10^{-7}$	1.1.3.
	Na_2O	0.077	$6.3X10^{-8}$	$4.9X10^{-9}$	1.1.3.
	K_2O	0.080	$1X10^{-10}$	$8X10^{-12}$	1.1.3.
	Nd_2O_3	0.010			
7	SiO_2	0.792	1.07	0.85	1.1.3.
	Al_2O_3	0.010			
	BaO	0.022			
	ZnO	0.012			
	Li_2O	0.022	$1.6X10^{-5}$	$3.5X10^{-7}$	1.1.3.
	Na_2O	0.080	$3.2X10^{-8}$	$2.5X10^{-9}$	1.1.3.
	K_2O	0.053	$1X10^{-11}$	$5.3X10^{-13}$	1.1.3.
	Nd_2O_3	0.007			
8	SiO_2	0.773	1.24	0.96	1.1.3.
	Sb_2O_3	0.002			
	BaO	0.113			
	Na_2O	0.100	$1X10^{-6}$	$1X10^{-7}$	1.1.3.
	K_2O	0.013	$3.2X10^{-11}$	$4.1X10^{-13}$	1.1.3.

*This data for 1673°K

TABLE 3

FREE ENERGY DATA OF BINARY SILICATES

	ΔF° (Cal.) 1533°K (G.Mole)
$BaO(c) + 2SiO_2(c) = BaSi_2O_5(c)$	-41,300
$CaO(c) + SiO_2(c) = CaSiO_3$	-21,050
$PbO(red) + SiO_2(c) = PbSiO_3(c)$	- 4,500 (est.)
$Li_2O(c) + 2SiO_2(c) = Li_2Si_2O_5(gl)$	-39,200 (est.)
$MgO(c) + SiO_2(c) = MgSiO_3(c)$	- 7,650
$K_2O(c) + 4SiO_2(c) = K_2Si_4O_9(gl)$	-81,000
$Na_2O(c) + 2SiO_2(c) = Na_2Si_2O_5(gl)$	-59,400
$2ZnO(c) + SiO_2(c) = Zn_2SiO_4(c)$	- 7,400

TABLE 4

SUMMARY OF ACTIVITIES CALCULATED USING ΔF_f°'s FROM TABLE 3

MeO_x	X_{MeO_x}	Log a_{MeO_x}	a_{MeO_x}	γ_{MeO_x}
BaO	0.33	- 5.86	1.38×10^{-6}	4.18×10^{-6}
CaO	0.50	- 3.00	1×10^{-3}	2×10^{-3}
PbO	0.50	- 0.613	2.43×10^{-1}	4.86×10^{-1}
Li_2O	0.33	- 5.59	2.57×10^{-6}	7.79×10^{-6}
MgO	0.50	- 1.09	8.13×10^{-2}	1.63×10^{-1}
K_2O	0.20	-11.54	2.88×10^{-12}	1.44×10^{-11}
Na_2O	0.33	- 8.47	3.39×10^{-9}	1.03×10^{-8}
ZnO	0.66	- 0.53	2.95×10^{-1}	4.47×10^{-1}

information may be available to pursue this technique during the next quarter. Charles (Ref. 1.1.3.) gives good data on binary alkali silicates while Chipman, et.al. (Ref. 1.3.1.) has presented the technique as have others (Refs. 1.2.5.; 1.1.23; and 1.2.1.).

B. Activities of Metals in Platinum

In the last quarter the estimation of the activities of metals in Pt received the greatest attention. Table 5 represents the best estimates made to date. Further improvements will be made in the second half of the 1971 fiscal year. Actual measurement carried out at Battelle will be a most valuable asset.

The activity of the various metals in Pt appearing in Table 5 are taken at a high Pt content. The mole fraction of the metal in Pt (X_M^{Pt}) corresponds to the point of "failure". "Failure" would occur: (1) if a liquid phase was formed; (2) if an intermetallic compound formed; or (3) if a large increase in the Pt lattice parameter occurred on addition of the metal. Most of the metal-platinum phase diagrams of interest are not available. From those which are available, ~ 1 at.% of the metal in Pt can be dissolved in the Pt before failure would be expected.

1. Estimations Based Upon Direct Measurement of Activities and Upon Experimental Observations

The values presented in Table 5 are derived from estimates calculated from Appendix IV. Direct measurement of activities and empirical observations are used where available. Estimates based on theoretical models have not been added at this time. In the next half year the Battelle empirical study will be completed; it is expected to

TABLE 5

SUMMARY OF ACTIVITIES OF METALS IN PLATINUM AT 1533°K

Component	Activity
Calcium	10^{-4}
Lithium	10^{-6}
Aluminum	10^{-8}
Barium	10^{-9}
Titanium	10^{-5}
Iron	10^{-3}
Antimony	10^{-3}
Cerium	10^{-8}
Sodium	10^{-6}
Potassium	10^{-6}
Boron	10^{-8}
Arsenic	10^{-3}
Neodymium	10^{-8}
Lead	10^{-3}
Zinc	10^{-3}
Silicon	10^{-5}

provide activities of Li, Ca, Al, and Si. Other elements in small amounts may also be detected. With at least these four activities, the theoretical methods of estimating activities can be reliably tested.

2. Estimations Based Upon Theoretical Models

Several authors have attempted to correlate various empirical observations using different chemical models. The ultimate in chemical modeling would predict all desired variables from fundamental principles. The field of estimating thermodynamic data, however, is not graced with such a universal model to date. Several authors have presented chemical models which could be used to predict heats of formation of chemical compounds. Thermodynamic activities can be calculated from this variable, as is done in Appendix IV. In several cases their ultimate goal was not to estimate heats of formation but to estimate some other chemical property. Pauling (Ref. 3.2.3.) was interested in finding a fundamental variable which would quantitatively describe the attraction of atoms for bonding electrons. B. W. Mott (Ref. 3.2.2.) has used an expression related to the heat of formation to predict whether or not a binary alloy system formed an immiscibility gap. P. Goldfinger has found an empirical ratio which has been used principally to estimate dissociation energies of heterogeneous diatomic gas molecules. During the past quarter, an attempt has been made to determine if these three chemical models could be used to estimate heats of formation of the platinum compounds of interest. Varley and Kubaschewski have developed methods for estimating heats of formation directly. Their work has also been reviewed to determine if their estimating methods would reliably predict the heats of formation of the platinum compounds of interest.

a. Electronegativity

Electronegativity is defined as a measure of the attraction of an atom in a molecule for bonding electrons. Pauling (Ref. 3.2.3.) determined electronetativities for fourteen elements using bond dissociation energy data of gaseous diatomic molecules. For the other elements of interest, he was able to calculate electronegativities from enthalpies of formation using the equation:

$$-\Delta H_f^\circ[AB_n(s)] = 23.06n(E_A-E_B)^2 \qquad \text{Eq. 1}$$

where ΔH_f° is the enthalpy of formation of compound AB_n(solid) and E_A and E_B are the electronegativities of elements A and B.

Our objective was to use Pauling's electronegativities to determine the enthalpies of formation of various platinum compounds. Table 6 gives a summary of ΔH_f° values calculated from Pauling's electronegativities compared with measured values reported in the literature.

