Joining of Ceramics
for High Performance Energy Systems
Mid-term Progress Report
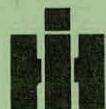
1 August 1979 to 31 March 1980

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RESEARCH REPORT

JOINING OF CERAMICS FOR HIGH PERFORMANCE ENERGY SYSTEMS

MID-TERM PROGRESS REPORT

Reporting Period: August 1, 1979 to March 31, 1980

REPORT SR80-R-4681-04

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ABSTRACT

The subject program is primarily an exploratory and demonstration study of
the use of silicate glass-based adhesives for bonding silicon-base refractory
ceramics (SiC, Si_3N_4). The projected application is 1250-2050°F relaxing
joint service in high-performance energy conversion systems (Ref. 1). The
five program tasks and their current status are as follows.

Task 1 - Long-Term Joint Stability. Time-temperature-transformation
(TTT) studies of candidate glass adhesives, out to 2000 hours simulated
service exposure, are approximately 50 percent complete.

Task 2 - Environmental and Service Effects on Joint Reliability. Start
up delayed due to late delivery of candidate glass fillers and ceramic
specimens.

Task 3 - Viscoelastic Damping of Glass Bonded Ceramics. Promising
results obtained over approximately the same range of glass viscosity
required for joint relaxation function ($10^{7.5}-10^{9.5}$ poise). Work is
approximately 90 percent complete.

Task 4 - Crack Arrest and Crack Diversion by Joints. No work started
due to late arrival of materials.

Task 5 - Improved Joining and Fabrication Methods. Significant work has
been conducted in the areas of refractory pre-glazing and the application
and bonding of high-density candidate glass fillers (by both hand-artisan
and slip-spray techniques). Work is approximately 50 percent complete.

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INTRODUCTION

The subject program has the objective of providing a general technology base for the improved joining of silicon-based ceramic components of high performance energy systems. Joining processes adaptable to ceramic tube heat exchangers and ceramic turbine assemblies will be emphasized. The current contractual effort of Solar Turbines International, an Operating Group of International Harvester Company, under DOE Contract DE-AC05-79ET15359 represents a follow-on of specialized ceramic joining work initiated under DOE Contract EY-76-C-05-5251 (Ref. 1). Particular joining concepts under investigation for silicon carbide (SiC) and silicon nitride (Si_3N_4) include: (a) relaxation joints (glass bonding agents); and (b) compliant-interlayer joints (primarily metallic bonding agents). See References 1 and 2.

The program work is divided into five main tasks:

Task 1 - Investigation of Long-Term Joint Stability

Task 2 - Determination of Environmental and Service Effects on Joint Reliability

Task 3 - Viscoelastic Damping of Glass Bonded Ceramics

Task 4 - Crack Arrest and Crack Diversion by Joints

Task 5 - Improved Joining and Fabrication Methods

The overall technical effort of the program is scheduled over a period of 16 months with submission of the draft final technical report at the end of the 16th month (see Fig. 1, Program Schedule).

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	Months From Start of Contract

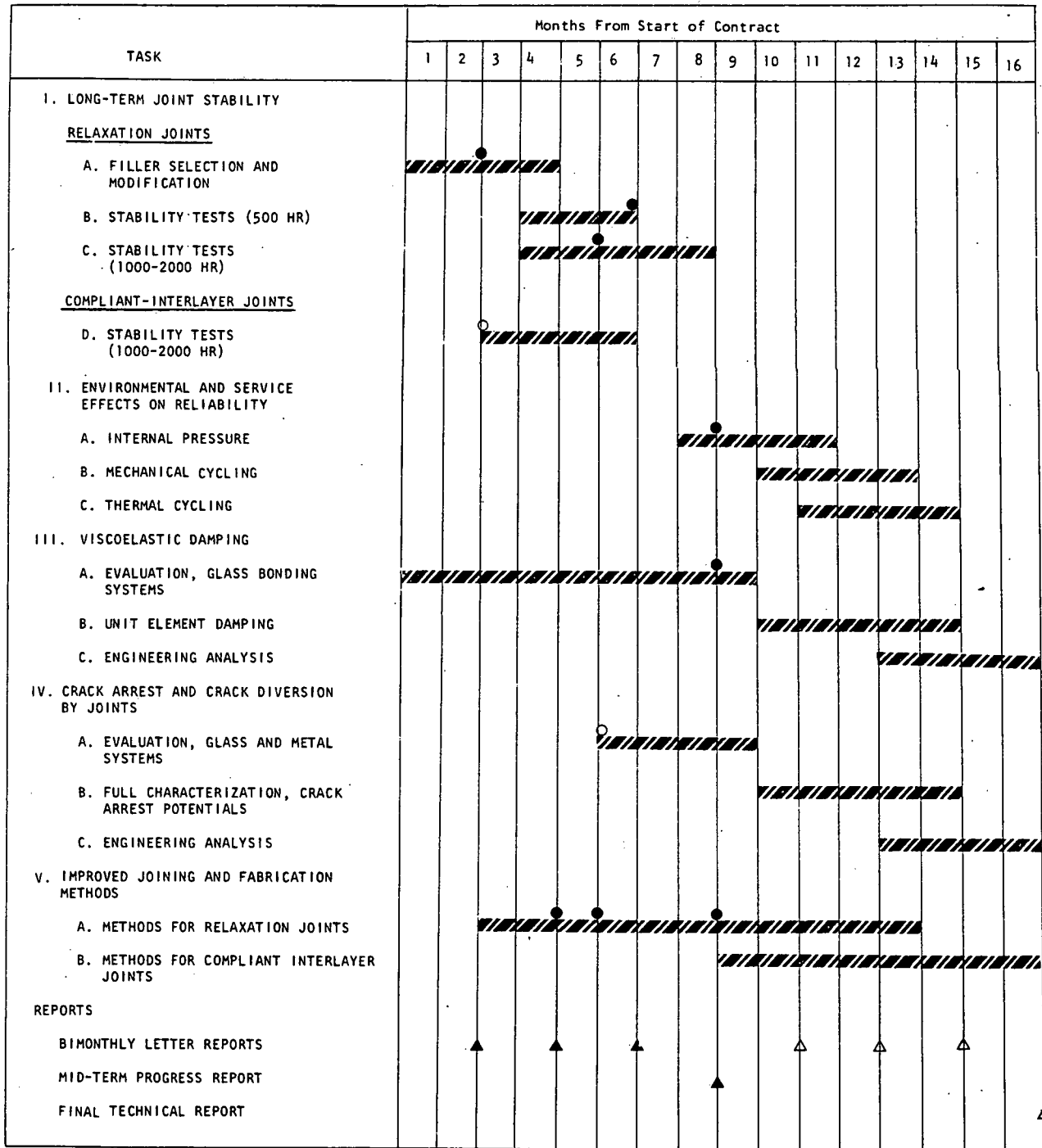| TASK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
I. LONG-TERM JOINT STABILITY																
RELAXATION JOINTS																
A. FILLER SELECTION AND MODIFICATION																
B. STABILITY TESTS (500 HR)																
C. STABILITY TESTS (1000-2000 HR)																
COMPLIANT-INTERLAYER JOINTS																
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B. METHODS FOR COMPLIANT INTERLAYER JOINTS																
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BIMONTHLY LETTER REPORTS																
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FINAL TECHNICAL REPORT																

Figure 1. Program Schedule

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BACKGROUND AND PROGRAM PLAN

The subject program is primarily a continuation of development of the specialized and novel Relaxing-Joint Concept (Ref. 1) for joining silicon-based ceramics (SiC and Si_3N_4). As opposed to the rigid, immobile, permanent-type joints afforded by silicate-based crystalline cements or silicon-metal brazes, the relaxing-joint concept employs special silicate-glass adhesives, which in specific viscosity ranges (approx. $10^8 - 10^{10}$ poise), permit appreciable (and reversible) translation of shear-joint faying surfaces under variable light service loadings. This potential for reversible joint translations (1/4" - 1/2") serves to alleviate peak assembly service strains, and thereby reduces the probability of ceramic component failure under both steady-state and cyclic stress-temperature regimes. (The relaxing-joint concept is described in more detail in Appendix A.) In a typical tube-sleeve telescoping shear-joint, depicted schematically in Figure 2 for a Solar-designed HX module, the vitreous silicate-glass adhesive is processed and applied much like an in-situ metallic braze, with the important exception that glass "glide-paths" are provided external to the original faying surfaces to permit reversible joint translations of up to 1/2 inch. (Fig. 2 and Ref. 1)

It was learned in prior work (Ref. 1) that no single glass composition or composite vitreous adhesive can operate over the entire range of desired joint service temperature (viz. 1050°F - 2050°F), providing the desired range of glass visocity for the relaxing-joint function (viz.; $10^8 - 10^{10}$ poise). Rather, it is more practical to select individual glass bonding agents to provide the proper viscosities over narrower, adjoining temperature increments of the broader temperature range, as outlined below. See Table 1.

In addition to the unique joint function of relaxation movement, other important functions and attributes of glass-bonded joints demonstrated in prior work (Ref. 1) include: (a) retention of glass/ceramic bond integrity following repeated relaxation cycles; (b) gas-pressure sealing ability at RT and at elevated joint service temperatures; and (c) the potential for transferring light service loads between the joined ceramic components. In the current program effort, which is largely exploratory, (see Ref. 2), additional glass-joint functions under evaluation include: (d) the potential for viscoelastic damping of vibration in ceramic assemblies (Task 3; Ref. 2) and the potential for arrest of fast-growth cracking in ceramic assemblies (Task 4, Ref. 2). See Figure 1, Program Schedule.

INNER SiC TUBE

HEATING METHOD: INDUCTION
ATMOSPHERE: AIR

PREGLAZED GLASS ADHESIVE

OUTER SiC TUBE

Preglazing Operation on Preoxidized SiC Ceramic
(Faying Surfaces of Tube-Sleeve Joint).

