DOE/NASA/0054-79-1
NASA CR-159706

# SINTERED SILICON NITRIDE RECUPERATOR FABRICATION

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**January 1980**

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Under Contract DEN 3-54

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(NASA-CR-159706)   SINTERED SILICON NITRODE           N80-15263
RECUPERATOR FABRICATION  Final Report
(General Electric Co.)   40 p HC A03/MF A01
                                   CSCL 11B            Unclas
                                              G3/27   46505
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for
**U.S. DEPARTMENT OF ENERGY**
**Conservation and Solar Applications**
**Office of Transportation Programs**

# FOREWORD

This is a final technical report submitted under Contract No. DEN 3-54 "Ceramic Recuperator Fabrication Technology", which was originally scheduled from August 9, 1978 to May 24, 1980. The contract was cancelled on February 2, 1979 for the convenience of the Government but was later renegotiated so that a Phase 1 demonstration of feasibility could be completed.

This study was performed at the General Electric Company Space Sciences Laboratory, Valley Forge, Pennsylvania, in the Materials Research and Development Section, managed by Louis R. McCreight. The principal participants in the program and their roles are:

| | |
|---|---|
| Dr. Wen Chiu | Consultant-Heat Exchanger Design |
| John Laffreda | Analysis of Heat Exchanger Designs |
| Arno Gatti | Metallurgist - Silicon Nitride Material |
| Harry W. Rauch | Ceramist - Sealing Glasses |
| William Laskow | Laboratory Technician - Processing and Fabrication |

This program was sponsored by the NASA-Lewis Research Center for the Department of Energy and was managed by John A. Misencik of the NASA-Lewis Research Center.

# SUMMARY

This report presents the results of a one-year effort to advance the technology of Ceramic Recuperator Fabrication Technology using pressureless, sinterable, silicon nitride or silicon-aluminum-oxygen-nitrogen (Sialon) materials, which are being developed in our Laboratory, funded by the Department of Energy through the NASA-Lewis Research Center. The program was originally organized as three technical tasks (plus a Reporting and a Reliability and Quality Control Task) as follows:

| | |
|---|---|
| Task I | Process Feasibility |
| Task II | Recuperator Module Fabrication |
| Task III | Recuperator Evaluation |

The contract was cancelled on February 2, 1979 for the convenience of the Government. However, the contract was renegotiated so that a Phase I demonstration of feasibility could be completed as approximately a one year effort. GE-130 Sialon, which is 94.5 w/o $Si_3N_4$, was considered the material of choice for the application. However, its use in the recuperator was dependent on further development to increase its final fired density. This task was not completed. Feasibility of the approach was therefore demonstrated using GE-128 Sialon which contains 66 w/o $Si_3N_4$, and it is readily sinterable to theoretical density with excellent strength, oxidation and corrosion resistance.

Three key elements of the necessary technology for developing a refractory recuperator were successfully demonstrated during this contract and are:

1. Extrusion and firing of thin-walled exchanger tubes to high density
2. Development of a sealing/brazing technique using a refractory glass
3. Behavior of Sialon materials in corrosive environments containing sodium salts and slightly reducing combusted gaseous atmospheres as well as air and hydrogen.

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# SECTION 1

# INTRODUCTION

Extensive efforts are underway to develop more fuel-efficient vehicular power plants which currently utilize a significant fraction of the available petroleum products. Among the approaches being considered are continuous combustion gas turbine and Stirling cycle engines along with elevated operating temperatures and various methods of waste heat recovery. In this program the objective is the demonstration of feasibility of recovery of waste heat from a Stirling engine at 1370 C (2500 F) utilizing a recuperator constructed of ceramic materials.

Both in the proposal and in the program, some design work was performed to provide on the one hand an efficient, compact, practical recuperator for an automotive Stirling engine and on the other hand a design which would be feasible for fabrication from ceramic materials. This design effort is reported in Section 2 of this report.

Simultaneously the materials from which to construct a high temperature recuperator were being considered in the primary program effort. The operating conditions, in particular the temperature, as well as eventual production requirements if the development is successful dictate the use of non-critical ceramics. Of these, two families of high performance engineering ceramics are quite comparable in most respects and offer the most likelihood of success. They are silicon carbide and silicon nitride. While silicon carbide offers a higher thermal conductivity, its higher modulus and thermal expansion generally cause it to be more thermal shock sensitive than silicon nitride. In addition, the use of sinterable silicon nitride compositions containing some alumina offers the potential for a more corrosion-resistant, alumina-silica surface protective layer than the more nearly pure silica skin on either silicon carbide or nitride. Therefore, our initial approach was to simultaneously demonstrate the forming processes with a previously developed sinterable silicon nitride designated as GE-128 and to work toward obtaining full density in some advanced compositions containing more silicon nitride which were designated as GE-129 and -130.

Joining and sealing of these materials using a powdered glass "braze" was also successfully demonstrated in this program.

In addition to these primary program activities, a small parallel effort to assess the corrosion resistance of the silicon nitride under accelerated conditions which somewhat simulate the exhaust and road salt associated with automotive operating conditions was performed. Serious corrosion problems of this type had previously caused oxide ceramic regenerators to be markedly changed in composition. While these tests were not completely definitive, no sign of a corrosion problem was detected.

# SECTION 2

# RECUPERATOR DESIGN

## Summary

Design considerations of a high temperature ceramic recuperator for an automotive Stirling engine led to a recommendation for a cylindrical, counterflow, channel type as most feasible and responsive to NASA's requirements for automotive applications. The selection was made based on General Electric experience with various Stirling engine programs and many high temperature materials and devices and in particular the silicon nitride materials.

Extensive analysis was carried out to study the tradeoff between the heat transfer, pressure drop, reliability, size and cost. Based on the tradeoff study design, configurations were recommended for various pressure drop levels. A triangular duct cross section was initially chosen but the problems of maintaining straightness during extrusion caused a change to a rectangular duct cross section. This indeed proved easier to produce with the desired straightness. It is believed however that with some further refinements in the die design, a triangular tube could also be produced.

The design consists of these hollow channels mounted in the annulus between and parallel to the axis of two large diameter tubes and attached to the outside of the recuperator inner tube. The hot exhaust gases would be carried in the hollow rectangular tubes, while inlet air would pass through the spaces formed between the adjacent hollow tubes. Small samples of hollow tubing and flat plates made of sintered silicon nitride were successfully assembled with a glass sealing material to demonstrate the preliminary feasibility of the concept during the recently completed Phase I. Larger modules (25mm x 150mm x 150mm) as depicted in part of Figure 3 were intended to be the next step in the program if it had proceeded.

This section discusses the design approach and analysis leading to our recommended recuperator configuration.

## 2.1 CURRENT STIRLING ENGINE PROGRAMS

Of many Stirling engine programs undertaken by General Electric Company, two major ones involve recuperator design and development for the fossil-fuel combustors.

Since 1975, GE has conducted product development of a heat-activated heat pump for both residential and commercial use under contract to DOE and the Gas Research Institute. The objective of this program is to develop a viable commercial product of a gas-fired heat pump which will allow both energy conservation and operative cost savings as compared to alternative gas heating and electric cooling systems. The system uses a 3 kW free piston Stirling engine driving a Rankine cycle vapor compressor.

Part of the program effort is to develop a high efficiency, compact, quiet, low cost and reliable combustor for the Stirling engine. Figure 1 depicts the layout of the combustor developed. The design goal for the recuperator effectiveness was set at 60%. The final design configuration of the recuperator is a counterflow heat exchanger consisting of triangular shaped flow paths alternatively for the hot combustion exhaust and cold air. The recuperator wall is made from corrugated stainless steel sheet metal. For domestic heat pump application, pressure drop across the combustor is designed to be less than 50mm of water so that no special air blower is required. Therefore relatively large channel gaps, (5.5mm), for the recuperator were designed which results in the recuperator pressure drop (air plus gas sides) being a mere 5mm water at 510 C pre-heat air temperature. The measured recuperator effectiveness exceeds 70%. Figure 2 shows the test results of this recuperator design.

A similar recuperator design concept was adopted in a program for the NASA-Lewis Research Center. The objective was to produce a preliminary design of a Stirling general-purpose test engine at the 25 HP level. The engine is to have high reliability and versatility over a wide range of test conditions, and have the capability of permitting components of different designs to be tested interchangeably or with only minor engine modifications. The recuperator was designed for 50% effectiveness with a pressure drop of 4mm water.

