CONF-810377--1

LA-UR-81-1643

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SUBMITTED TO: ASME Technical Report System for publication
Paper presented March 23-25, 1981 at WESTEC Conf.

University of California

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CERAMIC HEAT EXCHANGERS: MANUFACTURING TECHNIQUES AND PERFORMANCE

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ABSTRACT

The objective of the ceramic heat pipe program being conducted at Los Alamos is demonstration of the practical feasibility of this technology for the solution of severe high temperature recuperation functions. Ceramic heat pipe recuperators have been theoretically shown to offer distinct advantages over conventional ceramic heat exchangers from the standpoint of efficiency of heat recuperation and economics. The main stumbling block to their widespread utilization is related to the problems of materials for construction and the details of fabrication and assembly. This paper describes some of the performance objectives of ceramic heat pipes and describes some aspects of the materials technology program aimed at solving the problem of economic ceramic heat pipe fabrication.

INTRODUCTION

Ceramic heat exchangers offer the only practical means for high effectiveness recovery of heat from exhaust gases or chemical process streams at temperatures above 930°C. Alternative heat exchange devices employing metallic surfaces can be used in this temperature range only if the hot gas temperatures are reduced by dilution or if surface temperatures are lowered by deliberate design to reduce the thermal coupling from the gas. These restrictions lower the overall effectiveness of the heat exchanger and reduce heat recovery, as fuel saving in recuperation of furnaces is a direct function of the surface temperature of the heat exchange surface. Figure 1 shows the percentage of fuel savings, compared to an unrecuperated furnace, for a typical natural gas fired furnace using 110% stoichiometric air and employing a counterflow recuperator. The upper level for operation of stainless steel surfaces in this environment is indicated in the figure. In high temperature process heat transfer applications where an entire process may be carried out above the limits of metallic heat exchange surfaces the ceramic heat exchanger offers the only possibility for heat recovery.

CONVENTIONAL CERAMIC HEAT EXCHANGER DESIGN

Because of the advantages of ceramic heat exchangers in industrial application, they have been used in one form or another for many years. The traditional design of ceramic heat exchange surfaces for industry has consisted of units built up of short sections of ceramic tiles joined with ceramic cements. Their major drawback has been the leakage which develops between the gas streams through the multiplicity of joints in the units. Repair of the leaks requires major disassembly of the exchanger, a process which

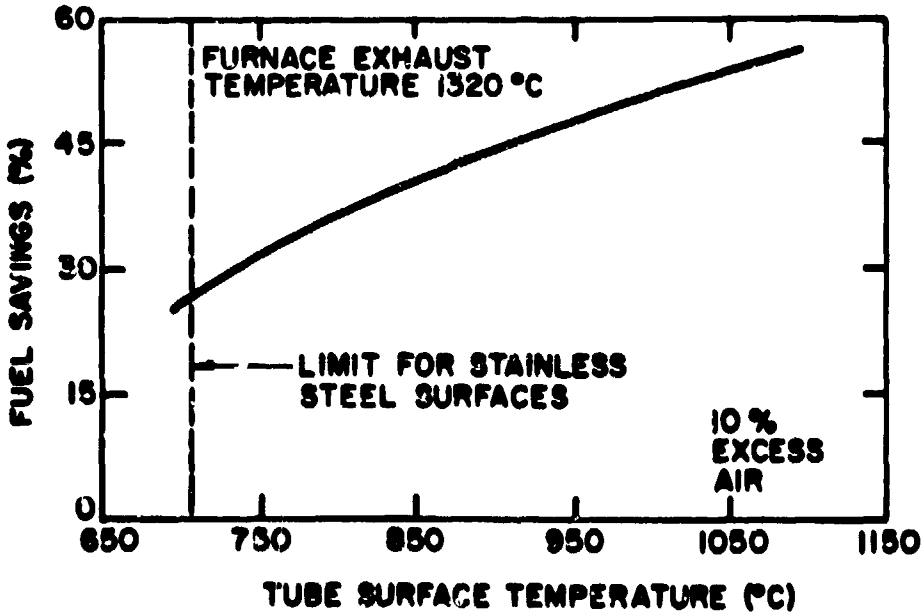

Fig. 1. Potential Fuel Savings as a Function of tube surface temperature.

may entail weeks of down time. In recent years the availability of higher quality ceramics has led to the development of alternative ceramic heat exchanger designs. Both plate and fin and tube and shell exchangers have been developed using ceramic materials. Plate and fin units offer the advantage of compactness and high surface density. The tubular units are generally configured much like metallic tube and shell heat exchangers. Both of these designs have problems which are fundamental to the materials of construction. Low thermal shock resistant material requires careful warmup and cooldown and the basic lack of ductility of the ceramic material requires that provision be made for differential expansion of the components of the exchanger. Repair or replacement of tubes in the field is difficult as is the fabrication of reliable joints between ceramic components and between ceramic and metallic surfaces. As a result, the present designs all incorporate some sort of pressure-loaded sliding seal in their design and consequently suffer from seal leakage at operating temperature.