HEATING METHOD: INDUCTION
PRESSURIZATION: DEAD-WEIGHT LOADING (LIGHT)
ATMOSPHERE: AIR

Hot Joining and Telescoping Assembly
of SiC Tube-Sleeve Joint
[Heating Method: Induction -
Pressurization: Dead Weight Load-
ing (light) - Atmosphere: Air]

HEATING METHOD: INDUCTION
HEATING ATMOSPHERE: AIR

A

A

A

Formation of Preglazed Glide Paths (A) on Tube-Sleeve Joint
(Preoxidized SiC Ceramic) Heating Method: Induction
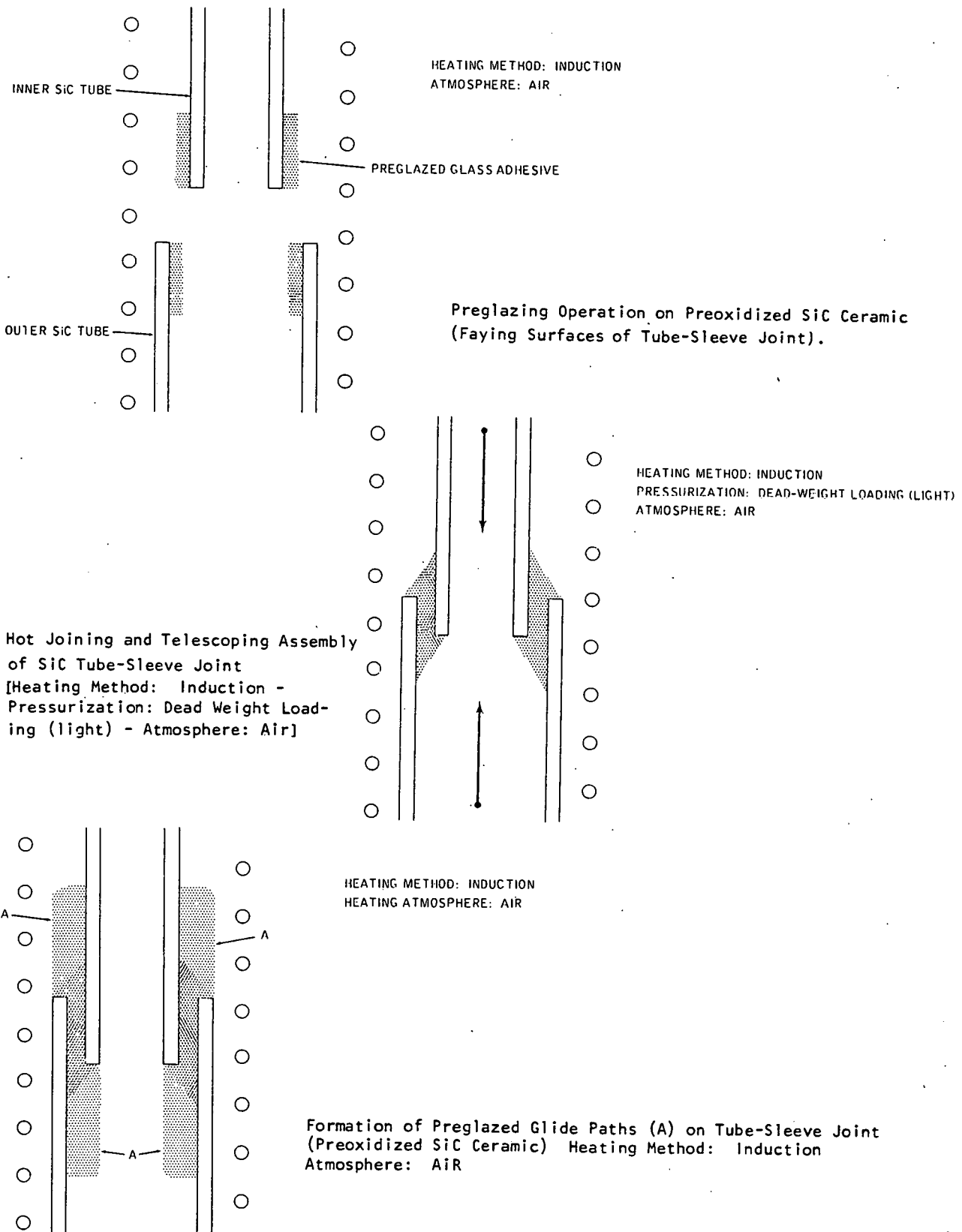Atmosphere: AiR

Figure 2.   Joining Process Sequence for Glass-Bonded Ceramic Tube Joint
(Simple Telescoping Design)

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Table 1

Candidate Glass Adhesives (Ref. 1)

Basic Silicate-Glass System	Service Temp. Range (°F)	Specific Glasses Evaluated (Ref. 1)
Soda-Lime	1050 - 1250°F	Corning 0080 Corning 6750
Borosilicates	1250 - 1500°F	Corning 7760 Corning 7800 Corning 7740 (Pyrex) Ferro RV-3324
Aluminosilicates	1600 - 1850°F	Corning 1720 Corning 1723
Two-Phase or "TPG" Glasses (Developed at Solar, Ref. 1)	1800 - 2050°F	TPG-1 to TPG-9* (SOLAR)

*Controlled fine physical mixtures of aluminosilicates and high-silica glasses (e.g., Corning Vycor or Fused Silica)

The feasibility of the Relaxing Joint Concept (App. A) and its applicability to actual ceramic assembly joining were well demonstrated in the initial DOE contract work (Ref. 1) and in a related manufacturing design and development contract on ceramic heat exchangers (DOE sponsored) conducted concurrently at Solar (Ceramic Heat Exchanger with Relaxing Joint; Ref. 3).

Predominant emphasis in program planning for the current work effort (Ref. 2) is in characterization and correction of significant joining problems inherent with glass adhesives, revealed in the initial contract work (Ref. 1). These joining problems and related program tasks are outlined below.

2.1 TASK 1 - LONG-TERM JOINT STABILITY

Long-term stability of glass-bonded ceramic joints is of paramount importance to energy-systems which incorporate and depend upon them; certainly out to 10,000 service hours, min. Stability in this context means reliable long-term retention of joint integrity, shear strength, vitreous structure, relaxation function and gas-sealing ability. All silicate glasses are structurally metastable at joint service temperatures, and have the potential to gradually lose their glassy, vitreous structures on long-term service holding, either through internal crystallization of equilibrium phases (devitrification) and/or alteration of their initial single-glass structure to one or more new glass forms (phase separation). Both types of transformation by definition, act to change vital viscosity/temperature characteristics (Fig. 3) upon which relaxation function and gas-sealing function are highly dependent (Refs. 1, 2 and 4). Volume changes accompanying these transformations,
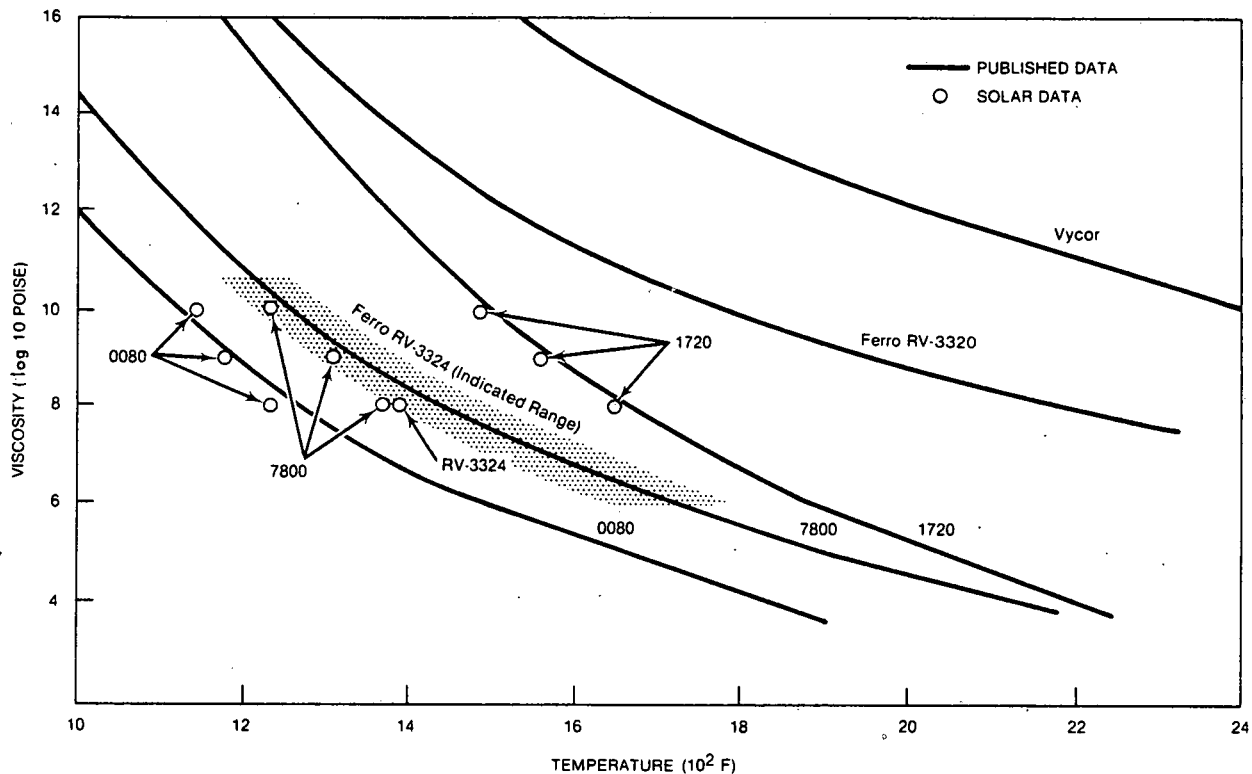
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Figure 3. Viscosity Versus Temperature for Glasses

typically glass shrinkage (Ref. 4), also can adversely affect the structural integrity of both the glass-fillers themselves and the glass/ceramic-interface bonds. Consequently, maintenance of glass-joint stability and function over the long-term are strongly dependent upon long-term retention of initial glassy structure at service temperatures, with only minimal structural modification tolerated in service. In early exploratory studies of glass stability (isothermal holding at proposed service temperatures, out to 500 hours, Ref. 1), the various candidate glasses showed extreme variation in apparent stability of microstructure and viscosity. Specifically, most of the borosilicates and soda-lime glasses showed considerable potential for stability; while the aluminosilicates and their two-phase glass derivatives exhibited considerably less stability, with viscosities so greatly increased after 500 hours holding that relaxation-function was essentially lost (Ref. 1).

In the current program plan (Task 1), the more promising candidate glass adhesives from prior work (Table 2) are being subjected to isothermal service temperature exposures in progressive steps out to 2000 hours, with close monitoring of any structural changes (through petrography and SEM/EDX analysis) as well as any associated viscosity changes. Time-temperature-transformation (TTT) diagrams will be constructed for each candidate glass. The most stable and promising glasses will then be chosen for further characterization and possible modification in subsequent tasks. (See Section 4, Planned Future Work.) If no suitably stable glasses are found for certain

Table 2

Long-Term Stability Testing; Isothermal Air-Exposure Regimes

Candidate Glass Filler (Collet Form)	Glass Type	Proposed Service Temperature Range* (°F)	Isothermal Exposure Temperatures & Times (Air Furnace)	
			Temperature (°F)	Time (Hr)
Corning 0080	Soda-Lime (73% Silica)	1120-1270	1050 1250 1450	100, 200, 500, 1000, 2000
Corning 6750	Baria-Lime (61% Silica)	1060-1230	1650	
Corning 7740	Borosilicate (81% Silica)	1240-1480		100, 200, 500 1000, 2000
Corning 7800	Borosilicate (75% Silica)	1250-1440	1050 1250 1450	
Corning 7760	Borosilicate (79% Silica)	1180-1400	1650	
Ferro Corp. RB-3324	Borosilicate (79% Silica)	1300-1450	1850** 2050**	
Corning 1720	Alumino-Silicate (62% Silica)	1500-1655	1250 1450 1650 1850	100, 200, 500, 1000, 2000
Ferro Corp. RV-3320	88% Silica	1850-2200	1650 1850 2050	100, 200, 500, 1000, 2000
Corning Vycor	96% Silica	Stability Baseline		

* Range corresponding to 10^8-10^{10} poise (viscosity)
** Only RV-3324 and 7760

segments of the desired 1050-2050°F range of service temperaturs, the most stable commercial glasses defined above will serve as bases for development of modified (new) glass adhesives to fill these open segments.

Work on Task 1 stability studies has been significantly delayed by late arrival of required candidate glasses from Corning Glass Works and Ferro Corp. (see Table 2). These glasses, in frit and cullet forms, arrived three to five months later than originally scheduled (see Program Schedule, Fig. 1).

Thermal exposure regimes out to 1000 hours are now complete, with 2000-hour exposures currently underway. (See Table 2.) However, because of the material delays, microstructural information for TTT diagrams is only available (to date) for the 500-hour exposures (see Section 3).