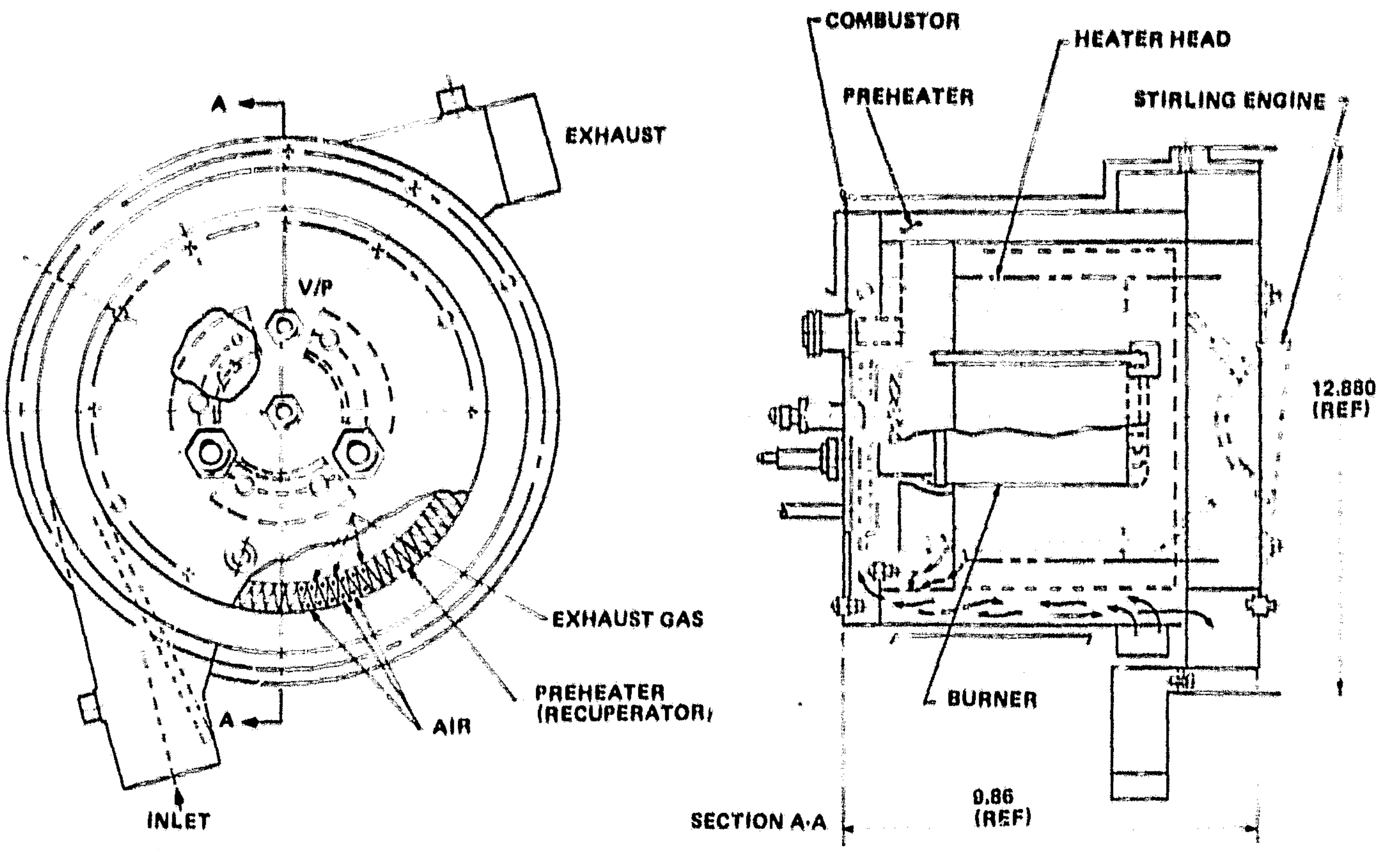

Figure 1. Layout of a Stirling Engine Combustor Incorporating a Preheater with Corrugated Flow Channels

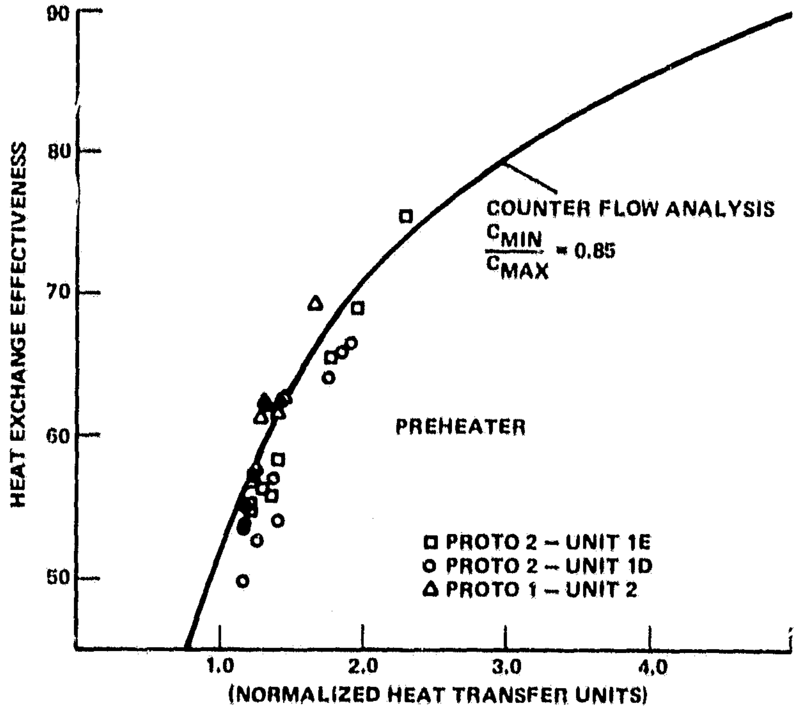

Figure 2. Effectiveness of a Stirling Engine Recuperator for a Heat Pump

Extensive experience in the above related programs has been applied to the present program in developing a ceramic recuperator.

## 2.2 DESIGN CONSIDERATIONS

In the present program the size and design of the flow passages in the subscale recuperator modules shall be similar to the flow channels of a full size automotive recuperator. Methods of manifolding the flow channels and of mating the recuperator to the engine are also to be included in the proposed design and fabrication development. At the initial phase of the program, the 4-215 automotive Stirling engine developed by Ford Motor Company and Philips of Holland** has been taken as the basis of the preliminary recuperator design. Table 1 lists the requirements set forth in the RFP and some additional assumed operating and size requirements based on the 4-215 engine.

Table 1. Ceramic Recuperator Requirements

| | |
|---|---|
| Air flow | up to (0.14 Kg/sec)* at temperature |
| Combustion products (gas) | up to (0.144 Kg/sec)$^+$ at a mean temperature of 1500 F |
| Air inlet pressure | 0.1 MPag (15 psig)* |
| Maximum pressure drop | (0.01 MPag) (1.5 psig)* for air side plus gas side |
| Effectiveness | 0.9 min. at max. power output |
| Maximum ceramic temperature | 1370 C* or higher |
| Interpath leakage | less than 5%* |
| Combustor outer housing | 400mm in diameter |
| Combustor plus Burner height = | 350mm |
| Recuperator Effectiveness | greater than 90% |

*Specified in the RFP

$^+$Assumed diesel fuel combustion with 1,050,000 BTU/hr firing rate at 30% excess air, 170 hp output @ 80% combustor efficiency and 55% engine efficiency.

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**VanGiessel, R. and Reinink, F., "Design of the 4-215 D.A. Automotive Stirling Engine," SAE paper 770082

In addition to the requirements listed in Table 1, other criteria to be considered in evaluating the recuperator design are:

1. Light weight
2. Potential low cost
3. Durability
4. Manufacturing feasibility
5. Best mating with the engine heater head

Overall assessments of the above design considerations concluded that a stationary recuperator appears to be more reliable than a rotary type.

During the last quarter of 1978, NASA provided an additional set of test data for a Ford 4-245 Stirling engine which are shown in Table 2. The high effectiveness and low pressure drops are typical of a rotary type recuperator which has a large frontal flow area and short flow path. In our view of this stationary recuperator, the size requirement could become impractically large in order to accomplish similar effectiveness and pressure drops. However, the elimination of power required to rotate the regenerator will be enough to offset the higher pressure drop penalty for a stationary design.

## 2.3 HEAT TRANSFER ANALYSIS

The heat transfer analysis was conducted using the Kays and London NTU-method*. A heat exchanger effectiveness is characterized by the operating condition of the working fluid, $C = Cp\ m$, and the number of heat transfer unit, $NTU - AU/C_{min}$, where $A$ = total heat transfer area and $U$ = overall heat transfer coefficient. NTU is indicative of the heat exchanger size and complexity. For the combustion process in an automotive application, $C_{min}/C_{max}$ is around 0.85.

Table 3 lists the maximum achievable effectiveness for three types of heat exchangers and their respective NTU's needed to obtain a 90% effectiveness.

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*Kays, W. M. and London, A. L., Compact Heat Exchangers, 2nd Edition, McGraw Hill Book Co., 1964.

Table 2. Recuperator Performance of Ford 4-245 Engine

|  | Full Load | Part Load | Idle |
|---|---|---|---|
| **Hot Side** |  |  |  |
| Flow Rate (g/sec) | 222.3 | 54.39 | 14.79 |
| $T_{in}$ (°C) | 1036 | 754 | 734.8 |
| $T_{out}$ (°C)* | 243 | 149 | 135.8 |
| $P_{in}$ (atm) | 1.030 | 1.0041 | 1.001 |
| $P_{out}$ (atm) | 1.007 | 1.0001 | 1.00 |
| $\Delta P$ (psi) | 0.34 | 0.06 | 0.015 |
| **Cold Side** |  |  |  |
| Flow Rate (g/sec) | 210.96 | 52.86 | 14.79 |
| $T_{in}$ (°C) | 52.3 | 97.7 | 83.1 |
| $T_{out}$ (°C) | 969.5 | 740 | 726.7 |
| $P_{in}$ (atm) | 1.153 | 1.015 | 1.003 |
| $P_{out}$ (atm) | 1.137 | 1.0115 | 1.002 |
| $\Delta P$ (psi) | 0.24 | 0.05 | 0.015 |
| Effectiveness (%) | 93.2 | 97.9 | 98.7 |
| Overall all $\Delta P$ (psi) | 0.58 | 0.11 | 0.03 |
| *Adjusted with flow leakage |  |  |  |

Table 3. NTU Requirements for Heat Exchanger at $\rho \text{Min}/\rho \text{max} = 0.85$

|  | Theoretical max. E @ NTU → ∞ | NTU Required for E = 90% |
|---|---|---|
| Counter-flow | 100% | 5.75 |
| Cross-flow with both fluids unmixed | 100% | 43 |
| Parallel flow | 63% | — |

It then becomes apparent that to obtain a 90% effectiveness, yet cost-effective and compact recuperator, the best configuration is a counter-flow type heat exchanger. It can be a tube-shell or a channel-path configuration. The selection must be based on ease of fabrication, manifolding and installation, large heat transfer surface-to-volume ratio, and reliability.