For some compounds large discrepancies exist between observed and calculated heats of formation. The reasons for these discrepancies are listed below with some possible alternatives to assist in making Pauling's equation more applicable to the alloy systems being studied.

(1) The electronegativity of an element is not completely independent of the element being bonded as would be the ideal case. The value of the electronegativity assigned to an element does depend upon its valence state and upon the family of compounds from which the electronegativities have been determined. Pauling's values of electronegativities were determined mainly from heats of formation of halides and hydrides. It is desired to [illegible] heats

of formation of metallic platinum compounds where the bonding is quite different from that encountered in halides and hydrides. For example, Pauling calculated the electronegativity of beryllium from the compounds: $BeCl_2$, $BeBr_2$, BeI_2, and BeS and obtained an electronegativity value for beryllium of 1.44, 1.47, 1.47 and 1.44. Rounding these values to two significant figures, the electronegativity value assigned to Be was 1.5. If the heat of formation of a Be-Pt compound is desired, using the electronegativity values of the beryllium halides and sulfide of 1.5 may be erroneous.

A possible solution may be to recalculate a new electronegativity value based upon the heats of formation of known platinides. Pauling's equation has worked quite well in providing an empirical relation between heats of formation and the slowly varying parameter electronegativity within certain families of compounds. Just as the heat of formation of the alkali chlorides decreases proceeding from Li to Cs, one may also expect the heat of formation of the platinides to decrease going from lithium to cesium. At high platinum concentrations the alkali metals may be expected to donate their valence electron to the platinum lattice as they do to chlorine in the chlorides. This is to say that although the heats of formation of platinides may not correspond to a value calculated from the current electronegativity table based upon the formation of halides, the heats of formation of platinides may be expected to vary in a continuous fashion within the periodic table as do the halides. The empirical work at Battelle will give a heat of formation of the platinides of: Li, Ca, Al, and Si. With these values one could recalculate an electronegativity for platinum which may be more reasonable in the platinide systems of interest. With

TABLE 6

COMPARISON OF HEATS OF FORMATION CALCULATED FROM ELECTRONEGATIVITIES WITH MEASURED VALUES

Compound	n	ΔH_f° (in kcal/mole Measured (1)	Pauling	Allred-Rochow	Sanderson
Ag_3Sb	3	5.5	1.6	31.9	15.2
AlAs	3	27.8	24.9	24.9	67.5
$AuSb_2$	2	4.7	5.6	21.3	10.2
$AuPb_2$	2	1.5	16.5	35.6	3.9
$AuCu_3$	3	6.5	17.3	7.5	0
Ba_2Sn	4	90.0	92.0	111.4	109.4
$BaPb_3$	2	42.0	37.3	90.13	53.7
Ca_3Sb_2	6	174.0	152.0	166.8	176.4
$CaSi_2$	2	36.0	37.3	37.3	21.3
Ca_2Pb	4	51.5	58.8	155.4	83.0
$CaZn_5$	5	33.0	41.4	56.4	73.6
$CeAl_4$	4	39.0	14.7	26.8	35.4
CoSi	1	24.0	0.2	0.9	1.7
$CoSi_2$	2	24.6	0.5	1.8	3.4
Cu_2Sb	2	3.0	1.0	5.6	9.3
$CuAl_2$	2	9.5	7.4	1.0	1.8
$MgCu_2$	2	8.0	22.5	9.3	4.7
Mg_2Cu	2	6.8	22.5	9.3	4.7
FeAl	3	12.2	6.3	0	0.3
Li_3Sb	3	43.0	76.1	83.5	122.1
Li_2Sn	2	27.3	37.2	46.0	61.9
Na_2Se	2	82.0	125.0	132.9	167.8
$NiAl_3$	3	36.0	6.2	1.6	0.3
Mg_2Ni	2	15.6	16.6	9.4	0.1
$MgNi_2$	2	16.8	16.6	9.4	0.1
$BeCu_2$	2	11.25(2)	7.4	1.0	0.8
Be_2Cu	2	11.0(2)	7.4	1.0	0.8
$MgCo_2$	2	5.55	16.6	7.4	0.1
$MgCu_2$	2	7.2	22.6	9.4	4.7
MgCu	2	6.0	22.6	9.4	4.7
Th^2Cu_2	2	12.84(2)	16.6	9.4	8.9

NOTES: (1) Values from Ag_3Sb to $NiAl_3$ from Ref. 3.1.19; Values from Mg_2Ni to $ThCu_2$ from Ref. 3.1.12.

(2) These values are ΔF_f°

this new value for the electronegativity of platinum, one could then calculate the heats of formation of other platinides of interest, for example the platinides of: Na, K, Mg, Sr, and B. Some feeling for the success of such as estimation will be more evident when the experimental work at Battelle is completed and more thermodynamic data is available.

(2) Pauling's main intention in deriving the electronegativity scale was not to estimate heats of formation but to define a parameter which varied systematically across the periodic table and described quantitatively the attraction of an atom for bonding electrons. As a result, Pauling's equation using the heat of formation to derive electronegativities transforms a highly varient parameter, the heat of formation, to one that is less sensitive, the electronegativity scale. A small variation in electronegativity therefore corresponds to a large variation in the heat of formation.

Pauling also attempted to relate the bond dissociation energies of heterogeneous diatomic gas molecules to the bond dissociation energies of the corresponding homonuclear diatomic gas molecules using the expression:

$$D[AB(g)] = 1/2\ \{D[A_2(g)] + D[B_2(g)]\} + 23n(E_A-E_B)^2 \qquad \text{Eq. 2}$$

An empirical fit was also found using the relation:

$$D[AB(g)] = \{D[A_2(g)] \cdot D[B_2(g)]\}^{1/2} + 30n\ (E_A-E_B)^2 \qquad \text{Eq. 3}$$

where D[AB(g)] is the dissociation energy of AB(gas) and corresponds to the reaction $AB(g) \rightarrow A(g) + B(g)$, D[AB(g)] may be more reliably predicted from Pauling's electronegativities using Equation 2 than

$\Delta H_f^\circ[AB_n(s)]$ using Equation 1. D[AB(g)] is certainly less sensitive to the electronegativity expression of Pauling than $\Delta H_f^\circ[AB_n(s)]$. P. Goldfinger has found an empirical ratio which remains constant throughout a family of compounds and which relates $\Delta H_f^\circ[AB(s)]$ from D[AB(g)]. It is discussed further in a later section.

(3) In ionic and covalent solids the value of n appearing in Pauling's equation is usually quite straightforeward to assign: $n_{Na} = 1$; $n_{Ca} = 2$; $n_{Al} = 3$ and $n_{Si} = 4$ in the corresponding halides or oxides. As a bond becomes more metallic, the n value to be assigned becomes more nebulous. Should n equal 2 or 4 in Mg_2Ni? Table 6 shows that n = 2 gives good agreement to the observed $\Delta H_f^\circ(Mg_2Ni)$ although n = 4 gives better agreement to the observed value of $\Delta H_f^\circ(Mg_2Sn)$ (Ref. 3.1.2.).