2.2 TASK 2 - ENVIRONMENTAL AND SERVICE EFFECTS ON JOINT RELIABILITY

Combined environmental and stress conditions of joint service may adversely affect consistency of joint performance. For example, repeated mechanical relaxation or viscous sliding of the glass adhesive, cyclically back and forth, may gradually develop local structural defects (interfacial and internally) which could effectively lower viscosity, shear strength, and/or resistance to gas leakage. Thermal cycling of the relaxing joint in service, the most severe related to the system "on-off" cycles, can alsoimpose (transiently) high local and general strains on the glass adhesive and joint interface due to different thermal expansion coefficients, high ceramic modulii, and variable heating rates of the joint components. Desired viscous behavior of the glass adhesive typically occurs only within 100 to 200°F of the maximum service temperature to relieve the mechanically and thermally induced strains. At all lower temperatures, especially during "on-off" thermal cycling, the glass adhesive and joint interface are vulnerable to overstress and consequent distortion and structural damage.

These are essentially short term or transient phenomena. In addition to the unknown influences of repeated viscous movements (relaxation) and transient, thermally induced strains upon joint integrity, there are also the possibly adverse effects of long-term service-loading and long-term isothermal service holding periods, sometimes with high internal pressurization. Long-term, diffusion controlled reactions, such as glass devitrification and/or phase separation, as well as "passive" glass/ceramic interaction (Ref. 1) resulting in internal gas generation at the interface are typical of possibilities here.

To obtain useful information on all these potential trouble areas, logically connected with joint longevity, the following exploratory tests are planned.

- Redeterminations of pertinent glass-joint relaxation rates, effective viscosities, shear strength and gas tightness of selected glass/ceramic joint systems (recommended in Task 1) following both 500 hour and 1,000 hour isothermal holding periods in ambient-pressure air at nominal service temperatures.

- Redeterminations, as above, following 10 or more mechanically induced joint relaxation movements at one maximum or near maximum service temperature, simulating 10 "on-off" cycles. Here only the effects of <u>cyclic viscous glass sliding (push-pull)</u> would be isolated and evaluated; e.g., ±0.1 inch of relative movement, forward and reversed each cycle, over a typical joint overlap distance of 0.5 - 1.0 inch. The effects of repeated relaxation movements should be compared for the as-fired condition versus application after a critical isothermal holding period, as determined in the first test series above.

- Redeterminations, as above, following 10 or more thermal cyclings between RT and the nominal maximum service temperature, with specimen ends fixed to develop the potentially high <u>transient strains</u>

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typical of service "on-off" cycles. Again, the ability of the
relaxation joint to accommodate these transient strains should be
evaluated and compared for the as-fired condition versus applica-
tion after a critical isothermal holding period, as determined in
the first test series above.

Initiation of Task 2 work (which depends upon material recommendations from
Task 1) has been unavoidably delayed because of the 5-month late start of
Task 1 studies. (See above.) Rather than starting the 8th month, as origin-
ally scheduled, (see Fig. 1), Task 2 will now likely start the 12th or 13th
month.

2.3 TASK 3 - VISCOELASTIC DAMPING OF GLASS-BONDED CERAMICS

Effective damping of resonant vibrations in large ceramic assemblies will be
imperative to attain long service life objectives, inasmuch as crystalline
ceramics and ceramic cements (Si-base) typically possess little or no ability
for self-damping at all proposed use temperatures. Their totally elastic
response to vibration excitation (e.g., from gas flows in heat exchangers)
will result in the highest possible amplitudes and surface (fatigue) stresses.
Metals and polymers are easier to design for because they display strong
anelastic behaviors and inherent energy damping capacities associated with
local and general plastic deformation, atomic diffusion, internal friction,
magnetostriction, etc. (For these reasons, inherent damping abilities of
compliant-metal interlayer butt joints are expected to be very substantial.)
In complete contrast, the monolithic reaction sintered type of ceramic heat
exchanger (module or hot-pressed turbine blades reportedly) ring long and
loudly like a bell when tapped, (see Refs. 5, 6). Fortunately, glassy-struc-
tured ceramics, such as glassy porcelains (Ref. 7) or the glass adhesives
developed on the current program, also exhibit anelastic behaviors and are
believed to possess interestingly high capacities for damping in their soften-
ing temperature ranges (i.e., at elevated temperatures with corresponding
viscosities on the order of $10^8 - 10^{10}$ poise). (Ref. 7.) The potentials
for strong damping characteristics afforded in this temperature region
(<u>similar to the planned operational temperatures for relaxing joints</u>) are
believed due to the anomolously high activation energies required for viscous
flow and/or relaxation movements in the glass, resulting in large quantities
of energy (irreversibly) dissipated per cycle, when in a vibration mode.
For example, the typical activation energies for viscous flow near the glass
softening points are on the order of 200-250 kcals/mole; while those for
alkali-ion diffusion in glass are only 20-30 kcals/mole and the energy assoc-
iated with rupturing the strong silicon-oxygen bond is 109 kcals/mole,
(Ref. 7).

Taking effective advantage of the (anticipated) high damping capacities of
"soft" viscous glass adhesives in the service temperature range requires,
first of all, that the glass-bonded relaxing joints be placed in zones of
high dynamic strain. This can readily be accomplished in most ceramic heat
exchanger designs employing tube-sleeve relaxing joints, (see Ref. 3).

The planned exploratory experiment consists basically of measuring and comparing relative damping levels (using the logarithmic-decrement method; see Section 3) of a freely resonating and decaying SiC heat-exchanger tube (nom. 3 ft. long x 1.0 inch diameter; Refs. 2 and 3); with the monolithic NC-430 ceramic tube as primary baseline. This will be compared against (a) the same monolith tube with glass-bonded SiC sleeve attachment (mid-length position; no tube joint) and (b) the same tube, (but mid-length-position split) with glass-bonded, mid-length-position tube joint and glass-bonded SiC sleeve attachment. See Section 3. The glass filler to be used; Corning 7800; is a 1450°F (max.) adhesive which appeared most stable and promising in prior work (Ref. 1). A secondary baseline specimen selected is the split SiC tube with mid-length-position joint with SiC sleeve attachment, (same geometry as (b) above), but permanently bonded with crystalline silicon-metal braze. These specimens represent a typical range of possible ceramic HX tube connections (Ref. 3). In the exploratory testing to assess glass-joint damping potentials, the principal control variable is to be test temperature, with associated variance in glass-filler viscosity. Vibration frequency and initial amplitude will be held within narrow ranges. Resources permitting, further characterization of glass-joint damping potentials will encompass the effects of varying the resonant frequencies and vibration-strain amplitudes of similar tube-sleeve joint specimens, employing selected, promising glasses from Tasks 1 and 2.

Because the subject Task 3 work could be started with relatively little glass adhesive and available NC-430 silicon carbide tubing, already in-house and residual from prior programs cited (Refs. 1 and 3); the bulk of Task 3 studies were actually initiated and completed this period. (See Section 3 and Fig. 1.) This was done early in the program, while awaiting the (late) delivery of glass and ceramic materials required to initiate Tasks 1, 2 and 4 (g.v.).

2.4 TASK 4 - CRACK ARREST AND CRACK DIVERSION BY JOINTS

Both intrinsic damping (discussed above) and crack arrest and/or diversion could become important functions of properly designed joints; especially in ceramic assemblies where catastrophic large-scale failures must be avoided. Again, only the adhesive (filler) material and structure of a glass-bonded or metal-bonded ceramic joint are capable of safely absorbing and dissipating the energies of excessive service vibration and/or a crack propagating elastically through the ceramic substrate. The mechanics of fracture initiation and propagation in ceramics (and metals) are extremely complex. However, cracks of critical size in brittle, high modulus ceramics normally will propagate autogeneously under constant service stress; the fast cracking mechanism typically receiving far more than enough energy from the release of elastic strain (from continuing crack propagation) than needed to produce new fracture surface. There is, unfortunately, very little possibility of arresting the propagation of an active, critical-size crack or flaw in a monolithic ceramic structure, short of total catastrophic failure.

It is plausible, however, that certain filler-type joining materials, such as viscous glasses or ductile metal adhesives, if properly designed and positioned, could interact with a moving crack front to arrest, divert or otherwise immobilize the cracking mechanism. Conceivably, both butt joints and shear type joints could be utilized for such purpose.

It was conceived that the effectiveness of a given filler-adhesive in arresting and/or diverting an existing crack in a joined ceramic assembly would depend largely on certain desired physical attributes and mechanical properties of the filler; viz.

1. A significantly lower elastic modulus than the ceramic, to mitigate the stress-intensity factor of the crack (as it enters the filler), Ref. 2.

2. A lower minimum interatomic bond strength than that of the ceramic; to promote retention of the crack (propagation path) within the filler and/or along the filler/ceramic joint interface. (This constitutes crack diversion; Ref. 2.)

3. A high potential (unlike the ceramic) to safely absorb cracking-released energy through viscous flow or plastic flow of the filler, ahead of the crack front.

All three of the above favored attributes may exist simultaneously in a given filler; or just one or two. Because so much depends upon the composition and physical nature of the filler itself, no exploratory testing in this area is planned until the most promising specific filler adhesives (for all other described joint functions) are defined and identified in Tasks 1, 2 and 4 (see Fig. 1). Completion of the critical Task 1 study has been deferred approximately 5 months due to late receipt of candidate glass adhesives (see above).

2.5 TASK 5 - IMPROVED JOINING AND FABRICATION METHODS

Integrity of ceramic-joint structure is a vital foundation to all of the normal and special relaxing-joint functions cited in the preceding discussion (Tasks 1 through 4). Prior studies (Ref. 1) have outlined the need for improved joint processing and fabrication in certain areas, in order to obtain a desired consistant high level of glass/ceramic bond integrity. For example, good wetting, flow and bonding of the filler glass to the silicon-based ceramic is strongly dependent upon the pre-formation of a natural, strongly bonded silica-rich oxide on the ceramic faying surfaces. This pre-oxidation step is routinely accomplished by airfurnace oxidation at 2400-2500°F (24 (+) hours); but it is time-consuming; it risks partial melting and exudation of free silicon metal binder in the base ceramic; and, of most importance to joint function, produces only a vanishingly thin layer of natural silica oxide, several angstroms thick (Ref. 1.) As developed above, this thin silica layer is only marginally adequate to promote desired

filler-glass wetting and bonding. Moreover, it is not thick enough to serve as an effective physical barrier between filler and ceramic, to prevent undesirable glass/ceramic interaction and resultant CO or N_2 gas formation at the bond interface (Ref. 1). The current task work involves development and evaluation of special refractory, high-silica glass coatings (approximately 2-3 mils thick) applied as a pre-glaze (2250-2350°F) prior to filler-glass application; as a hopefully superior substitute for ceramic pre-oxidation. Desired objectives include (a) reliably superior glass wetting and ceramic bonding, (b) avoidance of silicon metal melting (within the ceramic) and (c) prevention of joint-disruptive reaction gases, forming at the filler/ceramic joint interface.

Another work area is that to develop high-density, essentially porosity-free and gas-bubble-free filler glass in the bond regions. Prior work with low-packing-density glass slurries (Ref. 1) revealed that after normal sinter-bonding, the resultant 90-95 percent dense fillers were adequate in providing mechanical bond strength and joint relaxation function, but were susceptible to premature failure under high-gas-pressure sealing conditions at elevated service temperatures (Refs. 1 and 3). The process solution sought in current task work is the initial application of approximately 100% dense filler glass to the ceramic faying surfaces (as in Fig. 2), by one of two possible glass-industry methods: (1) Hand-artisan (glass-blower) application of bulk high-density glass (rod, cullet, or frit) or (2) slip-spray application of very fine filler-glass powders to the faying surfaces (to achieve high-packing-densities), followed by routine sinter-bonding and glazing. (Refs. 1 and 2). In both methods, pre-glazing the faying surfaces with the refractory, high-silica coatings discussed above might also be carried out prior to filler glass application, to promote improved filler/ceramic bonding and to circumvent reaction-gas bubble formation at the bond interface.