## 2.4 COUNTER-FLOW RECUPERATOR WITH CORRUGATED FLOW CHANNELS

### 2.4.1 TRIANGULAR DUCTS

A recuperator concept which meets the above requirements with a relatively simple configuration uses corrugated triangular flow channels surrounding the combustor outer housing as is being developed at General Electric for other Stirling engines. Based on these experiences and the current experiences with the sintered silicon nitride materials, a preliminary design shown as an artist's rendering in Figure 3 has been evolved. It shows a more nearly complete recuperator (which is beyond the scope of the present program) as possibly being about 350mm ID x 400mm OD x 275mm high plus manifolds.

In the early phase of the program, the flow channels were being developed as extruded hollow triangular tubes with a 0.75mm (0.030") wall as shown on the left hand side of Figure 3. A design chart, as shown in Figure 4, was constructed for a 90% effective recuperator. The overall length and the pressure drop, ΔP, of the recuperator are plotted for different triangular flow channel configurations (channel height, $t$, and channel width, $\delta$).

Based on the initial design requirements as specified in Table 1, a section of $t = 25$mm and $\delta = 1$mm was recommended for fabrication development. The overall pressure drop for a full scale recuperator was estimated to be 0.01 mPa (1.5 psi) with a channel length of 275mm. The recommended subscale recuperator module having a 150mm x 150mm section is depicted in Figure 5, with appropriate manifolding for combustion gas and air flows.

### 2.4.2 RECTANGULAR DUCT

After initial attempts to fabricate ceramic hollow triangular tubes, it appears that a rectangular cross section is superior to the triangular shape from the points of view of ease of fabrication and structural integrity of the long tubes. In addition, after receiving the Ford

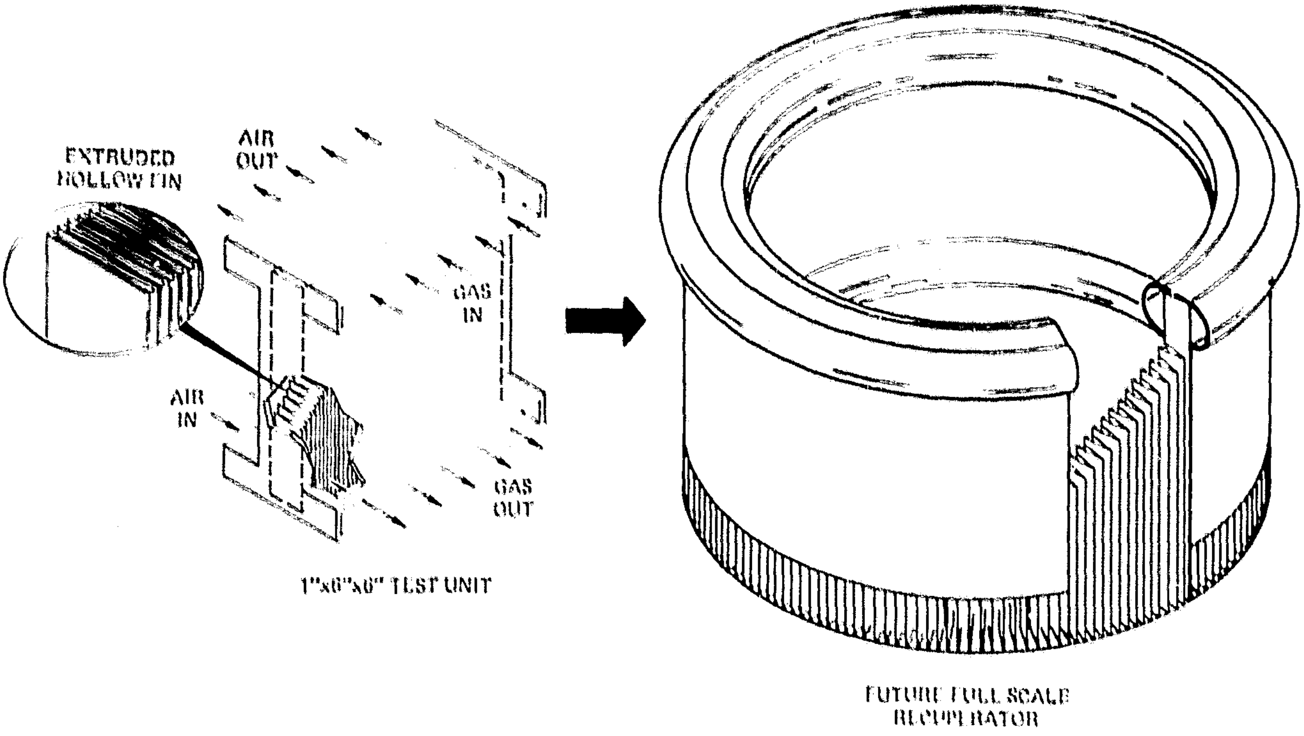

Figure 3. Preliminary Design of a Refractory Ceramic Recuperative Heat Exchanger for Operation at 1370 C is Shown on the Right with the Hollow Triangular Fin Tubing and a Test Module to be Built on this Program Shown on the Left

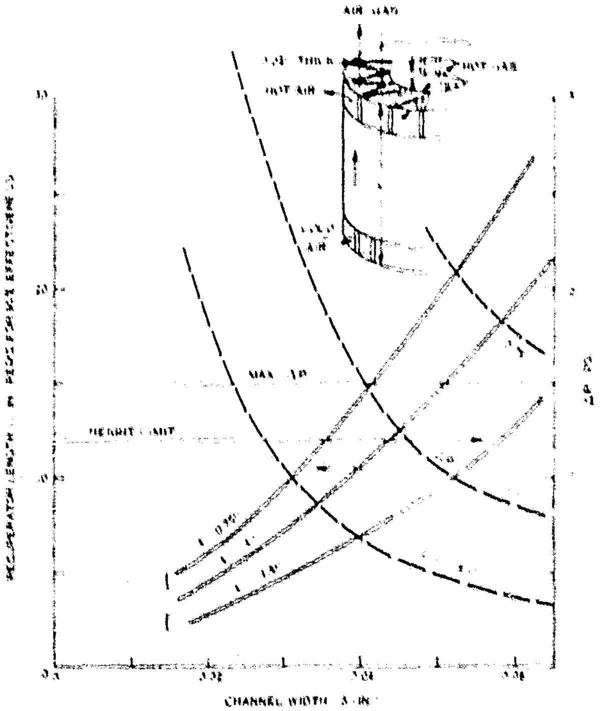

Figure 4. Automotive Stirling Engine Recuperator Design Chart with Triangular Channels Shown Schematically

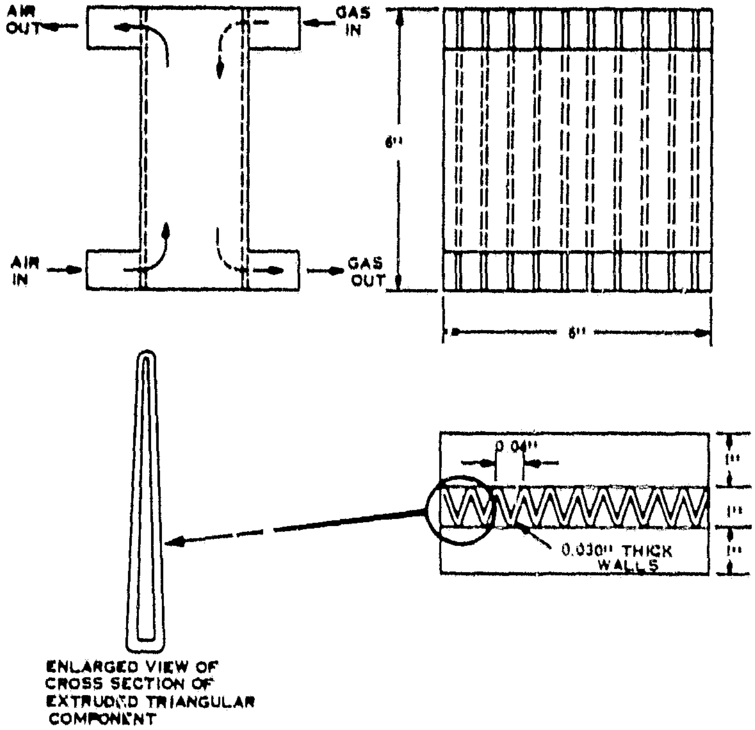

Figure 5. Subscale Recuperator Module

Stirling engine test data as summarized in Table 2, concern has been raised on how a stationary recuperator can be designed in order to achieve a low pressure drop comparable to that obtained in a Ford rotary recuperator.

Analysis of the recuperator with rectangular flow channels was carried out with essentially the same configuration as shown in Figure 3 (400mm OD for full scale recuperator). Figure 6 is the parametric plot for this design analysis. The design requirements were based on those tabulated in Table 1.

It can be seen from Figure 4 that in order to reduce the pressure drop, a longer recuperator length, L, and a larger duct cross sectional area (channel width, t, and channel gap, $\delta$ ) will be required. This will result in a larger size recuperator, with more weight and cost. Table 4 tabulates three different configurations corresponding to the design points denoted in Figure 6.