The activity of metals in Pt are desired at the Pt-rich side of the binary phase diagram. When more reliable data are available from the empirical Battelle study, a system for evaluating n may become apparent. Rather than examining heats for reactions such as:

$$LiPt_2 \rightarrow Li + 2Pt$$

it may be more meaningful to look for trends in $\overline{H}_{Li}^{xs}$ for the reaction:

$$Li(\text{pure}) \rightarrow Li\ (\text{in Pt soln, lim } x_{Li} \rightarrow 0) \qquad \text{Rx. 1}$$

$\overline{H}_{Li}^{xs}$ is approximately equal to $\overline{F}_{Li}^{xs}$ because the entropy for the above reaction is small by comparison. Therefore:

$$\overline{H}_{Li}^{xs} \simeq \overline{F}_{Li}^{xs} = RT \ln \gamma_{Li}(\text{in Pt soln, lim } x_{Li} \rightarrow 0)$$

In the latter case Li (in Pt sol'n, lim $x_{Li} \rightarrow 0$) is expected to have an n_{Li} value of 1. Similarly, Ca(in Pt sol'n, lim $x_{Ca} \rightarrow 0$) is expected

to have an n_{Ca} value of 2. In these cases, donation of the corresponding valence electrons to the Pt matrix is highly probable. Knowing $\overline{H}^{xs}_{Li}$ for Li, Mg, Al, and Si from the experimental Battelle study will be essential in evaluating this adoption of the Pauling equation.

b. Electronegativity Tables of Allred and Rochow and of Sanderson

Linus Pauling's electronegativity values are calculated from the empirically observed bond energies and heats of formation of compounds. The electronegativity values of Allred and Rochow and of Sanderson are derived from more fundamental parameters (Ref. 3.2.5.). The electronegativity values of Allred and Rochow are equated to the Coulomb force at the covalent radius of the monoatomic gas of the elements. Sanderson proposed a scale of electronegativities based upon the relative compactness of the atoms. The resultant electronegativity scales vary smoothly with atomic number.

The three scales of electronegativities were used to calculate the heats of formation of several metallic compounds using Pauling's equation [Eq. (1)] and are presented in Table 6. Of the three sets of values, those calculated using Pauling's scale are the closest to the measured values which is not surprising since his values have been based upon empirical thermodynamic data. As a result Pauling's electronegativity scale has been used in our study to date.

c. Mott's Immiscibility Criterion

Mott (Ref. 3.2.2.) proposed a model for predicting immiscibility in metal systems which was over 90% effective. He introduced a correction factor based on Pauling electronegativities

to the expression for immiscibility of Hildebrand (Ref. 3.1.40.). It was hoped that using Mott's expression for ΔH_f° would give calculated enthalpies which would more closely agree with measured values. The equation for ΔH_f° derived from Mott's work is:

$$\Delta H_f^\circ[AB_n(s)] = -23{,}060n\,(E_A - E_B)^2 + (1/2)(V_A - V_B)\left[\left(\frac{\Delta E_v}{V}\right)_A^{1/2} - \left(\frac{\Delta E_v}{V}\right)_B^{1/2}\right]^2 \quad \text{(cal/mole of } AB_n\text{)}$$

where V_A and V_B = atomic volumes of components A and B

ΔE_v & ΔE_v = heats of vaporization

E_A & E_B = Pauling's electronegativities

n = number of Pauling bonds.

Table 7 gives a comparison of the measured enthalpies of formation of selected intermetallic compounds vs. the enthalpies calculated from Pauling's electronegativities and finally the enthalpy calculated from Pauling's model with Mott's term.

The results were that the Mott factor, being a large positive number, gave in some cases a positive enthalpy of formation.

The conclusion was that the use of Mott's term was not justified in these estimations.

d. The Goldfinger Ratio: α

P. Goldfinger has found an empirical relationship which may be useful in estimating heats of formation for the Pt alloys of interest. For a given family of compounds, the ratio $\alpha = \Delta H_{at.}^\circ\,[AB(s)]/D[AB(g)]$ appears to be constant. $\Delta H_{at.}^\circ\,[AB(s)]$ is the

TABLE 7

COMPARISON OF HEATS OF FORMATION CALCULATED FROM PAULING'S ELECTRONEGATIVITIES AND MOTT'S CORRECTION WITH MEASURED VALUES IN Kcal PER MOLE

Compound	n	ΔH_f° (Kcal/mole)			
		Measured	Pauling	Mott Correction Term	Adjusted Value Pauling and Mott
Ag_2Se	2	- 5.0	-19.5	+ 9.7	- 9.7
Ag_2Te	2	- 7.0	-11.5	+18.1	+ 6.6
Ag_3Sb	3	- 5.5	- 1.55	+ 7.8	+ 6.5
$AuSb_2$	2	- 4.65	- 5.6	+16.3	+10.7
AuSn	1	- 6.4	- 5.7	+ 8.4	+ 2.7
$AuSn_2$	2	- 5.7	-11.5	+ 8.4	- 3.1
$AuPb_2$	2	- 1.5	-16.6	+24.6	+ 8.0
CoSe	1	-10.0	-13.0	+56.2	+43.2
CoTe	1	- 9.0	- 8.3	+79.6	+71.3
Co_5As_2	10	-26.6	-20.8	+26.5	+ 5.7
Co_2As	5	-13.5	-10.5	+26.5	+16.0
Co_3As_2	10	-27.2	-20.7	+26.5	+ 5.8
CoAs	5	-13.6	-10.5	+26.5	+16.0
Co_2As_3	15	-34.4	-31.0	+26.5	- 4.5
$CoAs_2$	10	-22.0	-10.5	+26.5	+16.0
CoSb	5	-10.0	- 7.0	+53.9	+46.9
$CoSb_2$	10	-13.2	-14.5	+53.9	+39.4

enthalpy of atomization of solid compound AB corresponding to the reaction: $AB(s) \rightarrow A(g) + B(g)$. $D[AB(g)]$ is the bond dissociation energy of gaseous AB corresponding to the reaction: $AB(g) \rightarrow A(g) + B(g)$.

The reaction of atomization of AB(s) can be expressed in two sequential reactions as follows:

$$AB(s) \rightarrow A(s) + B(s) \rightarrow A(g) + B(g)$$

and the corresponding enthalpy of atomization can be expressed as:

$$\Delta H^{\circ}_{at.}\ [AB(s)] = -\Delta H^{\circ}_{f}[AB(s)] + \Delta H^{\circ}_{at.}\ [A(s)] + \Delta H^{\circ}_{at.}\ [B(s)]$$

where $\Delta H^{\circ}_{f}\ [AB(s)]$ is the heat of formation of solid AB, the desired parameter.

Bond dissociation energies have been used to determine part of L. Pauling's table of electronegativities using the expression:

$$D[AB(g)] = 1/2\ \{D[A_2(g)] + D[B_2(g)]\} + 23n\ (E_A - E_B)^2$$

where the E_i's are the electronegativities of the corresponding elements A and B.

Using the two expressions, the Goldfinger ratio expected to be constant within a family of compounds becomes:

$$o = \frac{\Delta H^{\circ}_{f}[AB(s)] + \Delta H_{at.}\ [A(s)] + \Delta H_{at.}\ [B(s)]}{1/2\ \{D_o[A_2(g)] + D_o[B_2(g)]\} - 23n\ (E_A - E_B)^2}$$

Heats of atomization of the elements and bond dissociation energies of homonuclear diatomic gases are known and appear in the literature. Ref. 3.1.31. provides one such listing. One is therefore left with $\Delta H^{\circ}_{f}[AB(s)]$ as the only unknown in the "o" ratio. Unknown values can be matched with known values if the two compounds can be considered belonging to the same family.