3

PROGRAM STATUS

3.1 TASK 1 - LONG-TERM JOINT STABILITY

All candidate glass fillers scheduled for relaxing joint application in the subject program (Ref. 2 and Tables 2 and 3) have now been received, and placed in various isothermal air furnace exposure regimes to evaluate long term structural stability of the initial glassy structures. See Table 2 for a listing of each glass filler, along with the range of proposed service temperatures for each filler (corresponding to a required viscosity range for relaxation function of $10^{10} - 10^8$ poise) and the exposure test regimes currently underway. All glasses, except Corning 6750 which was received very late, have now passed the 500-hour exposure marks (Table 2) and are currently being evaluated for structural stability by metallographic-petrographic examination and SEM/EDX analysis of original glass versus (any) glass transformation products formed. Partial TTT diagrams have been constructed for Corning 7800 and 7740 borosilicate glasses (Figs. 4 and 5). These illustrate the superior structural stability of the 7800 glass over 7740 glass; particularly at 1450°F which is near the high temperature end of the normal borosilicate service temperature range. After 500 hours at 1450°F, the original glassy structure of 7740 glass is approximately 42 percent transformed, while the 7800 glass is only approximately 15 percent transformed. Last year's work showed that the effective viscosity of 7800 glass is little changed by this exposure; while 7740 glass experienced a major shift upward in viscosity (Ref. 1). 7800 glass also appears superior to 7740 at 1650°F (Cf. Figs. 4 and 5). It is hoped that 7800 glass (the most promising in last year's study) will show no more than 15 to 25 percent transformation at any service temperature exposure out to 2000 hours.

From the service stability viewpoint, the least promising borosilicate glass for 1400-1450°F application would appear to be Corning 7760. Out to 500 hours exposures at 1050°F and 1250°F, negligible transformation of 7760-glass structure was discerned (similar in this low-temperature aspect to Corning 7740 and 7800, above). However, after 500 hours exposure at 1450°F, $\geq 60\%$ transformation was obtained, making 7760 appear somewhat less structurally stable at 1450°F than 7740. This was unfortunate, inasmuch as Corning 7760 received the highest ranking in associated studies (Task 5) for best adaptability to hand-artisan application to ceramic surfaces and for high resistance to within-filler and bond-interface cracking on process cool-down (see Task 5; this section). Fortunately, the Ferro RV-3324 borosilicate glass (Tables 2 and 3) proved to be virtually equal in merit to 7760 in these same categories, as well as exhibiting remarkable structural stability in exposure tests to date. This is discussed below.

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Table 3

Listing of Candidate Glass Adhesive Materials; Relaxing-Joint Concept
(Task 1 - Ceramic-to-Ceramic Shear Joints)

| Glass Designation	Source (Mfr.)	Glass Type	Nominal Composition (% Wt) SiO_2	Al_2O_3	B_2O_3	Na_2O	K_2O	MgO	CaO	BaO	$F^{(-)}$	(Viscosity Data) Temperature (°C) Relative to — Relaxing Joint Concept 10^{10} poise	10^8 poise	Softening Point $10^{7.6}$ poise	Working Point 10^4 poise	Thermal Expansion Coefficient (10^{-7} cm/cm/C) (0-300°C)	Density (gm/cm³) RT	Elastic Modulus (E)/RT kg/mm² x 10³	psi x 10⁶
0080	Corning	Soda-Lime	73.0	1.0	-	17.0	-	4.0	5.0	-	-	~604 (~1120°F)	~688 (~1270°F)	696 (1285°F)	1005 (1841°F)	93.5	2.47	7.1	10.2
6750	Corning	Soda-Lime	61.0	11.0	1.0	15.0	-	-	-	9.0	3.0	~571 (~1060°F)	~666 (~1230°F)	676 (1249°F)	1040 (1904°F)	88.0	2.59	-	-
7740	Corning	Borosilicate	81.0	2.0	13.0	4.0	-	-	-	-	-	~671 (~1240°F)	~804 (~1480°F)	821 (1510°F)	1252 (2286°F)	32.5	2.23	6.5	9.1
7760	Corning	Borosilicate	79.0	2.0	15.0	2.0	2.0	-	-	-	-	~638 (~1180°F)	~760 (~1400°F)	780 (1436°F)	1198 (2188°F)	34.0	2.24	6.3	9.0
7800	Corning	Soda-Barium Borosilicate	74.8	5.6	9.6	6.4	0.5	-	0.9	2.2	-	~677 (~1250°F)	~782 (~1440°F)	795 (1463°F)	1189 (2172°F)	50.0	2.36	-	-
1720	Corning	Alumino-Silicate	62.0	17.0	5.0	1.0	-	7.0	8.0	-	-	~816 (~1500°F)	~901 (~1655°F)	915 (1679°F)	1202 (2196°F)	42.0	2.52	8.9	12.7
RV-3324	Ferro	Borosilicate	79.0	Proprietary								~1250°F (?)	~1450°F (?)						
RV-3320	Ferro	High-Silica	88.0	Proprietary								~1850°F (?)	~2050°F(+) (?)						
7913 (Ref. only)	Corning	96% Silica (Vycor)	96.5	0.5	3.0	-	-	-	-	-	-	-	-	1530 (2786°F)	-	7.5	2.18	6.9	9.8
7940 (Ref. only)	Corning	Fused Silica	99.9	-		(0.1% H₂O)						-	-	1580 (2876°F)	-	5.5	2.20	7.4	10.5

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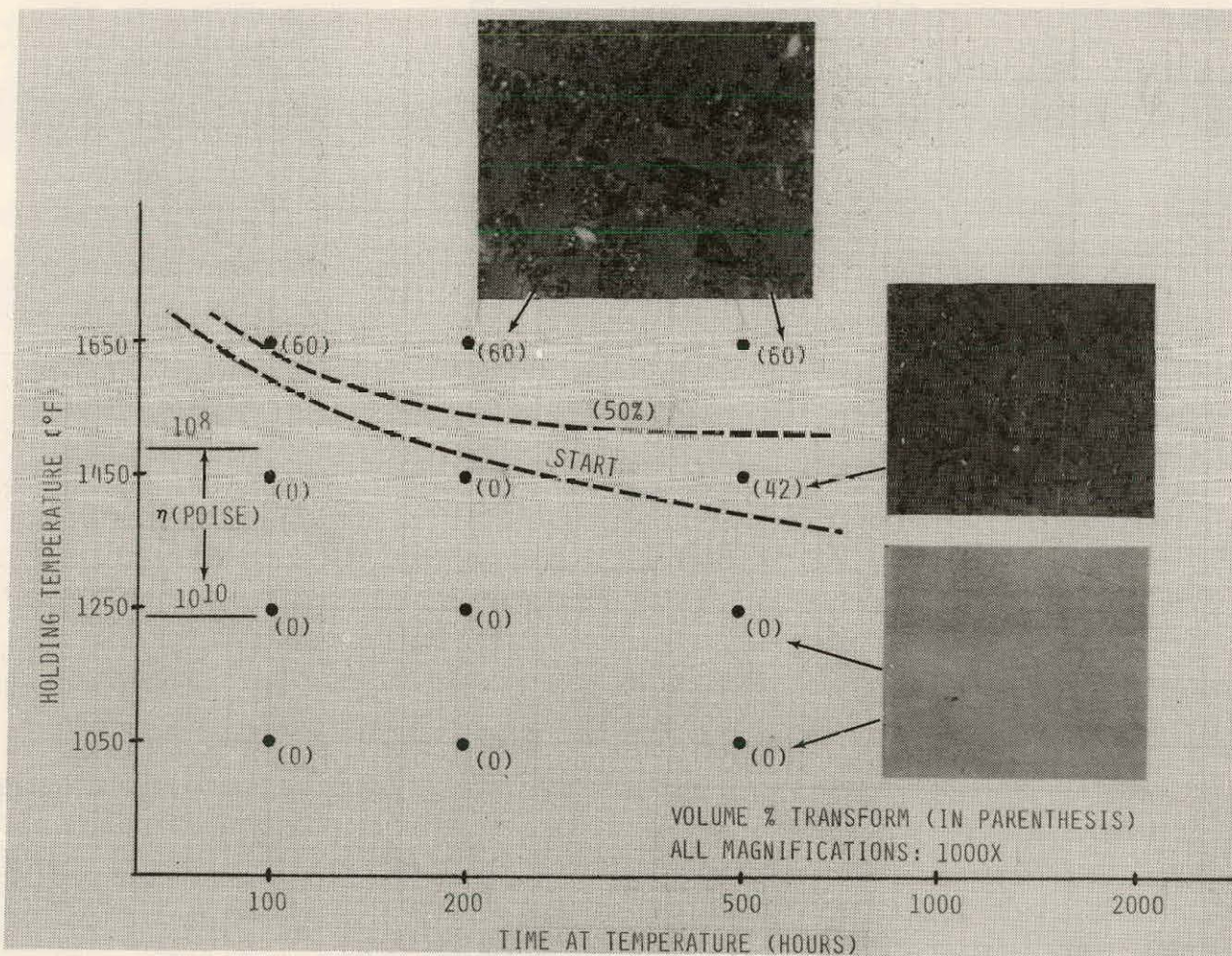
Figure 4. Time-Temperature Transformation (Corning 7740 Glass)
Initial Viscosity is Shown

Petrographic and SEM/EDX studies of the above borosilicate glasses indicate
that they generally transform by a phase-separation reaction i.e., into two
new glasses: (1) a somewhat higher silica, lower boric oxide glass than the
original glass, and (2) a somewhat lower silica, higher boric oxide glass
than the original. So long as the original, untransformed glass (and to some
extent, the compositionally similar first new glass above) remains as the
continuous, matrix glass and the constituent volume remains high ($\geq$50% Vol.),
then little change in effective filler viscosity is anticipated. (Ref. 8.)
Note the critical 50% volume transformation lines on the TTT diagrams cited
above. Of course, this assumption will have to be confirmed in subsequent
baseline relaxation-rate tests and related viscosity determinations (Task 2).