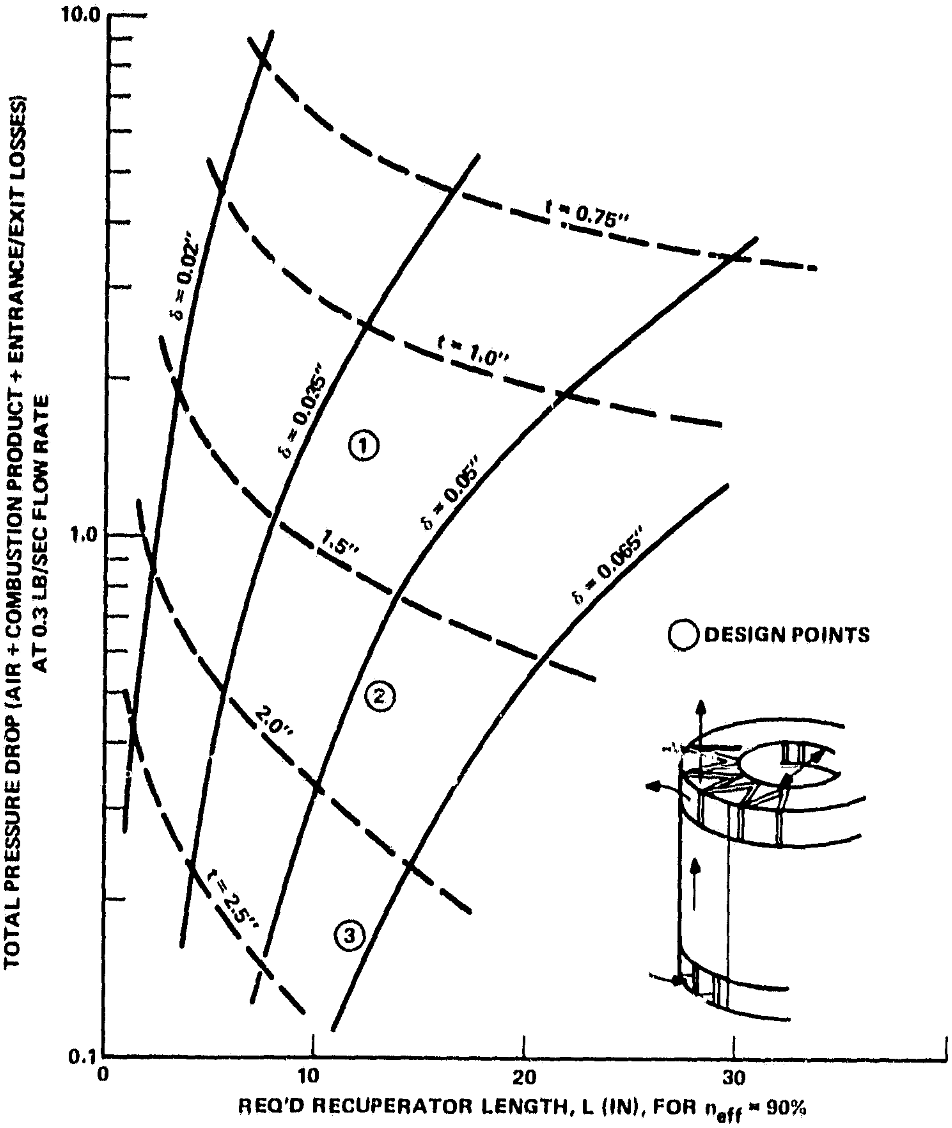

Figure 6. Parametric Plot of a Recuperator Design with Rectangular Flow Channel

It is apparent that as the channel cross section area increases, the lower ΔP can be achieved only at the expense of a weaker structure for a fixed wall thickness. The optimum selection of the final design, then, will be strongly influenced by the fabrication technique, material properties, and tradeoff of reliability and cost.

Table 4. Recuperator Designs with Rectangular Flow Channel

Effectiveness ≈ 90%
Channel wall thickness ≈ 0.75mm
Recuperator ID ≈ 400mm
Channel length, L ≈ 300mm

| Design Point | Channel Width, t | | Channel Gap, $\delta$ | | Overall $\Delta P$ | |
|---|---|---|---|---|---|---|
| | mm | (in) | mm | (in) | MPa | (psi) |
| 1 | 31.25 | 1.25 | 1.00 | 0.040 | .01 | 1.5 |
| 2 | 43.75 | 1.75 | 1.30 | 0.052 | .003 | 0.5 |
| 3 | 57.5 | 2.3 | 1.625 | 0.065 | .001 | 0.15 |

## SECTION 3

## EXPERIMENTAL

The Materials Research and Development Section of the General Electric Company's Space Sciences Laboratory has been active in studies on sinterable $Si_3N_4$ compositions since May 1972.(1) Current activities in this area have included a recently completed 3 year study of the ceramic processing of silicon nitride containing alumina and aluminum nitride by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio(2).

Processing studies were necessary because detailed knowledge of the "new" sinterable $Si_3N_4$ systems was not generally available. There was also a need to reproducibly fabricate sizeable specimens for test and evaluation. The sintering mechanism was complicated however because it involved a liquid phase which could vary in composition by both choice of starting materials and processing techniques. This liquid phase in turn had a profound effect on the mechanical properties, particularly at high temperatures. Studies included the fabrication and properties of compositions with deliberate additives and culminated in the description of the fabrication of $Si_3N_4$-based ceramics of up to 87 M/O $Si_3N_4$, with a minimum of second phase content and hence, good strength retention at high temperatures.

That earlier program formed the base for the present work. Sinterable compositions had been developed, what remained was to use that knowledge to fabricate recuperator components and modules and so a component fabrication and assembly sequence was developed and is shown in Figure 7. This sequence was followed during the program and comprises Phase I. Also as a part of Phase I a parallel study was made of the resistance of Sialon to sodium sulfate and sodium chloride corrosion at high temperatures. This would be a vital parameter in the use envisioned, especially for thin-walled recuperator channels.

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(1) See References at the end of the report.

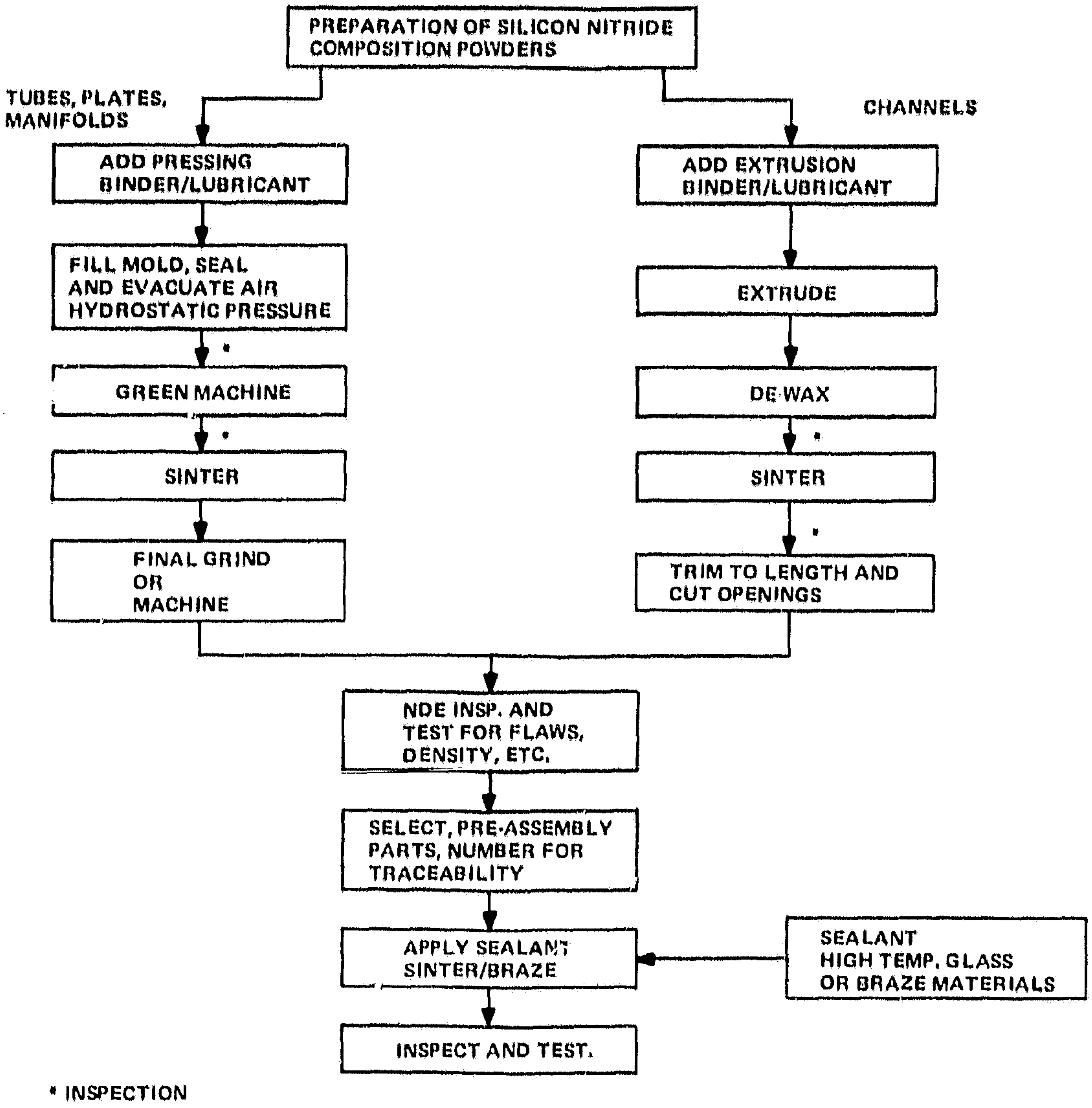


Figure 7. Component Fabrication and Assembly Sequence

## 3.1 POWDER PROCESSING

Sialon starting materials used during this work were processed by milling in a polyurethane-lined mill with Sialon balls as shown in the flow diagram of Figure 8. Wear of the Sialon balls was used to furnish the liquid phase necessary for sintering to high density together with a sintering aid composed of "mineralized" Sierralite Talc and Kyanite(3).