CERAMIC HEAT PIPE HEAT EXCHANGER DESIGN

The design characteristics desired in a high temperature ceramic heat exchanger are summarized in Table 1.

Table 1. Ideal Design Characteristics of High Temperature Ceramic Heat Exchanger.

- No sliding seals in fluid loop
- Independent heat exchange elements
- Field repairable or replaceable elements
- Ready access to surfaces for maintenance
- Inherent allowance for differential expansion

Review of these desired characteristics suggests that a heat-pipe heat exchanger configuration lends itself to the application. A schematic of this type of recuperator is shown in Fig. 2, illustrating the characteristics of interest.

The successful exploitation of these heat-pipe heat exchanger design characteristics in the high temperature regime requires the development of a heat pipe fabricated

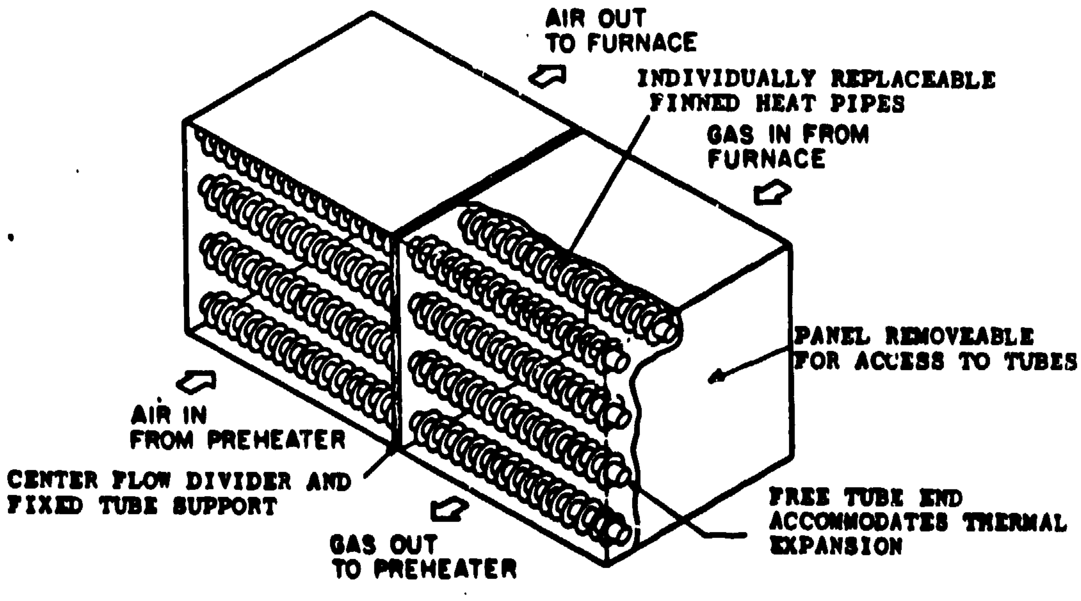

Fig. 2. Ceramic Heat Pipe Recuperator Arrangement.

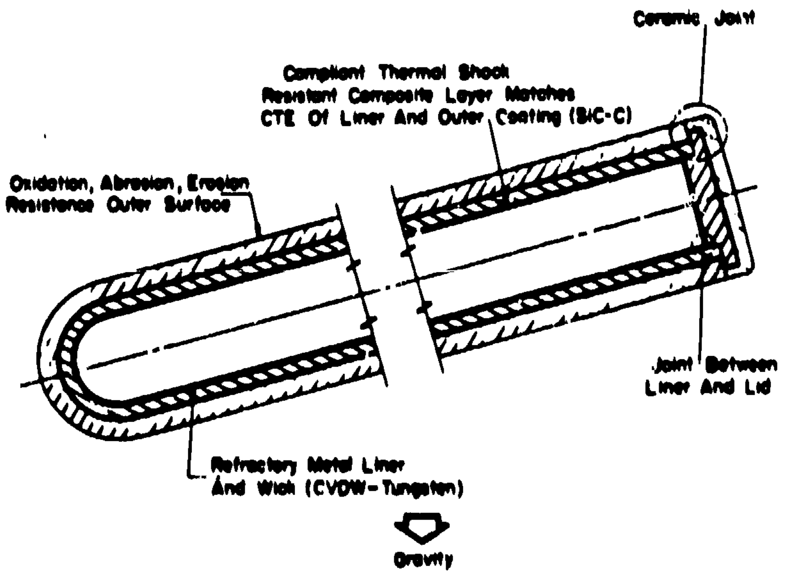

Fig. 3. Physical Characteristics of a Ceramic Heat Pipe.