The subject exploratory study has uncovered one particular area of concern;
viz., that considerably more rapid glass transformation occurs at (and likely
above) 1650°F, than $\leq$1450°F; true for all candidate borosilicate and alumino-
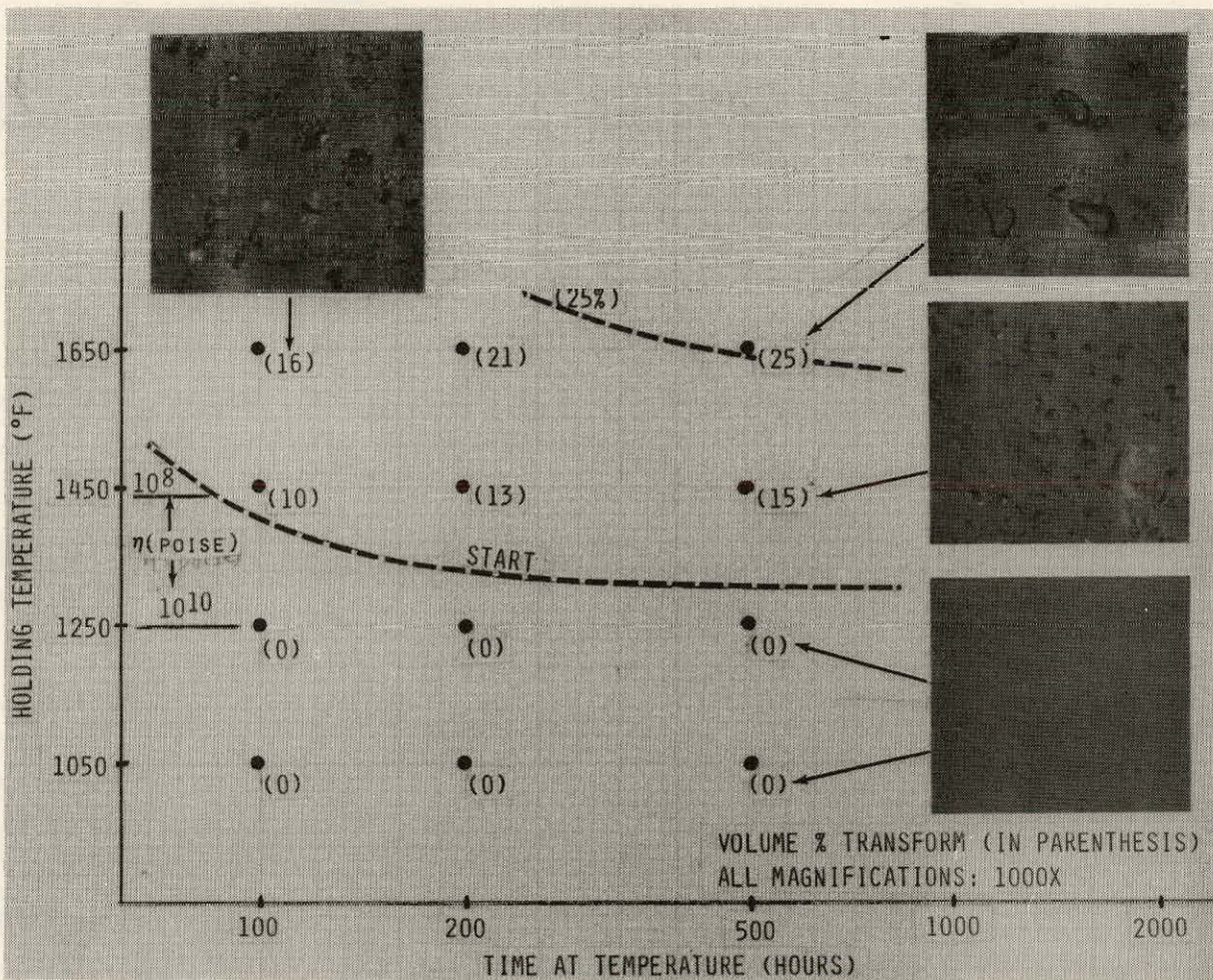silicate filler glasses examined to date, with the possible (and hoped for)

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Figure 5. Time-Temperature Transformation (Corning 7800 Glass)
Initial Viscosity is Shown

exception of RV-3324, see Figure 6. (RV-3324 glass was specifically formu-
lated by Ferro Corp. to provide superior long-term stability of glassy
structure, Ref. 1).

The practical significance of this still-tentative general observation is
that no commercial candidate glass may be suitable for long-term joint service
in the general vicinity of 1650°F and possibly above (i.e., to the conjugate
temperature). Note the partial TTT diagram for the representative alumino-
silicate glass, Corning 1720; which is nominally a 1500-1650°F glass based
upon viscosity and demonstration of relaxation function for the as fired
condition. (Fig. 7 and Ref. 1.) It is evident from 1720's strong transform-
ation tendencies at 1650°F and 1850°F that long-term structural stability is
doubtful for these and adjacent temperatures. Unlike the borosilicates, the
candidate aluminosilicate is reported to transform by precipitation of equil-
ibrium, high-alumina, crystalline compounds; viz. to mullite and/or anorthite.
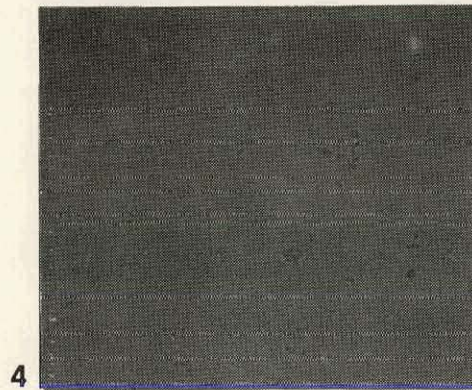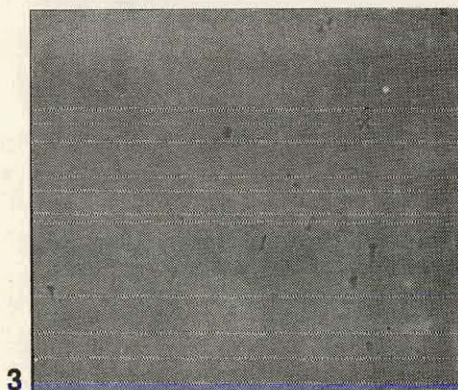(Ref. 1.) Continuous rigid, internal networks of these crystals, precipitated
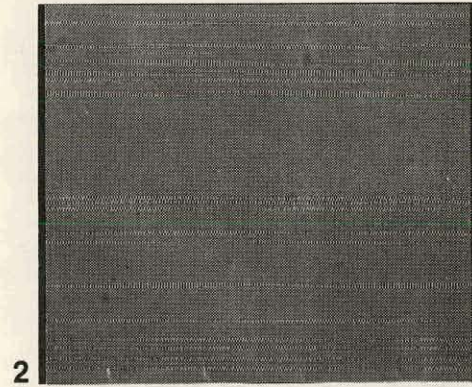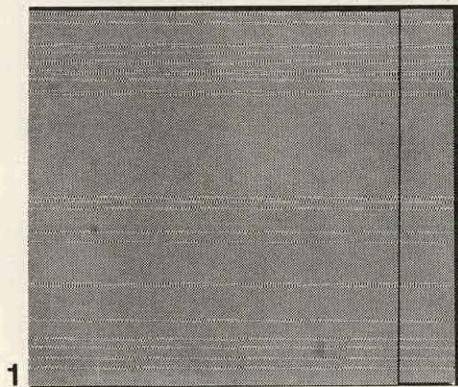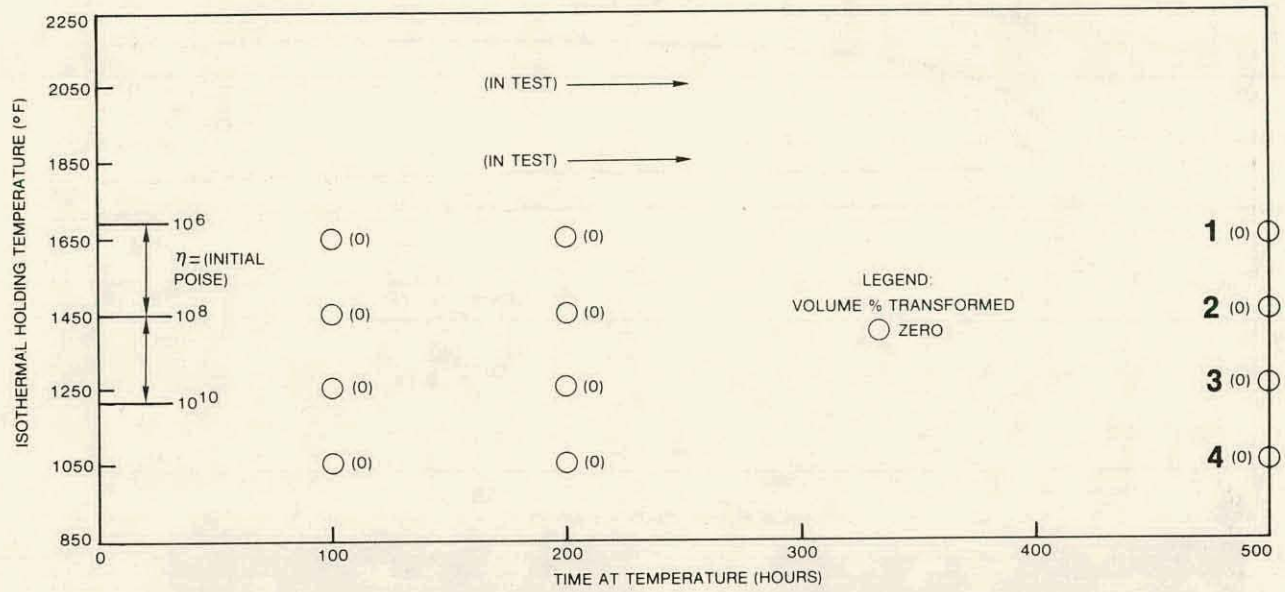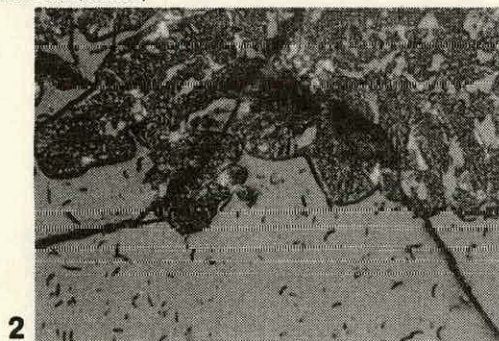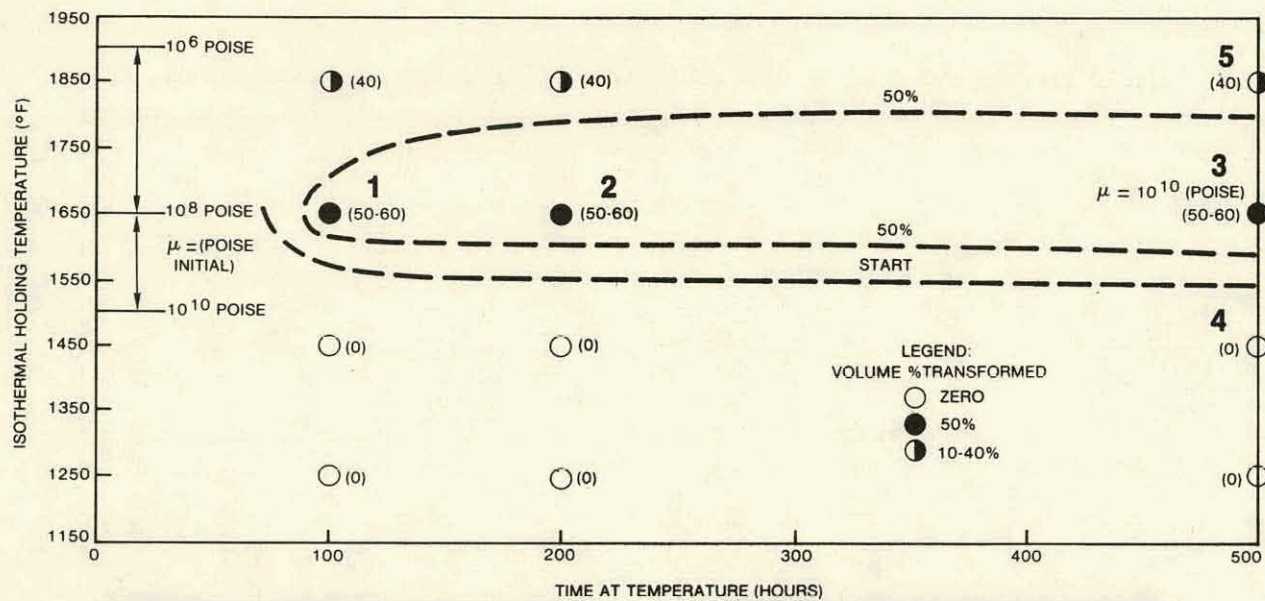
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Figure 6. Time-Temperature Transformation (TTT) (Ferro RV-3324 Glass)

Original Photomicrographs 500X
Reproduced 32% in Reproduction

Figure 7.   Time-Temperature Transformation (Corning 1720 Glass)

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during actual or simulated service, should (and do) effect marked increases in filler viscosity (true, based on prior experience, Ref. 1) and would if extensive, be far more detrimental to long-term stability than phase-separation.