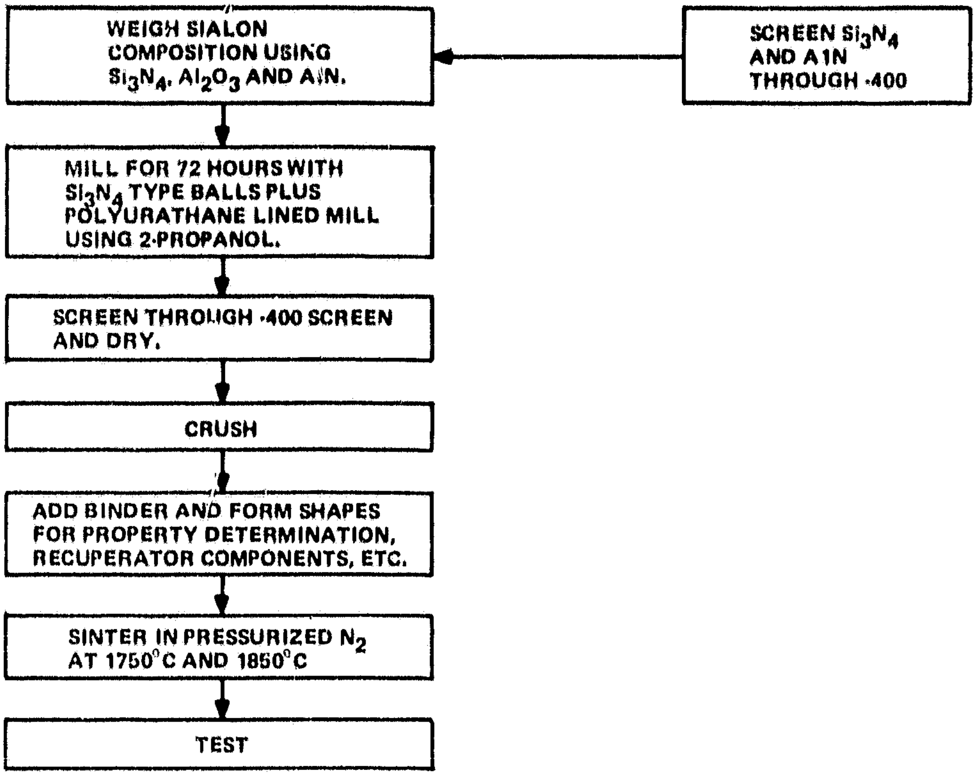


Figure 8. Flow Diagram of the Processing of GE Sialon Materials

Hydrostatic pressing, at pressures up to 400 MPa (50 KSI), was used to form the prepared powders into plate shapes. The development of a process which could form thin-walled, gas-tight tubing was a major task of this study. When the recuperator design is considered (channel cross-sections 25mm wide by 3mm thick with 1mm walls to 500mm long) it is apparent that extrusion would be the most practical process. Accordingly, plasticizer-binder-Sialon compounds with the potential to lead to good final sintered product were systematically studied. Of the six systems studied, one considered to be most easily adopted was comprised of a commercial wax compound and 60 w/o Sialon powder extruded warm (~50 C).

Plasticizer-binder-powder mixtures were "mulled" (mixed) in a small bench top muller built here. Figure 9 shows the muller as used to prepare wax powder mixtures maintained at about 100 C by applying external heat with a heat lamp and a hot air gun. An extrusion press was also designed and built which utilized a manually powered screw feed to exert pressure

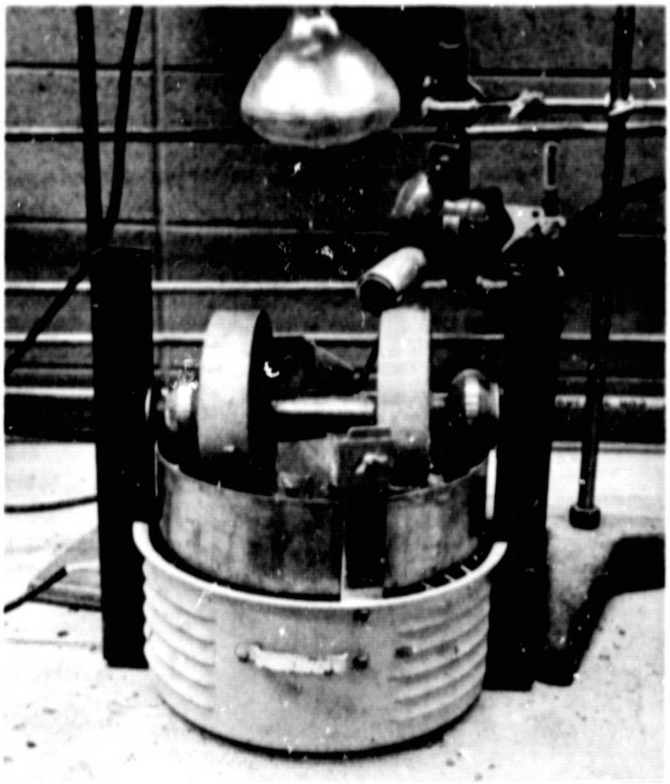


Figure 9. Photograph of the "Muller" Used to Mix Wax-Powder Materials for Subsequent Extrusion. Note Heat Lamp and Heat Gun Used to Maintain 100 C Mixing Temperature.

on a piston. The heat capacity of the press was such that if hot extrusion was needed, the die assembly could be brought to the temperature required and operated before it had cooled off too much. A disassembled-exploded view of the press is shown in Figure 10, with a portion of extruded recuperator channel in place.

## 3.2 BINDER REMOVAL

Binder removal and de-waxing by pyrolyzation was the only method used since none of the other binder systems tried was successful. The removal of binders from dense extruded shapes is not an easily predictable process and had to be determined by trial and error. Time-temperature conditions were adjusted until finally most ware could be de-waxed defect free. Further, during wax removal, the ware had to be supported to minimize distortion

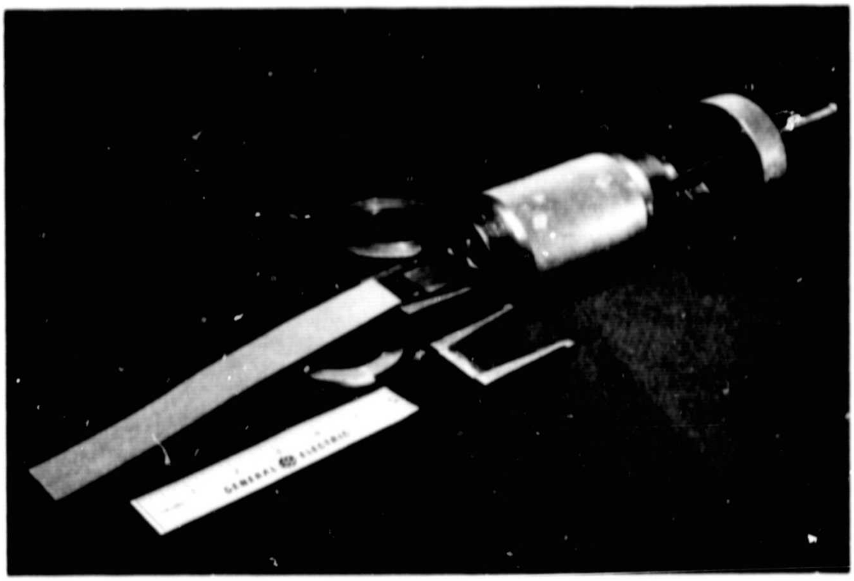


Figure 10. Disassembled-Exploded View of Laboratory Extrusion Press Used During this Study

and provide a sink for molten wax. The de-waxing schedule developed was to pack the parts in -900 mesh alumina powder and then fire in air at 220 C/hr to 200 C, hold 8 hours, then 20 C/hr to 350 C, and then firing to 1000 C, at 200 C/hr and furnace cool. The ware was carefully removed from the alumina bed and stored for final firing. The alumina packing powder meanwhile was de-lumped by screening and continuously recycled.

## 3.3 FIRING

At first, final firing of Sialon compositions was performed in a molybdenum box packed loosely with "Sialon" powder and covered with a molybdenum lid to control weight loss during firing. The molybdenum box was placed into a molybdenum retort, the mouth of which was covered with molybdenum foil and through which flowed nitrogen at a controlled rate. This assembly was fired in a hydrogen atmosphere. Later, a "Centorr" tungsten resistance furnace was added to our facilities with a maximum temperature capability to 2500 C in nitrogen-ambient with a hot zone 200mm (8") diameter by 300mm high. All firings after December 1978 were made in this facility, a photograph of which is shown in Figure 11. Ware to be fired was mounted on graphite fixtures and placed in the furnace. The furnace was then evacuated and back-filled with nitrogen to a pressure of 1/3 atmosphere above ambient. The furnace temperature reaches 1700 C in one hour using power surges of about 3000 amperes every 10 minutes. Recuperator channels were fired in this manner for 30 minutes at 1700 C and furnace cooled.