of ceramic materials and capable of operating for extended periods at temperatures above 930°C. The elements of such a heat pipe are shown in Fig. 3. The outer envelope of the heat pipe is formed of a ceramic material such as silicon nitride or silicon carbide, having good strength at temperature, high thermal shock resistance, and resistance to attack in oxidizing and reducing atmospheres. The ceramic envelope may require a liner of refractory metal to protect the tube wall from attack by the working fluid. In assembly the tube is evacuated, charged with the working fluid, and sealed with a vacuum tight seal. The heat pipes will normally operate in a gravity assist mode and the resultant minimal wicking requirements may be satisfied by texturing of the tube inner surface. The thermal transport capability of such a heat pipe configuration, using sodium, lithium, or potassium as a working fluid, will be in the required range for high temperature recuperation applications. Peak axial heat transfer density will occur at the end of the evaporator section of the heat pipe and will depend on the surface flux density and the length of the evaporator section. For surface heat fluxes typical of industrial recuperator applications, tube lengths of more than 3m may be used.

CERAMIC HEAT PIPE PROGRAM BACKGROUND

The development of a ceramic heat pipe tailored to the requirements of high temperature industrial recuperation is the subject of the Ceramic Heat Pipe Program being conducted by the Los Alamos National Laboratory for the Pittsburgh Energy Technology Center of the Department of Energy. The goals of the program include ceramic heat pipe development and demonstration, recuperator design employing heat pipes, and demonstration of the technology in a small-scale prototype and, finally, in a full-scale industrial application. The program scope covers basic materials investigations, fabrication and assembly method development, ceramic heat pipe performance testing and the analysis of application conditions and economics.

Work on the program began with material compatibility studies leading to the initial selection of pipe envelope materials, working fluids, and protective liner materials. Alumina-niobium-lithium and silicon carbide-tungsten-sodium combinations were selected for tests. The use of alumina materials with liquid metal working fluids was eliminated in early testing because of thermal shock failures. Tungsten-lined, chemical vapor deposited (CVD) silicon carbide heat pipes using sodium as a working fluid were

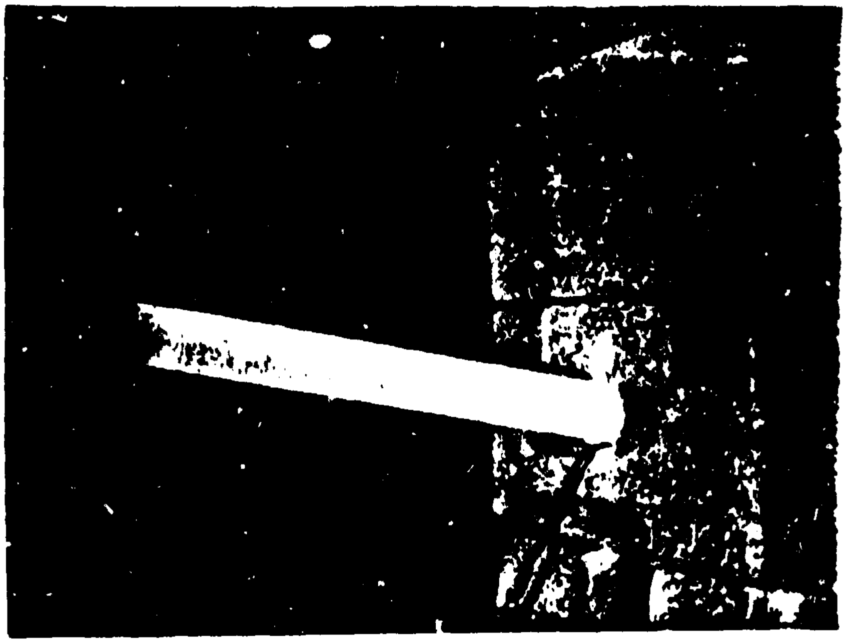

Fig. 4. CVD SiC Tungsten Lined Heat Pipe Operating in Air.

fabricated and operated in vacuum, air, and combustion gases at temperatures to 930°C. Figure 4 shows a CVD silicon carbide pipe at temperature in air. These pipes showed some liner-shell bond deterioration after operation for periods of approximately 100 h. One of the objectives of the current investigations is the improvement of this bond and, consequently, the operating life of the heat pipes through the use of different material combinations and assembly techniques.

These initial experimental heat pipes used brazed pipe closures which limited the operating temperature. Current efforts are directed to the development of welding of the tungsten liner as a means of tube closure.