Table 8 shows the variance of σ within several families of compounds evaluated by Goldfinger. To date, the relationship has not been fully investigated for intermetallic compounds. Preliminary evaluation shows that it may be quite good. Although it contains Pauling's electronegativity term, it is far less sensitive to discrepancies in values of electronegativities than the more direct Pauling relationship:

$$\Delta H_f^\circ[AB(s)] = -23n\,(E_A - E_B)^2 \quad \text{(Kcal/mole)}$$

As with the Pauling calculations, heats such as $\Delta H_f^\circ[LiPt(s)]$ will probably be replaced by $\overline{H}^{xs}_{Li}$ (in Pt sol'n, lim $x_{Li} \to 0$). This heat corresponds to the reaction:

$$Li(\text{pure solid}) \rightarrow Li(\text{Pt solid sol'n, lim of } x^{Pt}_{Li} \to 0).$$

$\overline{H}^{xs}_{Li}$ can be approximated from $\overline{F}^{xs}$:

$$\overline{H}^{xs} \approx \overline{F}^{xs} = + RT \ln \gamma_{Li}(\lim x_{Li} \to 0).$$

Assuming Henry's Law holds to 1 atomic % solute: $\gamma_{Li}(\text{at/im } x^{Pt}_{Li} \to 0) = \gamma_{Li}(\text{at } x^{Pt}_{Li} = 0.01) = [a^{Pt}_{Li}\ (\text{at } x^{Pt}_{Li} = 0.01)]/10^{-2}$. The current estimates of $a^{Pt}_{M}(x^{Pt}_{M} = 0.01)$ appear in Table 5.

The accuracy of the method, as can be seen from Table 8, is dependent upon which compounds are considered a family and upon which known ΔH_f°'s are matched to desired estimated values. The experimental runs at Battelle to be carried out in the next half year are expected to furnish $\overline{H}^{xs}_{Li}$(in Pt), $\overline{H}^{xs}_{Ca}$(in Pt), $\overline{H}^{xs}_{Al}$(in Pt), $\overline{H}^{xs}_{Si}$(in Pt) as well as others. One would expect to obtain quite good agreement in assuming Li, Na, and K to be in the same family of Pt compounds. Knowing the value of x_{Li} and σ_{Na}, σ_K could then be calculated.

TABLE 8

COMPARISON OF P. GOLDFINGER'S "d" PARAMETER FOR SEVERAL KNOWN COMPOUNDS

Compound	"d"
LiCl	0.71
NaCl	0.78
KCl	0.77
RbCl	0.74
CsCl	0.75
NaF	0.85
NaCl	0.78
NaBr	0.79
NaI	0.85
BeO	1.32
MgO	1.42
CaO	1.36
SrO	1.17
BaO	0.95
BeS	-
MgS	>1.68
CaS	1.54
SrS	1.45
BaS	1.19
GeTe	0.75
SnTe	0.83
PbTe	1.07
BF	0.51
AlF	0.54

e. Method of Estimation Used by Varley

J. H. O. Varley has derived an expression for the heats of formation of metallic compounds (Ref. 3.1.24, p. 900). It takes into account atomic sized differences, referred to as the strain energy term, and electronic interactions, referred to as the electrochemical factor. Varley's effort is an attempt to relate fundamental properties such as atomic radius, total number of electrons, and ground state and ionization energies to the heats of formation of compounds.

Table 9 compares values of heats of formation calculated from his model with those experimentally observed. Considering that his approach is so fundamental, agreement between heats from his model and observed heats is quite good. As can be seen from the table and as Varley points out in his paper, agreement is within $\pm$ 2 kcal./g.a. when the elements making up the compound are close to one another in the Periodic Table. (Exceptions are AuZn and AuCd.) When the elements are two or more Groups apart in the Periodic Table, errors of $\pm$ 5 to 15 kcal./g.atom appear common: CuSn, CuPb, AgSn, AgPb, AuSn, ZnMg, and ZnAl.

Because it is desired to estimate heats of formation of compounds of platinum with elements far removed from platinum in the Periodic Table, Varley's method is not accurate enough to be considered in this application.

f. ΔH_f° Versus ΔV

Kubaschewski (Ref. 3.1.19.) showed that the heat of formation (ΔH_f°) of a compound can be estimated from the change in volume (ΔV) that occurs when the two elements react to form the compound. His

plot of $-\Delta H_f^\circ$ vs. $-\Delta V$ gave a smooth curve for many binary compounds which included intermetallic alloys, oxides and halides. An accuracy of $\pm$ 6 kcal./g.a. is assigned.

Table 8 gives a summary of the measured heats of formation for a number of binary metallic compounds as reported by Kubaschewski. These values are compared with the ΔH_f° values estimated from Kubaschewski's curve of ΔH_f° vs. ΔV. When the estimated $-\Delta H_f^\circ$ is less than 10 kcal/g.atom, Table 8 shows that agreement between calculated and observed values is good. When the estimated $-\Delta H_f^\circ$ is greater than 10 kcal/g.atom, large discrepancies appear.

Examining the empirically derived estimates presented in Appendix IV, most of the platinum compounds of interest have $-\Delta H_f^\circ$'s greater than 10 kcal/g.atom; this method of estimation does not appear to be applicable in this case.

TABLE 9

ESTIMATED AND CALCULATED HEATS OF FORMATION
TAKEN FROM J. H. O. VARLEY (REF. 3.1.24.)

System		ΔH_f° (kcal/g.atom) for $A_{0.5}B_{0.5}$		
Acceptor	Donor	Calculated	Observed	Calculated Minus Observed
Cu	Zn	- 2.4	- 2.5	+ 0.1
Cu	Cd*	+ 0.06	+ 0.05	+ 0.01
Cu	Sn*	+ 4.72	- 1.15	+ 5.8
Cu	Pb*	+ 7.2	+ 1.89	+ 5.3
Cu*	Ag	+ 1.25	+ 0.8	+ 0.4
Ag	Zn	- 2.36	- 1.7	- 0.7
Ag	Cd	- 2.02	- 1.3	- 0.7
Ag*	Sn	+ 0.69	+ 1.37	- 0.7
Au	Cu	+ 1.56	- 0.9	+ 2.5
Au	Ag	- 1.70	- 0.945	- 0.8
Au	Zn	-14.5	- 5.5	- 9.0
Au	Cd	-16.4	- 3.9	-12.5
Au	Sn	-14.4	- 4.0	-10.4
Zn	Mg*	+ 0.865	- 4.27	+ 5.1
Zn	Al*	+ 0.050	+ 0.56	- 0.51
Cd	Zn	+ 0.750	+ 0.53	+ 0.22
Hg	Zn*	- 0.690	+ 0.17	- 0.86
Hg	Cd	- 1.89	- 1.10	- 0.79
Pb	Sn*	+ 0.115	+ 0.360	- 0.24

*Denotes liquid alloy

TABLE 10

ESTIMATED AND CALCULATED HEATS OF FORMATION
TAKEN FROM O. KUBASCHEWSKI (REF. 3.1.19)