## 3.4 CORROSION CRUCIBLES

For corrosion studies, GE 128 Sialon special crucibles and covering lids were fabricated by die pressing in the shaped dies shown in Figure 12. The crucibles and lids were pressed to 100 MPa (15 KSI) and fired for 1 hour at 1750 C in nitrogen using the molybdenum retort system described earlier. During reaction studies the crucibles were weighed, loaded with corrodants, reweighed, fired in a mullite retort in air, hydrogen or $CO_2$-$N_2$-$H_2O$ atmospheres, and weighted again. Changes in weight and microstructural changes as a function of time at each test condition were used to evaluate material performance.

## 3.5 SEALING AND BRAZING GLASS PROCESSING

Sealing and brazing glasses were processed by a fritting technique, ball milled in a high alumina mill and balls and screened to -200 mesh. The compositions used were first weighted out in 50-gram batches. The compositions were then melted at 1600 C in air, and water quenched twice to ensure homogenization of the resulting glass.

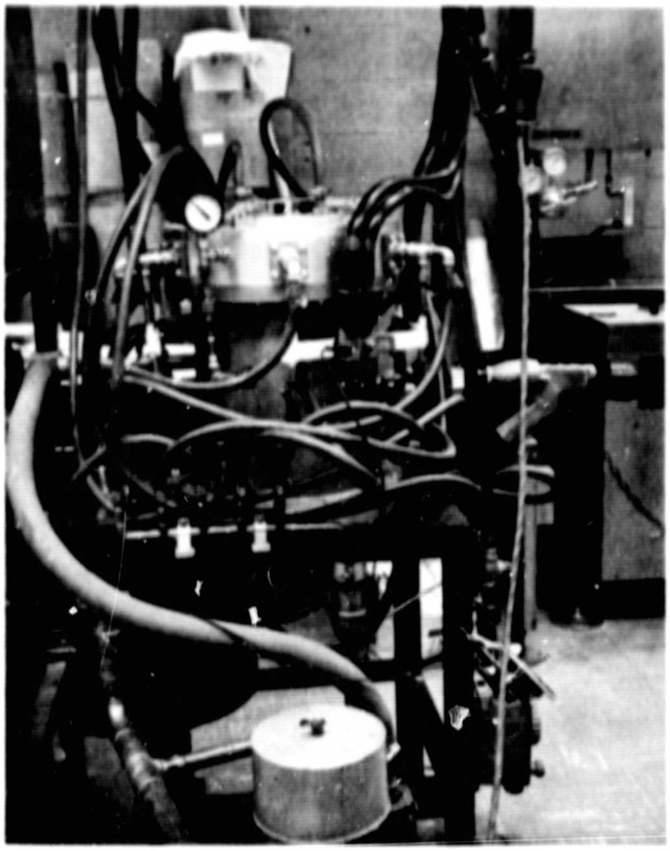


Figure 11. Photograph of Centorr Furnace Facility Capable of 2500 C Operation in Nitrogen Atmosphere

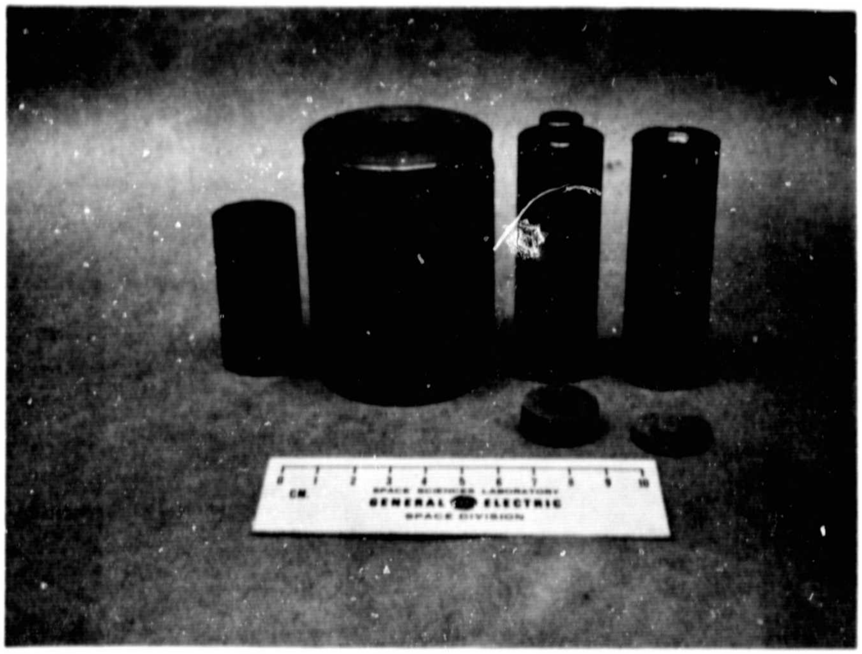


Figure 12. Photograph of the Dies Used to Form the Crucible-Lid, Combination (also shown) from GE-128 Sialon Material Used During Corrosion Studies

# SECTION 4

# RESULTS AND DISCUSSION

## 4.1 MATERIALS SELECTION

It was proposed that GE-130 material be developed for use as recuperator hardware because it offers the potential of improved properties such as thermal conductivity. This development should be readily accomplished since GE-130 material has a high $Si_3N_4$ content; thus it should have intrinsic properties that are similar to hot pressed or reaction sintered $Si_3N_4$, a material which is considered desirable recuperator application. The GE-130 material contains 94.5 w/o $Si_3N_4$; it can be sintered at 1750 C, but at present it does not sinter to a density that can guarantee gas tightness. Not much progress was made on this aspect of material development before the program was curtailed. However, it was decided that feasibility could be demonstrated during Phase I of the program with the use of GE-128 material which is readily sinterable to high density and insure gas tightness. GE-128 is also an acceptable material for recuperator hardware applications because it possesses excellent strength, oxidation and corrosion resistance and, aside from a slightly lower modulus, has other properties that are identical to $Si_3N_4$. Four-hundred gram batches of GE-128 were prepared as previously described and processed as needed throughout this study. GE-130 and GE-128 are compared in Table 5.

Table 5. Materials and Compositions Used During This Study

| GE Designation | Composition in weight percent and vendors | | |
|---|---|---|---|
| | $Si_3N_4$<br>AME<br>(England) | $Al_2O_3$<br>Linde A, Air Products Div. | AlN<br>Cerac/<br>Pure |
| 128 | 66 | 24 | 10 |
| 130 | 94.5 | 4 | 1.5 |

*Composition before processing

## 4.2 COMPONENT FABRICATION

### 4.2.1 PLATE

Two mm thick x 40 mm wide by 160 mm long GE-128 Sialon plates were fabricated by isostatic pressing, sintering and diamond sawing to be used as side walls during modular construction. This material has a fired density of 3.05 gm/cc which is 99% of theoretical (3.08 gm/cc) and is gas tight.

### 4.2.2 RECUPERATOR CHANNELS

Recuperator channels were successfully fabricated during this program as a result of a systematic study made to identify a binder-lubricant system which would work satisfactorily. Six binder-lubricant systems were tested before a workable one was developed. A summary of these results is shown in Table 6. As can be seen, all of the systems except the LN-27-266-2 wax had undesirable characteristics ranging from unable to extrude, to

Table 6. Summary of Sialon Extrusion Binder Studies

| Binder System | Results |
|---|---|
| Alcohol + Orange Shellac | Separates, "rattlesnakes". Does not extrude |
| Polypropolyne | Extrusion temperature too high. Difficult to add solids |
| PVA-Sterate(1) | Extrudes but less than 50 w/o solids, walls collapse |
| Buytal Sterate-Reten(1) | Extrudes but less than 50 w/o solids, walls collapse |
| Mixed waxes | Separates, rattlesnakes, collapses at high extrusion temperature |
| LN-27-266-2 wax(2) | Extrudes well at 58° w/o solids |

(1) Water based, reacts with sialon mix.

(2) Commercial mixture purchased from J.F. McCaughin Co., Rosemead, California.

extrusion without sufficient solids content ( >50 w/o) or wall sagging. Examples of extruded channel in final configuration are shown in Figure 12. This channel can be extruded to any length desired. Its final fired cross section dimensions are 25 mm wide x 3 mm thick with a 1 mm wall thickness. The original cross section design did not have the center rib shown, however, upon firing,channels without ribs sagged after firing usually closing the channel. Some sagging still persists and it is recommended that still another rib (2 equi-spaced) be added which will further support the channel walls during firing.

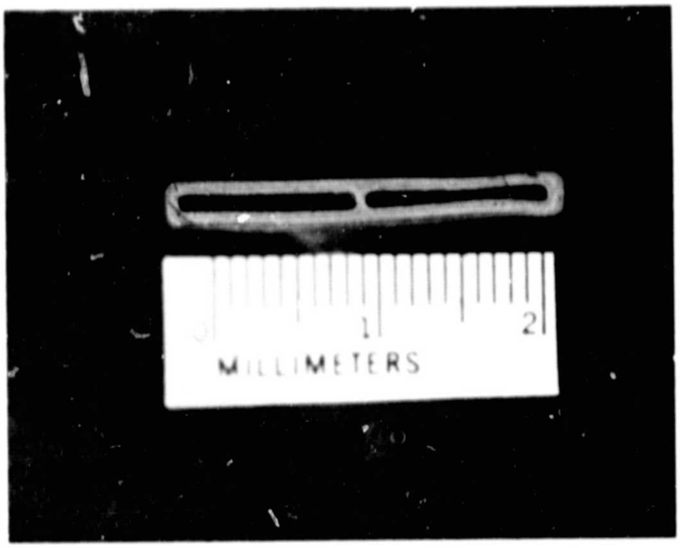
Solid rod, square in cross-section with radiused corners (50 $mm^2$) was extruded to provide material for mechanical property studies and density determinations in the as-fired condition since such measurements are needed and are difficult to perform on channel material. Table 7 shows the green and fired densities obtained. Also included in the data is the average room temperature MOR strength of this material tested without further regard for surface finish. As can be seen, this material has a reasonable strength which is indicative of the strength of extruded and fired channel. A more definitive test would require internally pressurized burst tests which were not done due to the lack of funds.