In view of the above emerging situation, attempts will be made next period to develop new high-stability glass fillers to accommodate stable-joint service and relaxation function over the temperature range of approximately 1500-2050°F. Prior work (Ref. 1) has shown that desired filler viscosities in this temperature range can be obtained by slurrying and sintering of controlled fine-powder admixtures of a very stable, high silica, very high viscosity glass (e.g., fused silica, Vycor, or RV-3320) to a matrix of a lower-than-desired viscosity glass (e.g., 7740 or 1720). This results in an intimate physical mixture of two finely dispersed glasses; termed "TPG" or "two-phase glasses". (See Ref. 1.) Unfortunately, as discussed above, both 7740 and 1720 are now known to be quite structurally unstable in the above temperature interval of interest; which likely explains why the initial viscosities of prior TPG glasses proved unstable on long-term service holding (Ref. 1). In the planned TPG-glass study of the current program, emphasis will be on controlled fine powder mixtures of the ostensibly very stable RV-3324 glass with Vycor, fused silica and RV-3320.

3.2 TASK 2 - DETERMINATION OF ENVIRONMENTAL AND SERVICE EFFECTS ON
              JOINT RELIABILITY

No work was conducted on Task 2 this reporting period. Initiation of Task 2 work must logically await final recommendations on preferred glass adhesives from Task 1 (see Fig. 1).

3.3 TASK 3 - VISCOELASTIC DAMPING OF GLASS BONDED CERAMICS

Excessive in-service vibration of ceramic components and ceramic assemblies is a valid design concern, particularly for high performance, and hopefully fail-safe, energy systems which cannot tolerate any major ceramic failures. Unlike most engineering metals which possess inherent damping capabilities and plasticity, engineering ceramics are predominantly elastic in response, exhibit negligible self-damping at all service temperatures to 1800°F (see Fig. 8), and are quite sensitive to excessive vibration. Therefore, great care must be exercised in system design to avoid resonant frequencies and associated high amplitudes during service. Obviously, this avoidance of critical amplitudes is difficult to guarantee entirely in complex energy systems involving ceramics.

It has been reported that some glassy ceramics, such as glassy porcelains, exhibit appreciable viscoelastic self-damping over certain ranges of temperature and viscosity (Ref. 7). One primary objective of Task 3 is to determine whether or not specific glass adhesives (from Task 1) will also confer significant self-damping to joined ceramic structures. Based upon
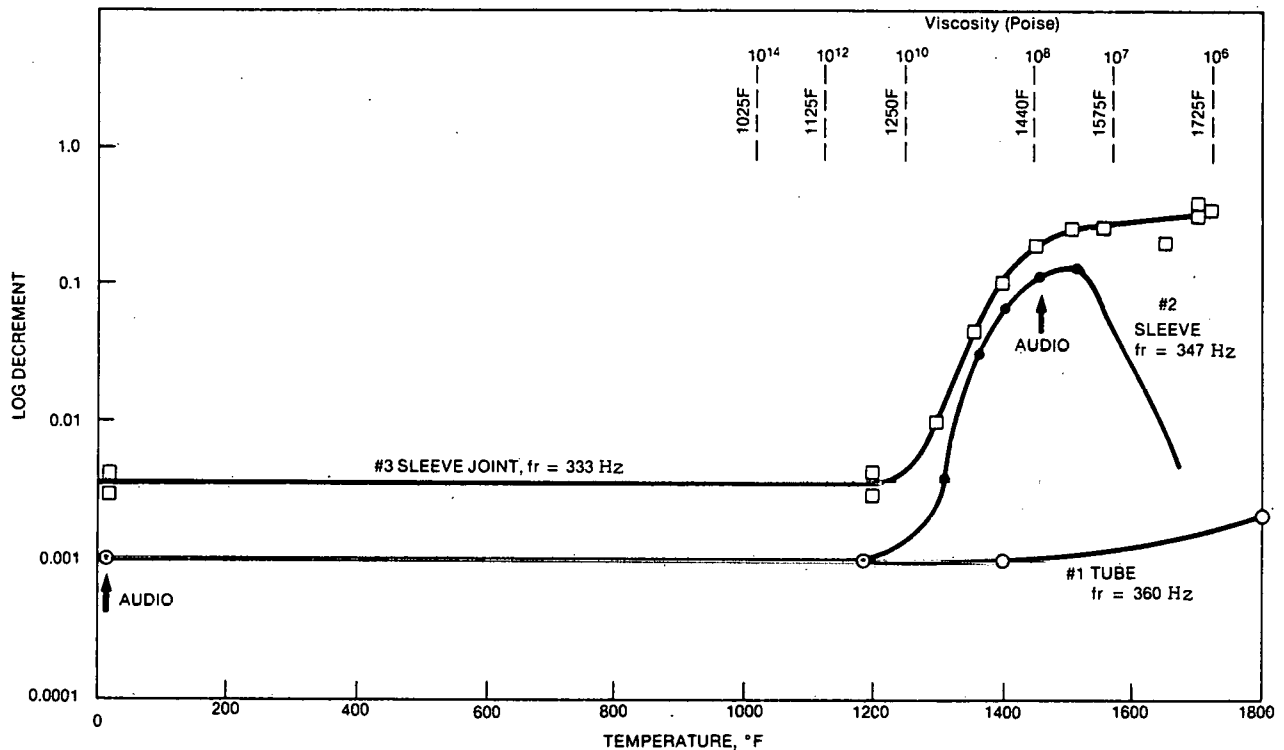
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Figure 8.   Log Decrement for RSSC Tubes with 7800 Glass
Bonded Sleeve

upon the referenced study with porcelains, maximum viscoelastic damping
might be expected over roughly the same viscosity range as required for
proper joint relaxation function, namely a viscosity range of approximately
10^8 to 10^{10} poise (Refs. 1 and 7). Three related tubular test specimen
configurations were adopted for the study of ceramic joint damping at basic
resonant frequency.

Type NC-430 (RSSC) silicon carbide tubes of the variety used in a recently
completed ceramic heat exchanger study (Ref. 3) were utilized for specimen
material. Residual Corning 7800 glass (Ref. 1) was adopted for the demon-
stration glass adhesive, because it was the most stable and promising glass
identified in prior work at Solar (Ref. 1). The baseline specimen (No. 1)
consisted of a monolithic silicon carbide tube alone, without a tube joint or
sleeve attachment (nominal dimensions; 1.00in. OD x 0.24 in. wall x 36.0 in.
length). The second specimen (No. 2) consisted of the same basic monolith
tube, but with a short NC-430 tube sleeve attachment, glass bonded over the
tube at the mid-length position. (Nominal dimensions of the tube sleeve:
1.02 in. ID x 0.15 in. wall x 3.0 in. length; concentric tube joint gap
clearance [glass filled] = 0.010 in.).

The third test specimen (No. 3) had the same external appearance and nominal
dimensions as the second specimen described above. It was, however, a glass-
bonded tube joint with sleeve, inasmuch as the 36-inch long basic tube was
first cut in half, prior to being reassembled and glass-bonded together, along

with the tube sleeve attachment (see schematic, Fig. 9). Joint separation between the tube halves was set at 0.062 inch. The concentric tube joint gap clearance (glass filled) was 0.010 inch, as in the second specimen. Each of the three tube specimens was tested in sequence, by being suspended at the nodal points within a furnace chamber and then struck with a rubber mallet to induce a resonant vibration of a constant initial amplitude, which was then allowed to decay freely. See Figure 9 for a schematic diagram of the experimental setup. This test comprised a self-damped oscillator with no driving force (Ref. 9). Note that the glass adhesives were placed in the central regions of highest dynamic strain, to realize most effective damping for each test temperature and specimen configuration.

The logarithmic decrement method was employed to characterize the relative damping capabilities of the three specimens at different isothermal test temperatures in the range, RT to 1800°F (see Refs. 2 and 9 and Figs. 8 and 9): Logarithmic decrement, δ, is defined as the ratio of (a) energy absorbed or damped out per dynamic cycle, over (b) the maximum (initial) cyclic strain energy. Expressed mathematically:

$$\delta \ = \ \left(\frac{1}{n}\right) \ \ln \ \left(\frac{X_o}{X_n}\right) \qquad\qquad \text{Eq. 1}$$

where   n   =   number of cycles experienced during the decay test period

              X_o =   the initial dynamic amplitude

              X_n =   the dynamic amplitude, n cycles later.

The results of damping tests conducted this period are given in Table 4 and illustrated in the comparison damping curves (δ versus T) of Figure 8.

The following observations have been made regarding the above test data.

- The baseline, monolithic ceramic tube (Specimen No. 1) exhibits very little self-damping potential at any test temperature (RT – 1800°F), and rings like a bell at all test temperatures to 1800°F (see Fig. 8).

- The two specimens with glass bonded ceramic sleeve attachments (Specimens No. 2 and 3) also exhibited minimal self-damping at the lower range of test temperatures (viz. RT to 1200°F). However, at 1300°F and above, significant self-damping was obtained; which is tentatively attributed to viscoelastic absorption of vibration energy by the 7800 glass adhesives (Fig. 8). For the monolithic tube with sleeve attachment (Specimen No. 2), damping reached an apparent maximum at 1500°F; with the value of log decrement at 1500°F more than two orders of magnitude greater than the RT value!

FURNACE

MICROPHONE

FURNACE

RESONANT FREQUENCY

SIGNAL
PROCESSOR

AMPLITUDE
(X)
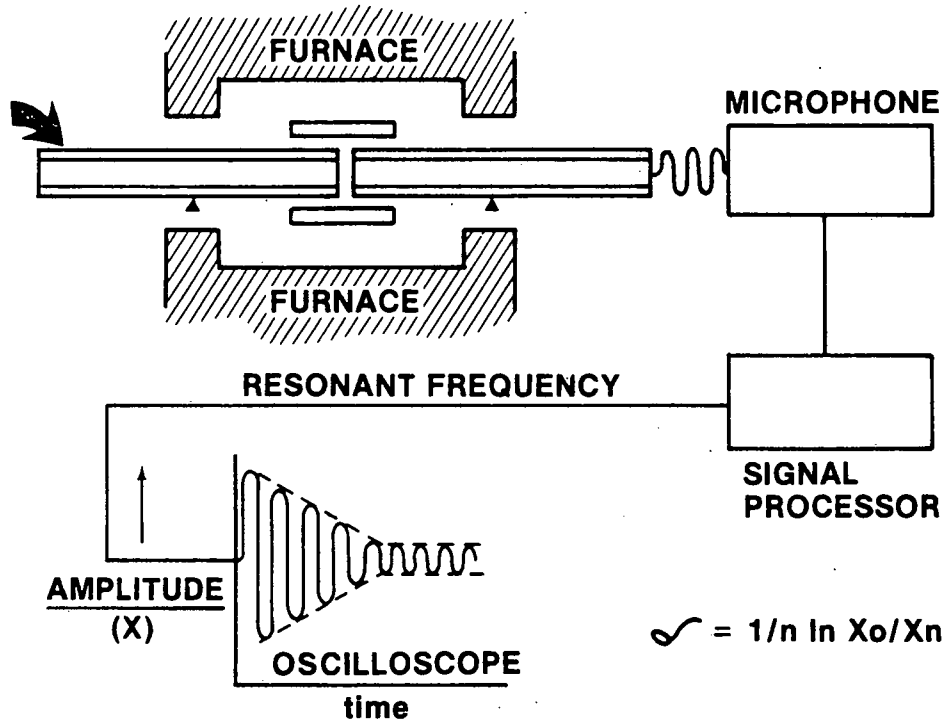
OSCILLOSCOPE
time

$\mathcal{J} = 1/n \ln X_o/X_n$

Figure 9.   Schematic of Ceramic Tube Damping Test (Glass-Bonded
Tube Specimen Suspended at Nodal Points, Within Furnace)

- The viscosity of 7800 glass at 1300°F is about $10^{9.5}$ poise; at
  1500°F about $10^{7.5}$ poise. This is about the viscosity range expec-
  ted for effective viscoelastic damping (Ref. 7). Very likely, at
  temperatures <1300°F, the 7800 glass is too stiff for effective
  viscoelastic response; and >>1500°F, the glass becomes too fluid to
  transfer viscoelastic shear.