Compound	ΔH_f° (kcal/g.a.) (Ref.3.1.19)	ΔV (%)	ΔH_f° (kcal/g.a.) (From Graph)	Calculated Minus Observed
Ag_2Te	- 2.3	+ 0.4	+	2.3
$AuSb_2$	- 1.6	- 4.8	- 3	- 1.4
AuSn	- 3.2	- 2.0	- 1	+ 2.2
$AuSn_2$	- 1.9	+ 0.8	+	1.9
$CoSn_2$	- 2.4	- 9.5	- 6	- 3.6
CoAl	-13.2	-14.7	- 10	+ 3.2
$MgNi_2$	- 5.7	-12.0	- 8	- 2.3
NiTe	- 4.5	-16.9	- 10	- 5.5
Ni_3Si	- 8.9	-18.2	- 11	+ 2.1
$ReSi_2$	-20.7	-33.1	- 30	- 9.3
FeSi	- 9.6	-40.7	- 41	+31.4
FeAl	- 6.1	-15.1	- 21	+14.9
CoAl	-13.2	-19.3	- 25	-11.8
Ni_3Al	- 9.2	- 8.0	- 14	- 4.8
Cu_3Sb	- 0.6	-20.5	- 26	-25.4
Cu_3Sn	- 1.8	- 9.0	- 15	-13.2

*For compounds Ag_2Te through $ReSi_2$ the value for ΔV was calculated from reported density data, for compounds FeSi through Cu_3Sn ΔV was calculated from lattice constants.

IV. SUMMARY AND CONCLUSION - SECTION 2A

The thermodynamic activities of oxides in laser glass melts and of the corresponding metals in platinum are desired. An extensive literature search on the subject appears in Appendix I. Estimates of activities based upon these findings appear in Tables 2 and 6

Several theoretical models correlating the thermodynamic properties of chemical compounds have been reviewed. Adoption and modification of L. Pauling's electronegativity model and of P. Goldfinger's model show the most promise of reliably predicting the thermodynamic properties of the platinides.

As with any estimation, comparison to measured values is the most valuable tool The empirical study to be carried out at Battelle in the remainder of the 1971 fiscal year will be of great assistance.

V. ACKNOWLEDGEMENT - SECTION 2A

The consulting assistance of Dr. Wayne L. Worrell, Dr. Charles B. Alcock, and Dr. Carl Alexander has been most fruitful. Several noted authors researching the area have responded generously to requests for the references which appear in Appendix I. Members of the Owens-Illinois Technical Center staff have contributed suggestions relating to the practical application of this effort.

2B Particle Detection

An integral part of any program to reduce damaging particles from laser glass must be a method of detection of such particles.

Several methods of detection have been advanced by workers in the field. These include, for example, small angle scattering and holographic techniques. However, none of these approaches has proven completely reliable. In the final analysis, the most reliable procedure to date for detecting damaging particles consists of subjection of the glass to a high power laser pulse. Even this leaves something to be desired because of the dependence of the damaging threshold on the pulse width of the laser emission.

Previous particulate damage work under this contract during fiscal year 1969 utilized Owens-Illinois' high peak power laser. However, this system is now being used in the holographic study of surface damage currently being pursued under this contract. For this reason, another high power laser is being adapted as a tool for the final evaluation of melting procedures resulting from the thermodynamics study being made under this contract. This laser utilizes government equipment from Redstone Arsenal and is in the final stages of modification. It will emit energy in a Q-switched pulse sufficient for detecting damaging particles.

3. SURFACE DAMAGE

3A. Introduction

Damage to the surfaces of elements of glass and ruby laser systems has been a problem since the genesis of the Q switched laser. Although most studies of this damage have been limited to the lasing material, the problem also includes beamsplitters, lenses, prisms, etc. The solution to the problem for the lasing elements will probably extend itself to these other elements.

The damage usually takes two distinctive forms depending on whether it occurs in the entrance region of the laser pulse into the sample or in the exit region. Generally, the first phenomenon to be noticed as the energy density of the laser pulse is increased is a small, rounded plasma at the entrance point. An even smaller plasma of different shape is noted at the exit at the same or slightly higher energies. As the energy density is increased these plasmas grow in size until slight excoriation and/or pitting is seen at the exit. At still higher densities this exit pitting becomes greater and excoriation is also noticed in the entrance face. When the laser pulse becomes energetic enough to self focus inside the sample, a relatively severe increase in the size of the surface pit is sometimes observed.

It should also be noted that exit surface pitting sometimes seems to occur in conjunction with self focusing. An exit pit is often seen to lie on a line with self focusing tracks inside the material.

Several theories have been put forth in an attempt to explain the mechanism through which surface damage is brought about. At least two of these theories involve the plasmas which accompany the deterioration

of the surfaces. There is evidence which suggests that these plasmas initially arise from desorption by the laser pulse of impurities which have been absorbed by the glass surface. That this is the case, and that surface damage is related to these plasmas, is evidenced by experiments which show that the damage threshold increases significantly when the surfaces are chemically treated in such a way as to remove any impurities.

The two theories alluded to above postulate the damage to come about as follows:

1.) A plasma is initiated by desorption of surface impurities and grows as the laser pulse proceeds through it. Thermally energetic ions bombard the surface, leading to thermal erosion, crazing, and eventually pitting.

2.) The plasma is again initiated by thermal desorption, but in this theory the damage is caused by a shock wave born of the rapid expansion of the plasma as the laser pulse expands it by further desorption of impurities. This shock wave is strong enough to cause fracturing of the material.

Other theories unrelated to the formation of a plasma contiguous to the damage area have been proposed. Several of these are based upon the conception of shock waves generated interior to the material and propagating to the surface where they cause fracturing. The differences among these theories lie in the several mechanisms they postulate to cause the shock wave. Two of these are as follows:

1.) Electrostrictive forces "squeeze" the material, sending a shock wave both backward and forward along the beam.

2.) The shock wave is created in conjunction with self focusing inside the sample. It is postulated that this self focusing is often present even though no damage track is observed, either because the track is too small to "see" or because no damage actually occurs.

One of the two phases of the surface damage program now being carried out under this contract deals with determining the causes of damage. All except one of the theories discussed above postulate the existence of high intensity shock waves in the glass. In one of these theories the shock is assumed to originiate at the surface from where it propagates into the material, while in the other shock theories the wave is postulated to originate within the sample from whence it moves to the surface. Hence, if it can be ascertained first whether a shock wave of sufficient magnitude to cause fracture exists in the material, and second, from whence this wave originates, then a large step will have been taken toward validating or invalidating some of the damage theories presented. Owens-Illinois is presently attempting to make this ascertainment in a most direct manner. The technique of double exposure, stop action holography is being used to detect shock waves in a glass sample through which a high power laser pulse has been passed. By taking several holographs at various times relative to, say, the leading edge of the damaging pulse from the high power laser, the region of origin of any shock wave present will be determined.

The other phase of the program is predicated on the assumption that the plasma accompanying surface damage is in part or in whole responsible for the damage. Hence, if by treatment of the surfaces we can either strengthen the surface or prevent the formation of a

plasma, then we can eliminate, or at least decrease, surface damage. In this phase chemical etching procedures are being explored which will remove impurities and retain the polished surface. Also, ion exchange techniques are being used in attempts to mechanically strengthen the surfaces.