Table 7. Green and Fired Densities of Extruded GE-128 Sialon

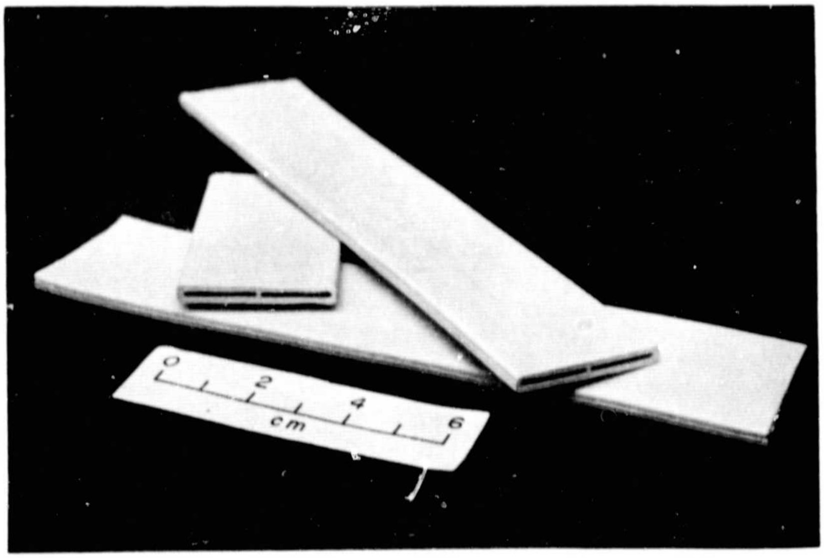
| Sialon Treatment | Density gm/cc | % of Theoretical* | Firing Shrinkage (%) | Room Temp. MOR as Fired |
|---|---|---|---|---|
| Extruded and dewaxed | 1.25 | 58 | - | |
| Fired 30 min. at 1750°C in $N_2$ | 2.96 | 98 | 25 | (39.1 KSI)<br>(260 MPa) |

*Based on a theoretical density of 3.02 gm/cc

An x-ray diffraction trace was also made of extruded, dewaxed and fired GE-128 Sialon material, Figure 13. The results show a typical β' Sialon trace as shown in Figure 14.



Fired Cross-Section



De-Waxed Channel

Figure 13. Examples of Extruded GE-128 Sialon Channel Fabricated During This Study.

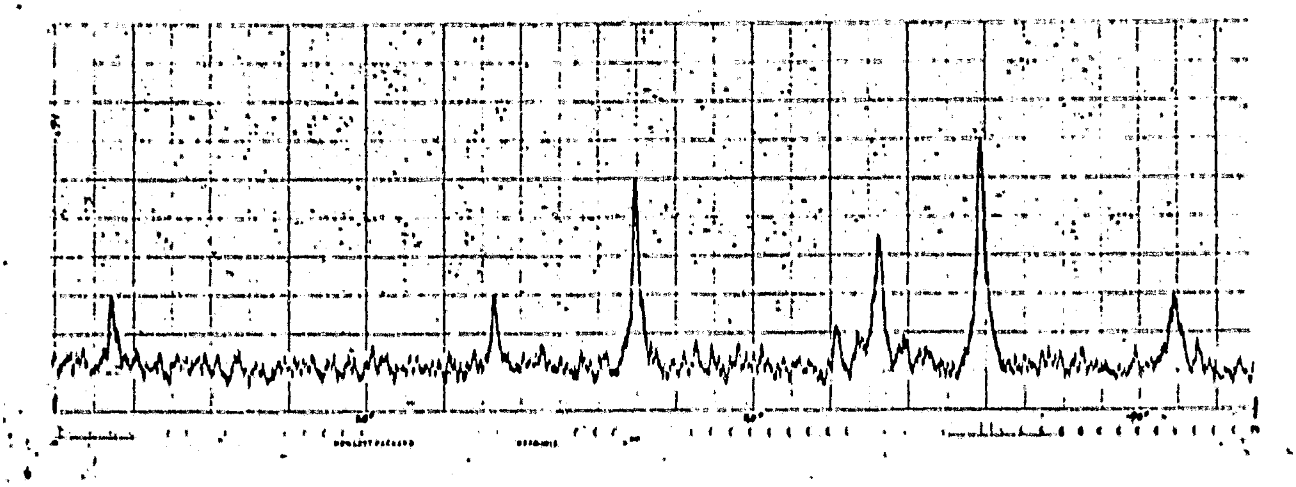


Figure 14. X-Ray Diffraction Trace of Extruded, De-Waxed and Fired GE-128 Sialon

## 4.3 SEALED AND BRAZED SIALON MATERIALS

The initial work in the development of glass sealing and brazing materials was with borosilicate and magnesium aluminosilicate glasses with and without additions of powdered fused silica. However, a composition (HS-110)$^{(4)}$ which represents the glass phase at the grain boundaries in hot-pressed silicon nitride was evaluated and found to be ideal for the application. The borosilicate/silica and magnesium aluminosilicate/silica mixtures wet sialon very well and appear to form strong bonds. However, considerable bubble formation was observed in all of these combinations and could be a structural weakness. HS-110 glass wets sialon very well and produces very strongly bonded sialon/sialon pieces.

The molar composition of the HS-110 glass is $Al_2O_3 \cdot 4.5\ CaO \cdot MgO \cdot 11SiO_2$. A slurry of the HS-110 glass in alcohol using -200 mesh powder was used to provide a very thin film of glass particles on small (25 x 50 mm) pieces of sialon. The slurry was dried and the sialon pieces were fired. In one instance, two of the glass-coated sialon surfaces were mated before firing. Two temperature/time schedules, 1250 C/55 minutes and 1320 C/1.5 hours, were investigated. Both schedules produced nicely glazed sialon surfaces and very strongly bonded sialon/sialon specimens.

Various samples of sub-modular brazed assemblies were then made using HS-110 glass slurries. Examples of these brazed assemblies are shown in Figure 15. A cross-section of a brazed section showing the glass (meniscus) formed between a channel and wall section is shown in Figure 16. These brazes were all made by firing for 5 minutes at 1400 C in air atmosphere. A larger module was then brazed using several sintered sialon channels and large sintered sialon plates. This sialon ceramic heat recuperator sub-module is shown in Figure 17. Full sized modules were not made only because our present channel firing furniture was designed for feasibility work and can only handle 100 mm long pieces.

## 4.4 CORROSION STUDIES

Corrosion studies were carried out using GE-128 Sialon crucibles described earlier. Small amounts (~ 0.5 gm) of $Na_2SO_4$, NaCl and carbon were added to the crucibles both individually and as mixtures. Included in each series was a blank crucible to assess the effects of atmosphere alone on the materials. The loaded crucibles and blanks were fired at 870 C and 1370 C in air, hydrogen and $Co_2$-$N_2$ and $H_2O$ to periods of up to 1000 hours. During air firing the blank gained about 4% in weight in 20 hours while the crucibles containing the various corrodants also gained about the same percentage. It is concluded then that in air atmosphere the sialon gains weight but is not affected by the corrodants which also persist as a white porous layer. Specimens fired in $H_2$ lost weight. The blank specimen lost about 2.4% in 20 hours while the crucibles containing the corrodants were emptied of their contents. It is further concluded that in hydrogen, sialon material loses weight but the process is not affected by the corrodants which are transported away by the $H_2$ gas stream. Runs at 1370 C in a simulated combustion atmosphere using $CO_2$-$N_2$ and $H_2O$ vapor were discontinued after 100 hours since the added $Na_2SO_4$ and NaCl had essentially vaporized away and/or reacted with the sialon and no further reaction was taking place. The samples are quite similar in appearance to the runs made in hydrogen in that no frothy glass layers formed (which are typical of air atmosphere runs). The temperature was then lowered to 870 C where the salt mixtures remain liquid and have a fairly low vapor pressure. After 1000 hours of operation, the appearance of the crucibles is similar to the 1370 C 100 hour runs in that no foamy reactions are evident. Further, the only apparent difference in weight gain between

Figure 15. Examples of Submodular Glass Grazes Made with HS-110 Glass, Extruded and Fired Sialon Channel and Pressed and Fired Plates

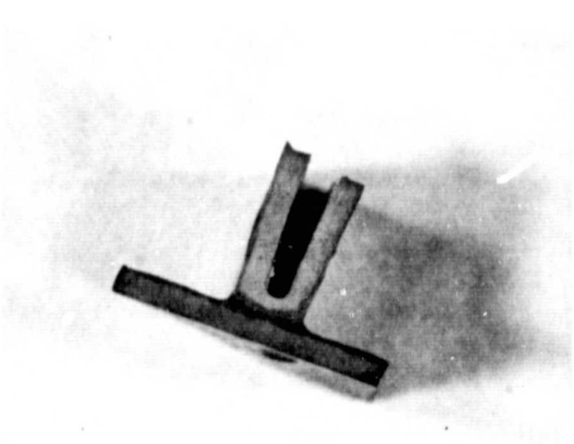


Figure 16. Cross-Section of a Glass Brazed Submodule Showing Minicus Between Extruded and Fired Sialon Channel and Pressed and Fired Sialon Plate

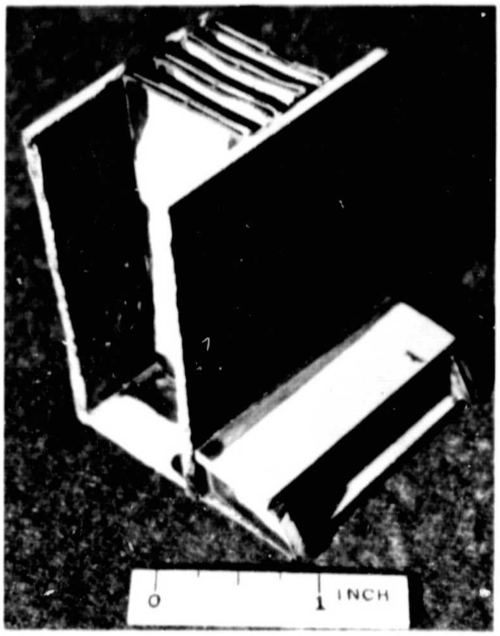


Figure 17. Glass Brazed Section of a Sialon Ceramic Heat Exchanger Module

the blank sample and the loaded crucible can be accounted for by the initial reaction which occurred within the first 100 hours. This series was terminated after 1000 hours. The data for these tests using $CO_2$-$N_2$-$H_2O$ mixtures are summarized in Figure 18.