- The tube-joint specimen with glass-bonded sleeve attachment (No. 3)
  exhibited very similar improvement in damping to the monolith with
  sleeve (No. 2), except that damping efficiency generally continued
  to improve up to the top test temperature of 1700°F (Fig. 8).
  This is believed due to minor slumping of the tube center >1550°F,
  so that the tubejoint end surfaces (>1550°F) undoubtedly contacted
  the tube-sleeve inside diameter surface. Consequently, viscoelastic
  damping was likely reinforced by surface-friction damping.

Based upon the above, it appears that significant viscoelastic damping of
ceramics can be achieved with a relatively small quantity of viscous glass
adhesive at service temperatures which provide the proper range of glass
viscosity (approximately $10^{9.5}$ to $10^{7.5}$ poise). The concept appears feasible
for both the ceramic monolith and joined ceramic assemblies.

A final series of damping tests was conducted with a fourth tube-joint
specimen; similar in design to No. 3 except that the central tube joint and
sleeve attachment were argon-brazed with pure silicon metal instead of being

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Table 4

Damping Test Results on Glass Bonded Ceramics (Task 3)

Specimen Descripton	Resonant Frequency Monitored (H_z)	Test Temperature (°F)	Logarithmic Decrement (δ)
No. 1 Monolithic Tube; RSSC (NC-430); Baseline (no glass)	360	RT 1200 1400 1800	1.0×10^{-3} 1.0×10^{-3} 1.0×10^{-3} 2.0×10^{-3}
No. 2 Monolithic Tube, RSSC (NC-430) With Glass Bonded* NC-430 Sleeve Attachment	347	RT 1200 1300 1350 1400 1450 1500 1550	1.0×10^{-3} 1.0×10^{-3} 4.0×10^{-3} 3.0×10^{-2} 6.0×10^{-2} 8.0×10^{-2} 1.2×10^{-1} 7.0×10^{-2}
No. 3 Tube With Glass Bonded* Center Joint (RSSC; NC-430) and Glass Bonded* NC-430 Sleeve Attachment	333	RT 1200 1300 1350 1400 1450 1500 1550 1600 1650 1700	3.5×10^{-3} 4.0×10^{-3} 1.0×10^{-2} 4.0×10^{-2} 1.0×10^{-1} 1.7×10^{-1} 2.2×10^{-1} 2.3×10^{-1} 1.4×10^{-1} 1.7×10^{-1} 3.1×10^{-1}

*Corning No. 7800 Glass

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glass bonded. This was to confirm that all significant self-damping measured in prior tests (Specimen Nos. 2 and 3) was, in fact, due to the glass adhesive alone, with no sensible contribution from the crystalline silicon-metal infiltrant and bonding agent of the NC-430 tube materials. The data shown in Table 5 supports the above assumption up to the melting temperature of silicon (2550°F).

3.4 TASK 4 - CRACK ARREST AND CRACK DIVERSION BY JOINTS

No work was conducted on Task 4 this reporting period due to late arrival of candidate glass adhesives.

3.5 TASK 5 - IMPROVED JOINING AND FABRICATION METHODS

Last year's study of glass bonding (Refs. 1 and 2) demonstrated that (brush-applied) powder slurry methods of glass application and air firing invariably result in filler glass joints possessing high concentrations of porosity and entrapped air bubbles. These high-porosity ceramic joints, although exhibiting adequate bond strength, good pressure sealing at room temperature, and predictable relaxation function, tend to fail prematurely under situations requiring gas pressure sealing at elevated service temperatures. This is believed due to sequential collapse of in-line porosity (Fig. 10), in effect

Table 5

Damping Test of Silicon-Brazed Ceramic (Task 3)

Specimen Description	Resonant Frequency Monitored (Hz)	Test Temperature (°F)	Logarithmic Decrement (δ)	Comments
No. 4 Tube With Si-Brazed Center Joint (RSSC; NC-430) and Si-Brazed NC-430 Sleeve Attachment	350	RT 1400 1800 2000 2200 2400 2500 2525 2550	1.0×10^{-3} 5.0×10^{-4} 4.0×10^{-4} 4.0×10^{-4} 5.0×10^{-4} 4.0×10^{-4} 7.0×10^{-4} 2.5×10^{-3} 7.0×10^{-3}	Rings like bell

↓
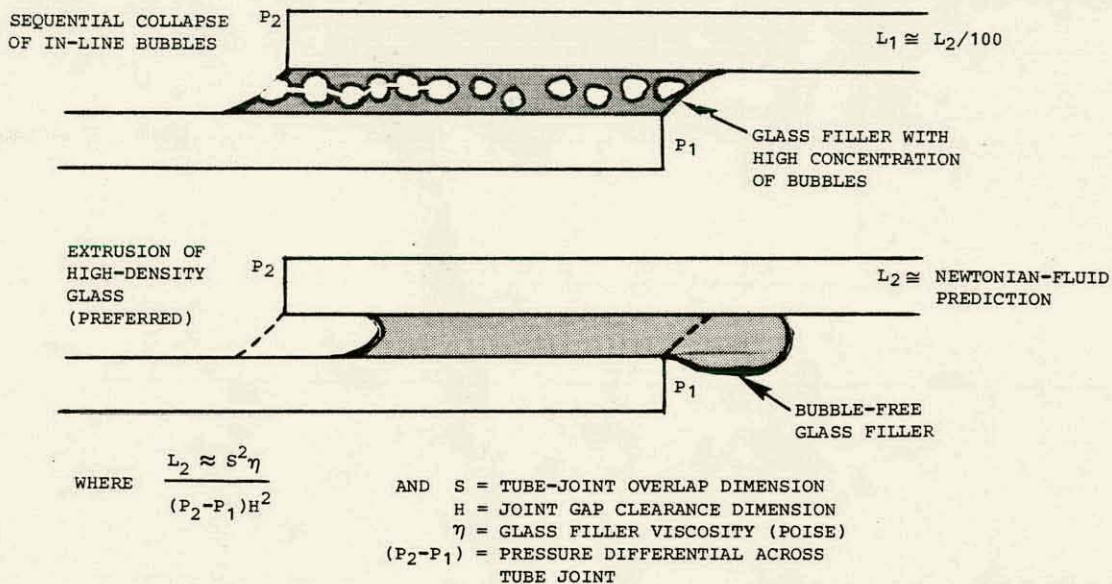
Silicon Braze Melts; Ringing Stops |

Figure 10. Advantage of Bubble-Free Glass Adhesive for Long-Life Pressure Sealing (L = Effective Joint Life, as a Pressure Seal)

forming a leakage-line conduit through the joint glass in 1/50 to 1/100 the time (L) predicted for bulk extrusion of the glass filler, based on Newtonian flow due to differential pressure (see Equation in Fig. 10). To cirvumvent this problem, work this year is concentrating on two alternative methods of glass application to the joint areas prior to telescoping assembly (Figs. 2, 11), hopefully to provide high-density, porosity-free zones of glass filler adhesive. The first involves ball milling the glass frit to very fine, homogeneous powders (-300 mesh) and precise high-pressure spraying a water-base slip of these powders onto the faying surfaces. This is followed by air firing at temperatures corresponding to $\eta = 10^4$-10^5 poise to form a very dense surface glaze. The second method involves hand artisan or glass blower related techniques to hand apply bulk, high-density glass to the joint regions (Ref. 2). Unfortunately, at low glass viscosities and corresponding high temperatures where both methods of glass application and bonding are facilitated (e.g., $\eta = 10^4$-10^5 poise), all candidate glasses have the potential to react with bare SiC faying surfaces to form carbon monoxide (CO) gas at the joint interface (Refs. 1 and 2). (An analogous reaction occurs with Si_3N_4 surfaces to form N_2 gas.) These bubbles either remain at the interface, which acts to inhibit good filler wetting and bonding, and/or evolve and become entrapped in the glass filler proper, to compromise gas pressure sealing capability at service temperature, as explained above. Typically, large entrapped bubbles can be minimized by hand working the glass at lower temperatures ($\eta = 10^{5.5-6.5}$); but then the glass becomes quite stiff and much more difficult to apply, and tiny interface bubbles still tend to form on bare SiC. Telescoping SiC tube joints (NC-430) made at these lower temperatures tend to fail by SiC/glass interface shear at low differential pressures in sealing tests (even at RT). One solution, which also has the added benefit of promoting good SiC/glass wetting and bonding, is the pre-oxidation of SiC faying surfaces (e.g. 2400-2500°F,
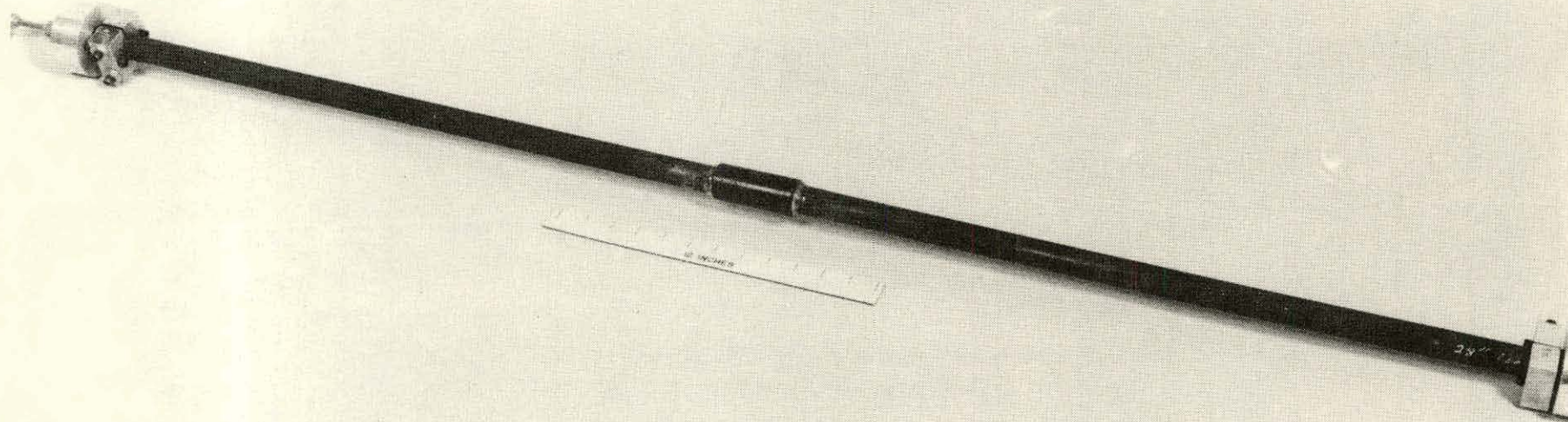
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Figure 11. Glass Bonded NC-430 Tube-Sleeve Joint Specimen
(Set Up for Pressure Sealing Tests)

24 hours, air atmosphere). The basic problem here is that the natural SiO_2 oxide film formed on the SiC faying surfaces during recommended pre-oxidation is just Angstroms thin, and only marginally serves as a physical barrier to the SiC/glass reaction at application temperatures which generate CO gas (Ref. 1). There is also the risk of melting the free silicon metal binder in the silicon-base ceramics during pre-oxidation, which can disrupt the protective oxide.