These two methods of attack are complementary. The one is an attempt to clarify the causes of damage, the implication being that once these causes are understood, the situation will be amenable to corrective measures. The other assumes what at the present state of the art seems to be a reasonable cause for damage and proceeds to try to eliminate this cause. As the study proceeds the two efforts will be closely coordinated. For example, if in the holographic portion of the study, a shock wave from the plasma is found to fracture the surface, then a mechanical strengthening of the surface is indicated.

3B. Holographic Study

The experimental apperatus for the holographic detection of shock induced strass patterns in a glass sample consists essentially of two lasers, a high power glass laser for damaging the sample and a ruby laser for making the hologram. The glass laser is capable of delivering more then 60 joules in a 30 ns pulse, this in a 2 cm^2 multimodal beam. The ruby laser can emit more then 2 joules in 20 ns when operated multimode; however, as it is now being used it delivers about 10 millijoules in 20 ns. This output is in the TEM_{00} mode and is accomplished by inserting a 1 mm diameter aperture into the oscillator cavity.

The two lasers are fired in a coordinated manner. The pulse of the ruby laser can be inserted into the sample to within ± 3 ns relative to the insertion of the damaging pulse from the glass laser.

The 10 mj output of the ruby laser is too high for the holographic film being used (AGFA 10 E75). For this reason, a neutral density filter with a transmission of less then 1% is used in the reference section of the holograph producing beam. A diffuser serves this purpose in the object beam.

In order to expand the 1 mm diameter beam emitted by the ruby laser, a short focal length diverging lense is used. Because of this, both the reference and the object beams are spherical, and intensities of the two at the position of the film are strongly dependent upon their respective path lengths. This leads to difficulties in obtaining correct exposures. A beam expander, which will yield a collimated beam, has been ordered to remedy this problem.

The technique for making a double exposure hologram is well known. First, a hologram of the sample, in this case a glass cube, is made. Next, the sample is subjected to the conditions of interest, in this case a high power laser pulse, and another exposure is made. The resulting hologram shows the sample with interference fringes due to changes in the sample between the two exposures "frozen" into it.

The diffuser in the object beam of our setup serves a purpose additional to that of effectively attenuating the beam as mentioned above. When a double exposure hologram is made without a diffuser in the object beam, there appears on the film an interferogram such as would be observed if the sample were placed in an interferometer and subjected to stress. Each fringe is a separate hologram. This pattern makes examination of the hologram difficult. However, when a diffuser is used in the sample beam, this trouble is no longer encountered; the gross interferogram no longer appears. There is, however, a tradeoff. The diffuser leads to speckle in the finished hologram, but this does not seem to be as serious as the interferogram obtained in the absence of the diffuser.

Work accomplished to date is as follows:

1. The ruby holographic laser has been received, assembled and characterized.

2. The glass laser has been modified to allow temporal coordination of the firing of the two lasers. This involved replacing by a Kerr cell the rotating mirror previously used to Q switch the laser. A considerable amount of effort was expended rendering the system operable with the Kerr Cell installed.

3. The desired relative timing of the firing of the two lasers has been achieved. This involved the design and installation of the electronics required to interconnect the lasers.

4. Exposure problems related to the geometry of the holographic setup and the energy output of the ruby laser have been characterized.

5. Double exposure holograms of stress induced fringe patterns in a transparent plastic block have been made using the Q switched ruby laser.

6. An attempt has been made to make double exposure holograms of a glass sample subjected to a pulse from the glass laser.

During the work of (6) the Kerr cell used in the glass laser was damaged on its output face. This damage was probably due to self focusing of the laser beam by the nitrobenzene used in the Kerr cell. This trouble has been encountered with two different cells now. The first cell was replaced, but it now appears that a Kerr cell will not be an effective method for Q switching the laser used in this experiment. The tendency of the cell to damage is not its only drawback; the laser pulse obtained using the Kerr cell is spatially very messy because of the characteristics of the nitrobenzene. For these reasons, we intend to replace the Kerr cell with a Pockels cell.

The following work is planned for the remainder of fiscal year 1971.

1. Installation of the Pockels cell will be accomplished.

2. In order to render data obtained more meaningful, the glass laser will be modified to emit a diffraction limited beam

4. The final goal of detecting shock waves in a glass sample subjected to a high power pulse from the glass laser will be pursued.

3C. Chemical Treatment of Surfaces

The test equipment which will be used for this study consists chiefly of a glass laser This laser is one of four being used in work under the contract, the other three having been described in previous sections of this report. It is capable of emitting more than five joules in a thirty nanosecond pulse. The spatial and temporal aspects of this pulse are currently being characterized

The study to be conducted will utilize the focused output of this laser. The beam will be focused on the surface to be studied. The damage threshold and integrated plasma characteristics will be noted for each method of surface treatment tried.

Work during the period July 1, 1970 to December 31, 1970, has included, besides the modification of the laser described above, a study of various surface treatments which might be effective in increasing the surface damage threshold. These are as follows:

1 Surface Cleaning

This treatment removes soils on the glass that could act as energy absorbers Cleaning techniques well known in the art of glass cleaning will be employed They include:

sulfuric acid - chromic acid

hydrogen perioxide

detergents and surfactants

vapor degreasing

ultrasonics, etc

2. Surface Etch

This treatment removes a layer of glass in addition to surface soils. The object here is to remove any grinding and polishing materials that have become imbedded in the glass during surface finishing The treatment involves the use of hydrofluoric acid, probably mixed with other acids or modifiers. This treatment may disturb the surface finish.

3 Monolayer Coatings

These coatings displace surface water and render the surface hydrophobic. The coatings include silicones, fluorides, and fluorocarbons

4. Dehydration

This is a simple heat treatment, perhaps under vacuum, to remove surface water.

5 Thermochemical Surface Modification

This treatment will prestress the glass surface through ion exchange techniques

The laser described in the opening paragraph of this section will be utilized in the initial stages of this work. However, later stages will be conducted with a diffraction limited beam in order to more accurately measure the effectiveness of the various chemical treatments

APPENDIX I

BIBLIOGRAPHY

The bibliography attached covers pertinent information obtained to this date. Those marked with an asterisk (*) have not yet been studied thoroughly.

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The systems are divided into groups depending upon the number of components contained, however, some papers discuss several systems and may contain information, for example, on binary and ternary systems.

1.1. Binary Systems

1.2. Ternary Systems

1.3. Quarternary Systems

1.4. Vapor Pressure

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3.1. General
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3.2. Electronegativity

3.3. Ternary Activities from Binary Data (Oxide Systems)

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3.2.6. Gordy, W., and Thomas, W.J.O., "Electronegativities of the Elements," Jnl. of Chem. Physics, Vol. 24, No. 2, Feb. 1956.

3.3. Ternary Activities from Binary Data (Relevant to Oxide Systems)

3.3.1. Toop, G.W., "Predicting Ternary Activities Using Binary Data," Trans. of the Metallurgical Society of AIME, Vol. 233, May 1965.