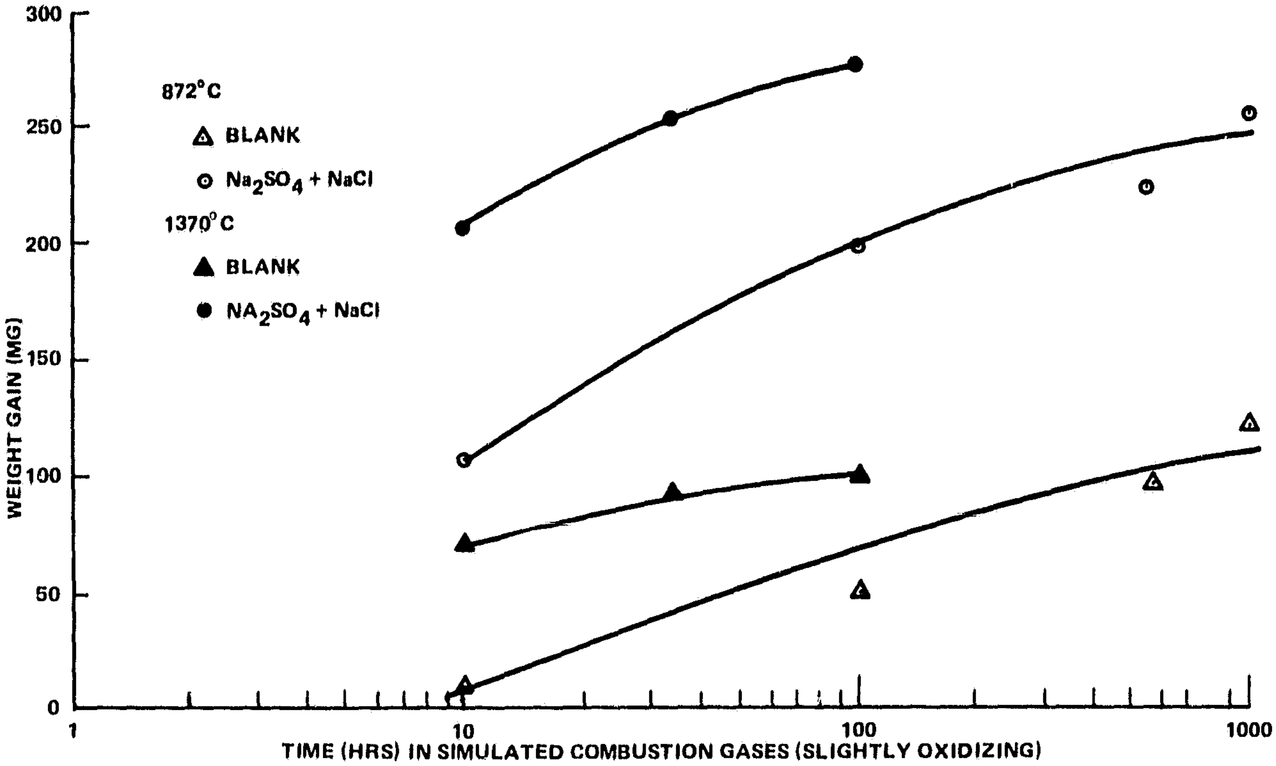


Figure 18. Corrosion Test Data of GE-128 Sialon in $CO_2$+$N_2$+$H_2O$ Atmosphere at 870 C with and without Sodium Salts Added.

Five representative corrosion study sialon crucibles were picked from the total number of 20 used, and were cross-sectioned and metallographically polished for electron probe x-ray microanalysis to detect sodium penetration into the bulk material. The samples examined are shown in Figure 19. Results for each sample are discussed below.

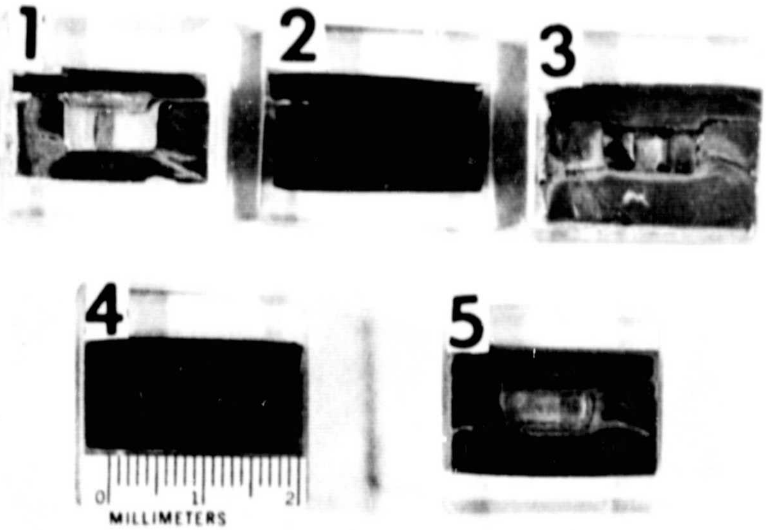


Figure 19. Cross-section View of Sialon Crucibles after Corrosion Testing

Sample no. 1 - 1370 C, 100 hours, $Na_2SO_4$ + NaCl, $CO_2 + N_2 + H_2O$

Sodium was found along the edges of the crucible and along cracks; no sodium was detected in the bulk sialon.

Sample no. 2 - Control Sample, 870 C, 1000 hours, $CO_2 + N_2 + H_2O$

No sodium was detected in the bulk or around the edges of the sialon material in the control sample.

Sample no. 3 - 1370 C, 100 hours, Air

Sodium was found along the outside surfaces and along cracks, no sodium was detected in the bulk sialon.

Sample no. 4 - 870C, 100 hours, $Na_2SO_4$ + NaCl, $C)_2 + N_2 + H_2O$

Sodium was found along the surface edges and in cracks but no sodium was detected in the bulk sialon.

Sample no. 5 - 1370 C, 100 hours, $Na_2SO_4$ + NaCl, $H_2$

Very little contamination product was observed on the sufaces of the crucible. No sodium was detected in the bulk sialon.

These results are parallel to those observed by Palko(5) for GE Sialon material tested at 870 C in combusted gases containing sodium contamination. Palko's tests were discontinued after over 16,000 hours with no significant reactions taking place.

# SECTION 5

# CONCLUSIONS

The feasibility of fabricating sintered $Si_3N_4$ channels and plates suitable for constructing a ceramic recuperator have been successfully demonstrated. Techniques were developed for extruding unlimited lengths of thin-walled channels using wax-powder mixtures which can be fired to high density. These materials are strong in the as-fired condition averaging better than 260 MPa (39 SKI) strength in modulus of rupture. The art of glass brazing using a HS-110 glass was also demonstrated so that module sections could be assembled from fired channel and plate components. Finally, it was concluded that Sialon materials do not react catastrophically with sodium salt-carbon mixtures at 870 C or 1370 C in atmospheres of air, $H_2$ or $CO_2$-$N_2$-$H_2O$ mixtures.

## SECTION 6

## RECOMMENDATIONS FOR FUTURE WORK

The development of sinterable $Si_3N_4$ compositions like GE-130, which contains 94.5 w/o $Si_3N_4$, should be continued. Further, since the technique for extruding and firing Sialon channels has been developed, further studies to characterize its pressurized high temperature behavior should be done while thermal cycling. Further, brazed components should also be tested for long-time stability as a function of pressurized high temperature and thermal cycling.

Finally, we feel that ceramic heat exchanger technology, utilizing assemblies developed during this work would be advanced toward eventual utilization if this program were to be funded in the future.

# SECTION 7

# REFERENCES

1. W. I. Wilson and K. H. Jack, paper presented to the American Ceramic Society, 74th Annual Meeting, Washington, D.C., May 10, 1972.

2. A. Gatti and M.J. Noone, "Methods of Fabricating Ceramic Materials," Technical Report AFML-TR-77-135, November 1977.

3. A. Gatti and M.J. Noone, "Ceramics in the Si-Al-O-N System Fabricated by Conventional Powder Processing and Sintering Techniques." Processing of Crystalline Ceramics, Edited by H. Palmour III, R.F. Davis, T.M. Hare, Plenner Publishing Company, 1978.

4. Ram Kossowsky, "The Microstructure of Hot-Pressed $Si_3N_4$," J.Mat.Sci., 8 1603-1615 (1973).

5. J.E. Palko, "A Review of Oxidation and Hot Corrosion of Silicon Based Ceramics," TIS, Gas Turbine Series, #77-MD-714, October 13, 1977.