Task 5 work this period has concentrated on augmenting the potential effectiveness of the natural surface oxide film as a reaction barrier; by laying down a much thicker refractory glaze (approx. 2-3 mils) on top of it, a glaze based upon a high silica commercial glass such as Ferro RV-3320, Vycor, or fused silica. These glazes are applied by a slip-spray technique and fired at 2250-2350°F, well under the melting point of the silicon metal binder of NC-430. Work to date indicates that borosilicate filler glasses such as Corning 7740 and 7800 can be applied to the subject pre-glazed surfaces at preferred high process temperatures, corresponding to $\eta = 10^5$ poise poise, with negligible bubble generation. Based upon the significantly increased difficulty in physically removing these same filler glasses from the glazed SiC surfaces, it is apparent that SiC/glass bond strength can also be improved. The acid test of the practical efficiency and utility of these high silica glazes will be made next period, when elevated temperature gas pressure sealing tests will be conducted with Corning 7740 and 7800 bonded tube-sleeve joints (as shown in Fig. 11), comparing glazed versus unglazed joint processing. Test temperatures will correspond to $\eta = 10^8$ poise and $\eta = 10^9$ poise, in the proposed service (relaxation) range. These test joints are typical of planned ceramic tube heat exchanger joints (Ref. 3). If the glazes work well, and enable attainment of predicted seal life, this will represent a significant advancement in the glass bonding of ceramics.

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SUMMARY AND PLANNED FUTURE WORK

Task 1 studies to characterize the long-term structural stabilities of various candidate glass adhesives are now approximately 50 percent complete. Work was delayed by late arrival of glass and ceramic test materials. Next period, time-temperature-transformation (TTT) diagrams for all candidate glasses should be completed (out to 2000 hours, 1250-2050°F). Selections of the most stable and promising glasses for relaxation joints will then be made, enabling initiation of principal work on Tasks 2, 4 and 5 (Fig. 1). Present indications are that most commercial candidate glasses will need to be modified to provide desired levels of structural stability at service temperatures $\geq$1650°F.

Task 3 studies, to characterize the potentials of glass-bonded ceramic joints for viscoelastic damping, were essentially completed this period. Both glass-bonded ceramic tube joints and simple glass-bonded sleeve attachments (to monolithic ceramic tubes) were shown capable of conferring one to two orders of magnitude increases in self-damping, at elevated temperatures corresponding to glass viscosities of $10^{7.5}$ to $10^{9.5}$ poise.

Task 5 studies, to improve glass-joint processing and quality, were initiated this period. Major effort was in two areas: (1) development of refractory pre-glazing techniques, primarily to facilitate filler-glass wetting and bonding at desired high-process temperatures, without attendant problems of gaseous reaction products; and (2) ball-milling and slip-spraying and sintering of filler glasses (as opposed to previous slurry methods) to obtain highdensity, porosity-free glass bonds. Future work next period, evaluating the long-term gas pressure sealing ability of test joints will assess the (anticipated) superiority of these advanced joining processes.

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APPENDIX A

SYNOPSIS OF THE CERAMIC RELAXING JOINT CONCEPT

APPENDIX A

SYNOPSIS OF THE CERAMIC RELAXING JOINT CONCEPT

Advanced engineering structures for energy conversion require ceramic components to be joined to other ceramic components, as well as to metallic support structures. Joints in high-modulus ceramic systems can be treated as both problems and opportunities. Problems arise because interfacial interactions at the mechanical and chemical level are difficult to control and because non-uniform load transfer between non-plastic members may lead to high stress concentrations. The innate brittleness of ceramics can be accentuated to a serious degree in joint regions due to normal changes in design section, random surface-point or line-asperity contacts, misalignment or misfit of faying surfaces, and similarly unavoidable real-world circumstances of production. On the other hand, joints also represent periodic interruptions in the continuity of an otherwise monolithic unyielding elastic structure; hence the opportunity aspect. The opportunity is vitiated by the use of mechanical bonding or conventional, high modulus, crystalline refractory cements. However, with proper joint design and bonding materials, advantage can be taken of these structural discontinuities to reduce both the local stress concentration at the joint (mentioned above) as well as the nominal stress levels in the main structural components. For example, the spatial intervals provided between joint interfaces can be filled with low-to-intermediate stiffness bonding materials possessing controlled compliancy characteristics (e.g., viscous glasses or heat-resistant ductile metal alloys). Properly designed, this type of joint might well be employed to reduce local stress concentration and to safely accommodate (alleviate) otherwise inordinate service-imposed stresses and strains through plastic or viscous flow (relaxation) of the joint filler; while concurrently operating in the conventional sense by providing a continuous medium for service-load transfer, gas sealing, heat transfer, etc. Joining systems incorporating the above features are basically the novel "compliant-interlayer" and "relaxating joint" concepts currently being explored and evaluated in the subject program, for possible future application to high performance energy systems.

The primary program objectives are the logical selection, successful demonstration and design characterization of various "viscous relaxing" and "compliant-interlayer" materials, in both shear joint and butt joint configurations representative of high performance energy systems. The specific ceramics of interest are silicon carbide (SiC) and silicon nitride (Si_3N_4), joined both to themselves and to different metallic superalloy (supporting) substrates. The overall range of joint temperatures considered is 1250 to 2050°F. Because joints typically are placed at sites below the maximum service temperature, this range is expected to cover service temperatures up to 2500°F.

Equally important functions of the viscous and/or compliant joining media are: (a) continued long-term physical separation of the ceramic faying surfaces, to effectively preclude misfit and asperity contacts; and (b) uniform transfer of service loads across the joint region. Gas sealing is also a vital joint function. For shear type joints, various silicate glasses of controlled viscosities are being studied as candidate adhesive materials. For butt type joints, the above glasses as well as various metallic alloys possessing desired yield strength and creep relaxation characteristics and inherent oxidation/corrosion protection are under primary evaluation as candidate compliant-interlayer materials.

Joints which connect ceramic components are extremely complex structures from the point of view of design. Thermal resistance, stress concentration and load transfer are three important design factors that are major sources of uncertainty. Design of metal structures presents far less severe problems than design with ceramics because the plasticity of metals reduces the design uncertainties. In contrast, the lack of plasticity in ceramic-to-ceramic joints maintains their high thermal resistance, high stress concentration factors, and poor load transfer. Work at Solar has shown that suitable filler materials in ceramic-to-ceramic joints can reduce these adverse design factors significantly, as well as decrease the risk of failure. Joints can be made to transfer steady-state loads but to relax when excessive loads arise, such as during transients.

The diagram in Figure A-1 illustrates the principles of the relaxing shear joint as applied to concentric joints between tubes (so-called sleeve joints). The viscous adhesive (e.g., a glass) has a viscosity/temperature relationship as shown. At the lower end of the useful temperature range for arbitrarily handling thermal transients up to 10°C/second, the maximum permissible adhesive viscosity is 10^{10} poise, if the stress in the system is to be retained below a peak safe design level of 10,000 psi. The arbitrary "design stress" level of 10,000 psi was selected to be representative of Type NC-430 sintered silicon carbide tubes (tentatively chosen for ceramic heat exchanger application, Ref. 3); which when tested in radial compression at Solar yielded the following Weibull plot data (Ref. 3).

Stress Limitations at Projected Low Failure Rates

Tube Temperature (°F)	Failure Stress (ksi) for Failure Rate (%)	
	0.5%	0.1%
RT	16.4	13.8
1500	11.1	8.7
1700	18.2	15.2
1900	15.5	12.9
2500	10.0	8.4

Just above the higher (opposite) end of the useful temperature range, the viscosity of the glass becomes too low to maintain gas-pressure sealing for the arbitrary design life of 10,000 hours (chosen for illustration). The

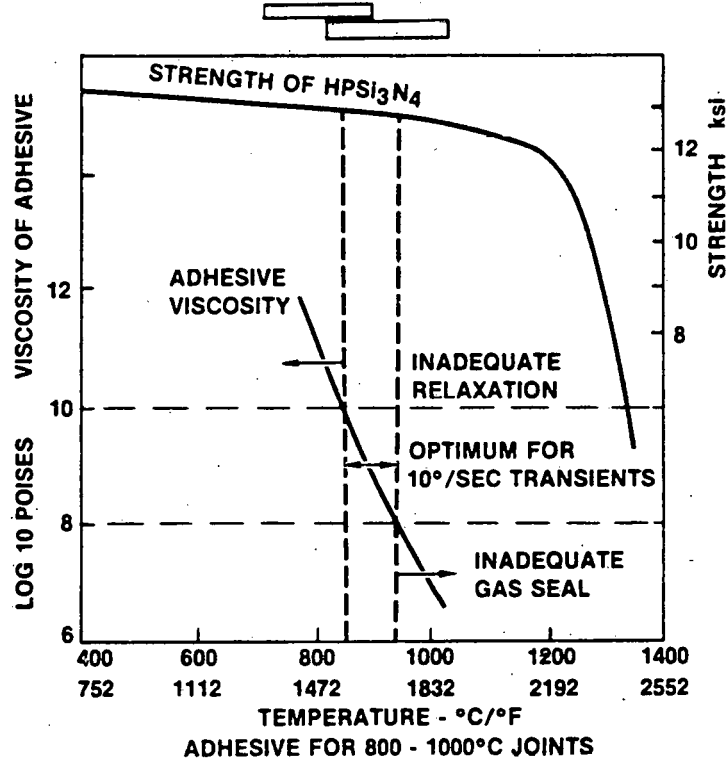REDUCTION OF SHEAR AND NORMAL STRESSES -
RELAXING ADHESIVES

Figure A-1. Stress Reduction at Shear Joints

limiting viscosity on this end is approximately 10^8 poise; i.e., to resist glass extrusion from the joint by the gas pressure differential across the joint seal (Fig. A-1). Both viscosity boundaries can be moved to some extent by a variety of methods including system design to change the design requirements and by joint design to optimize adhesive performance.

The proper function and advantage of the glass-bonded relaxation joint concept are as follows. When heated into the range of temperatures to provide 10^8-10^{10} poise glass viscosity, the joint faying surfaces must have the capability of rapid translation (telescoping) to new low stress positions, when activated by somewhat higher operating shear stresses and corresponding shear strains. Reversibility of such relaxation function is both imperative and implied. Consequently, through the relaxation function, operating shear stresses and strains on the joint and associated ceramic components are never allowed to rise to hazardous levels. Secondary but necessary functions of a viscous glass-bonded relaxation joint are: (a) retention of glass-bond integrity; (b) continuous separation of ceramic faying surfaces; and (c) maintenance of gas pressure sealing ability.