3.3.2. Richardson, F.D., "Activities in Ternary Silicate Melts," Trans. Farady Soc. 52 (1956).

APPENDIX II
CALCULATION OF METAL OXIDE ACTIVITY IN SILICA FOR GLASS NO. 5

Component	x_{MeO_x}	a_{MeO_x}	γ_{MeO_x}
SiO_2	0.593	0.63	0.37
Al_2O_3	0.025		
K_2O	2.12×10^{-7}	6.3×10^{-9}	1.3×10^{-16}
CeO	1.6×10^{-3}		
Fe_2O_3	9.4×10^{-8}		
Na_2O	2.42×10^{-7}	6.3×10^{-7}	1.5×10^{-15}
Li_2O	0.275	2.0×10^{-5}	5.5×10^{-6}
Nd_2O_3	0.005		
CaO	0.100	7.6×10^{-2}	7.6×10^{-3}

Mole fraction of network formers = $x_{SiO_2} + x_{Al_2O_3} = 0.593 + 0.025 = 0.618$.

Mole fraction of network modifiers =

$$x_{K_2O} + x_{CeO_2} + x_{Fe_2O_3} + x_{Na_2O} + x_{Li_2O} + x_{Nd_2O_3} + x_{CaO} = 0.382.$$

From Charles (Ref. 1.1.3.) the activity coefficient of Li_2O (γ_{Li_2O}) at a mole fraction of 0.332 is 2.0×10^{-5} at 1533°K. Since the activity is defined as the product of the activity coefficient and the mole fraction

$$a_{Li_2O} = (x_{Li_2O})(\gamma_{Li_2O}) = 0.275 \times 2.0 \times 10^{-5} = 5.5 \times 10^{-6}.$$

Similarly from Charles the activity coefficient of K_2O at a mole fraction of 0.382 is 6.3×10^{-9}; therefore

$$a_{K_2O} = (x_{K_2O})(\gamma_{K_2O}) = 2.12 \times 10^{-7} \times 6.3 \times 10^{-9}$$
$$= 1.3 \times 10^{-16}$$

Ray (Ref. 1.1.17) gives a value of γ_{CaO} of 7.6×10^{-2} at 1873°K.

Then $a_{CaO}^{1873°K} = (x_{CaO})(\gamma_{CaO}) = 0.100 \times 7.6 \times 10^{-2}$

$$= 7.6 \times 10^{-3}$$

APPENDIX III
CALCULATION OF ACTIVITIES AND ACTIVITY COEFFICIENTS FROM BINARY FREE ENERGY OF FORMATION DATA

$$BaO(c) + 2SiO_2(c) = BaSi_2O_5(c)$$

$$\Delta F^\circ_{1500^\circ K} = -41{,}300 \text{ cal/g.mole}$$

$$\Delta F = \Delta F^\circ + RT \ln \frac{a_{BaSi_2O_5}}{(a_{BaO}) \times (a_{SiO_2})^2}$$

Assume:

1) $\Delta F = 0$ (system at equilibrium)

2) Activity of $SiO_2 = 1$

3) Activity of $BaSi_2O_5 = 1$

then $\ln (a_{BaO}) = \frac{-\Delta F^\circ}{RT}$

$$a_{BaO} = 10^{-5.86} = 1.38 \times 10^{-6}$$

$$x_{BaO} = 1/3$$

$$\gamma_{BaO} = a_{BaO}/x_{BaO} = \frac{-1.38 \times 10^{-6}}{0.333}$$

$$\gamma_{BaO} = 4.18 \times 10^{-6}$$

APPENDIX IV
CALCULATION OF THE ACTIVITIES OF METALS IN PLATINUM

1. Silicon

1.1. Method 1

The activity of Si in Pt (a_{Si}^{Pt}) can be related to the free energy of formation (ΔF_f°) or the heat of formation (ΔH_f°) of a Pt-rich Si-Pt intermetallic compound, such as $SiPt_3$. ΔH_f° ($SiPt_3$) can be estimated knowing ΔH_f°'s of similar compounds.

$$\text{Si (pure solid)} \rightarrow \text{Si (in Pt)}$$

$$\Delta F_{rx} = \Delta F^\circ + RT \ln \frac{a_{Si(\text{in Pt})}}{a_{Si(\text{in Si})}}$$

Choosing Si (pure solid) as the standard state, $a_{Si}^{Si} = 1$ and $\Delta F_{rx}^\circ = 0$.

$\therefore \Delta F = RT \ln [a_{Si(\text{in Pt})}]$

Because both reactants and products of the reaction are solids,

$\Delta S \simeq \pm 2$ cal/deg. mole and $|\Delta H| >> |T\Delta S|$.

$\therefore \Delta H \simeq \Delta F = RT \ln a_{Si(\text{in Pt})}$

Adding Pt to both sides of the reaction, one obtains:

$$3Pt + Si(\text{pure solid, } 1533^\circ K) \xrightarrow{\Delta F_{rx}} Si(\text{in Pt, } 1533^\circ K) + 3Pt$$

ΔF_1 ↓

ΔF_5 ↑

$$Si(\text{in Pt, } 298^\circ K) + 3Pt(298^\circ K)$$

ΔF_4 ↑

$$Si(\text{in } SiPt_3, 298^\circ K) + 3Pt(\text{in } SiPt_3, 298^\circ K)$$

ΔF_3 ↑

$$3Pt + Si(\text{pure solid, } 298^\circ K) \xrightarrow{\Delta F_2} SiPt_3(298^\circ K)$$

Because ΔF_{rx} is path independent:

$\Delta F_{rx} = \Sigma \Delta F_i = \Delta F_1 + \Delta F_2 + \Delta F_3 + \Delta F_4 + \Delta F_5$

$\Delta F_2 = \Delta F_f^\circ (SiPt_3, 298^\circ K)$

$\Delta F_3 = 0$ because the Si, Pt, and $SiPt_3$ are in equilibrium within the $SiPt_3$ phase.

$\Delta F_4 = 0$ when the Pt and $SiPt_3$ phases are in equilibrium.

$\Delta F_1 \simeq \Delta F_5$ because ΔC_p for the reaction (rx) $\simeq 0$ and $\Delta F_i \simeq \Delta H_i$.

$$\Delta F_{rx} \simeq \Delta F_2 = \Delta F_f^\circ(SiPt_3,\ 298°K) = RT \ln a_{Si}^{Pt}$$

Solving for $a_{Si(in\ Pt)}$

$$\ln a_{Si(in\ Pt)} = \frac{\Delta F_f^\circ(SiPt_3,\ 298°K)}{RT}$$

$\Delta F_f^\circ(SiPt_3)$ has not been experimentally determined.

$\Delta H_f^\circ(SiNi_3)$ has been determined. Assume:

$$\Delta F_f^\circ(SiPt_3) \simeq \Delta H_f^\circ(SiPt_3) \simeq \Delta H_f^\circ(SiNi_3) = -35.5 \text{ kcal/mole (Ref. 3.1.19, p. 340)}$$

$$\text{Log } a_{Si(inPt)} = \frac{-(35,500)}{(2.303)(1.987)(1533)} = -5.07;\quad a_{Si(in\ Pt)} = 10^{-5}$$

1.2. Method 2

Assume:

$$a_{Si(Pt)} = a_{Si(Pd)}$$

$$a_{Si(Pd,\ 1550°C)} = 4.3 \times 10^{-5} \text{ for } x_{Si} = 0.26 \text{ (Ref. 2.4.2., p. 115)}$$

$$a_{Si(Pt)} = 4.3 \times 10^{-5}$$

1.3. Method 3

Assume:-

$$a_{Si(Pt)} = a_{Si(Re)}$$

$$Re_3Si \rightarrow 3\ Re + Si$$

$$\Delta G^\circ = A + BT \text{ Log } T + CT \qquad \text{(Ref. 3.1.19, p. 341)}$$

$$A = 24,600;\ B = 0;\ C = +5$$

$$\Delta G^\circ_{Re_3Si(1533°K)} = -31,760$$

$$\text{Log } a_{Si(Re)} = \text{Log } a_{Si(Pt)} = \frac{-31,700}{(2.303)(1.987)(1533)} = -4.53$$

$$a_{Si(Pt)} = 10^{-4.53}$$

1.4 Method 4

Assume:

$$a_{Si(Pt)} = a_{Si(Ni)}$$

$$a_{Si(Pt)} = a_{Si(Ni)} = x_{Si(Ni)}\ \gamma_{Si(Ni)} = 10^{-1} \times 10^{-4} = 10^{-5} \qquad \text{(Ref. 3.1.34, p. 1330)}$$

$$a_{Si(Pt)} = 10^{-5}$$

2. Calcium

$$Ca + 2Pt \rightarrow CaPt_2 \qquad \text{(Ref. 3.1.8, p. 246)}$$

No thermodynamic data is available.

Assume: $\Delta F^\circ_{CaPt_2} = -10\ K$ cal/g.a.

$$\text{Log } a_{Ca(Pt)} = \frac{(-10,000)(3)}{(2.303)(1.987)(1533)} = -4.27$$

$$a_{Ca(Pt)} = 10^{-4.27}$$

3. Lithium

$$Li + 2Pt \rightarrow LiPt_2 \qquad \text{(Ref. 3.1.8., p. 586)}$$

"Contamination free Li and Pt react in a violent exothermic reaction at 540°C in a vacuum or an inert atmosphere to form the compound $LiPt_2$." (Ref. 3.1.8., p. 586)

$$T_{Boiling\ (Li)} = 1329°C \qquad \text{(Ref. 3.1.19, p. 377)}$$

Assume that for the reaction to be violent, boiling of Li must occur.

$$\Delta H = C_p\ \Delta T + \Delta H_{vaporization\ (Li)}$$

$$C_p \sim 6.3 \qquad \text{(Ref. 3.1.35, p. 114)}$$

$$\Delta H_{vaporization\ (Li)} = 35.5\ K\ \text{cal at B.P.} \qquad \text{(Ref. 3.1.19, p.377)}$$

$$\Delta H = (6.3)(1330 - 540) + 35,500$$

$$= 40,500\ \text{cal/mole}$$

for an exothermic reaction ΔH is negative

$$\Delta H \sim \Delta F \qquad \text{(from 1.1)}$$

$$\text{Log } a_{Li(Pt)} = \frac{-40,500}{(2.303)(1.987)(1533)} = -5.77$$

$$a_{Li(Pt)} = 10^{-5.77}$$

4. Aluminum

4.1. Method 1

$$Al + Pt \rightarrow AlPt \qquad \text{(Ref. 3.1.8., p. 50)}$$

assume: $\Delta F^\circ_{AlPt} \simeq \Delta F^\circ_{AlNi} \sim \Delta H^\circ_{AlNi}$

$\Delta H^\circ_{AlNi} = 28,300$ cal/mole (Ref. 3.1.19, p. 342)

$$\text{Log } a_{Al(Pt)} = \frac{-28,300}{(2.303)(1.987)(1533)} = -4.03$$

$$a_{Al(Pt)} = 10^{-4}$$

4.2. Method 2

$$\Delta F^{\circ}_{Pt_3Al} \leq -52.6 \text{ cal/mole} \qquad \text{(Ref. 3.1.36)}$$

$$\text{Log } a_{Al(Pt)} = \frac{-52,600}{(2.303)(1.987)(1533)} = -7.5$$

$$a_{Al(Pt)} \leq 10^{-7.5}$$

Note: For aluminum method 2 is preferred.

5. Barium

$$Ba + 5Pt \rightarrow BaPt_5 \qquad \text{(Ref. 3.1.10., p. 273)}$$

No thermodynamic data is available.

Assume: $\Delta F^{\circ}_{BaPt_5} = -10\ K$ cal/g.a.

$$\text{Log } a_{Ba(Pt)} = \frac{(-10,000)(6)}{(2.303)(1.987)(1533)} = -8.55$$

$$a_{Ba(Pt)} = 10^{-8.55}$$

6. Titanium

$$3\ Pt + Ti \rightarrow TiPt_3 \qquad \text{(Ref. 3.1.8., p. 752)}$$

$$\Delta F^{\circ}_{TiPt_3} = -9.2\ K \text{ cal/g.a.} \qquad \text{(Ref. 3.1.13., p. 189)}$$

$$\Delta\text{Log } a_{Ti(Pt)} = \frac{(-9100)(4)}{(2.303)(1.987)(1533)} = -5.2$$

$$a_{Ti(Pt)} = 10^{-5.2}$$

7. Iron

$$a_{Fe(Pt)} = 10^{-3.46} (x_{Fe} = 0.01) \qquad \text{(Ref. 2.5.3., p. 338)}$$

8. Antimony

$$2Sb + 5Pt \rightarrow Pt_5Sb_2 \qquad \text{(Ref. 3.1.10., p. 1138)}$$

assume: $\Delta F^{\circ}_{Pt_5Sb_2} = \Delta F^{\circ}_{Ni_5Sb_2}$

$$\Delta F^{\circ}_{Ni_5Sb_2} = -36.4\ K \text{ cal/mole} \qquad \text{(Ref. 3.1.19, p. 340)}$$

$$2\ \text{Log } a_{Sb(Pt)} = \frac{-36,400}{(2.303)(1.987)(1533)} = -5.2$$

$$a_{Sb(Pt)} = 10^{-2.6}$$

9. Cerium

$$Ce + 2Pt \rightarrow CePt_2 \qquad \text{(Ref. 3.1.10, p. 460)}$$

$$\Delta F^{\circ}_{CePt_2} = -55 \text{ K cal/mole} \qquad \text{(Ref. 3.1.37.)}$$

$$\text{Log } a_{Ce(Pt)} = \frac{-55,000}{(2.303)(1.987)(1533)} = -7.84$$

$$a_{Ce(Pt)} = 10^{-7.84}$$

10. Other Activities

Na, assume $a_{Na(Pt)} = a_{Li(Pt)} = 10^{-5.75}$

K, assume $a_{K(Pt)} = a_{Li(Pt)} = 10^{-5.75}$

B, assume $a_{B(Pt)} = a_{Al(Pt)} = 10^{-7.5}$

As, assume $a_{As(Pt)} = a_{Sb(Pt)} = 10^{-2.6}$

Nd, assume $a_{Nd(Pt)} = a_{Ce(Pt)} = 10^{-7.48}$

Pb, assume $a_{Pb(Pt)} = a_{Sb(Pt)} = 10^{-2.6}$

Zn, assume $a_{Zn(Pt)} = a_{Sb(Pt)} = 10^{-2.6}$