CURRENT MATERIAL DEVELOPMENT FOR THE CERAMIC HEAT PIPE PROGRAM

The present material development program for the ceramic heat pipe program is directed to the development of tubular materials, coatings, and sealants consistent with the baseline configuration shown in Fig. 3. This consists of a core pipe structure of SiC-C composite with a lining of chemically vapor deposited (CVD) turgsten and an outer sealing and protective layer of CVD silicon carbide. Closure technique selected for the baseline is electron beam welding of the tungsten tube liner to a tungsten end cap with protection of the tungsten provided by a cap of ceramic joined to the tube material by a ceramic-to-ceramic joint. The current state of development of the processes involved is outlined in the following paragraphs.

The selection of material combinations for ceramic heat pipes is dictated by the limitations of physical and mechanical properties of candidate heat pipe materials. The general characteristics that are required of the ceramic heat pipe component are given in Table 2. Silicon carbide was selected for the baseline application because of its excellent high temperature oxidation and erosion resistance and its resistance to failure by thermal shock.

Table 2. Required Ceramic Heat Pipe Material Properties.

- High Mechanical Strength
- High Density (Vacuum Tight)
- Good Thermal Conductivity
- High Thermal Shock Resistance
- Good Oxidation Resistance

Because there are chemical compatibility, thermal expansion, and physical property restrictions imposed upon the fabricated assembly, it is necessary to incorporate many materials and processes in order to produce a design possessing the necessary physical, chemical, and mechanical properties required for service in severe environments. Key problem areas in construction are identified on Table 3.

The tungsten (W) liner is necessary in this design to serve as a barrier coating between the SiC and the molten Na working fluid in the heat pipe. Experience has shown that it is necessary to have intimate contact between the W liner and the outer ceramic envelope in order to have efficient heat transfer. Mismatch in coefficient of thermal expansion (CTE) between the CVD-W liner and the SiC can

Table 3. Key Problem Areas in Ceramic Heat Pipe Construction

- Quality Assurance
  - SiC/C Composite
  - SiC
  - W
- Mechanical and Physical Properties
  - Anisotropy
  - Reaction Zone Products
- Compatibility
- Scale-up For Production
  - Process Evaluation
  - Facility Engineering
- Alternate Manufacturing Processes
  - Production Rate Considerations
  - Economic Considerations

Table 4. Properties of Heat Pipe Constituents and Reaction Products.

Property	SiC	40v/o SiC-C	W	Si	W_3Si_2	WSi_2
Melting point, °C	2827	-	3410	1420	2340	2165
Density, g/cm^3	3.1	-	19.3	2.33	12.21	9.3
Thermal expansion/$^{o}C \times 10^{-6}$ α-SiC	5.68 5.32*	5.50	5 to 6	3.9	-	8.3
Thermal conductivity, w/mK	0.08 to 1.0	-	1.67	0.8	-	0.48
Hardness, kg/mm^2	2500-3000	-	-	715 to 960	-	1074

*700-2000°C

cause bowing, loss of bond, and spallation of either the SiC or W liner. A SiC-C composite layer between the W liner and the outer SiC is used to reduce CTE mismatch problems. This layer provides the compliance and dimensional stability necessary to maintain the integrity of the heat pipe.

The closure of the heat pipe presents a difficult problem. First a leak-tight joint has to be produced between the W liner and lid in order to encapsulate the working fluid. Secondly, a seal must be achieved between the SiC-C layer and lid, and finally the assembly must be overcoated with SiC. The final overcoat may be accomplished by either a CVD process using the decomposition of CH_3SiCl_3 or by a pack cementation process.

There are many potential problems associated with the materials combinations proposed in this design. Table 4 is a summation of some of the physical properties of the component materials of the heat pipe. These data show that there is a good match of the coefficients of thermal expansion between the various layers. Critical questions concern the compatibility of the reaction layer between the W liner and the SiC-C composite layer. The reaction products in this layer can be a source of difficulty with regard to component life and constitute a key area for evaluation in test.

The production of SiC-C composite tubing is a mature technology at Los Alamos. For more than twenty years Los Alamos has been a leader in the development of extruded graphites and carbides for various nuclear fuel element geometries. Figure 5 shows some tubular shapes being extruded and clearly demonstrates the practicality of high volume production of these kinds of components.

The microstructures developed in extruded and heat treated SiC-C composite material are far from ideal. A considerable amount of work is necessary to optimize the processing of the extruded composite. Because of the extremely refractory nature of SiC it is not possible to achieve optimal density of the processed composite. This composition will probably require the addition of various sintering aids in order to improve the density of the composite. The literature suggests that significant densification should be achievable with the addition of trace amounts of elements such as Mo, Ti, and/or B.

Coating Development

One of the most critical facets of the manufacture of ceramic heat pipes is related to the coating of refractory metal on the inside diameter of the ceramic or composite tube. All of our experiments to date have involved a base

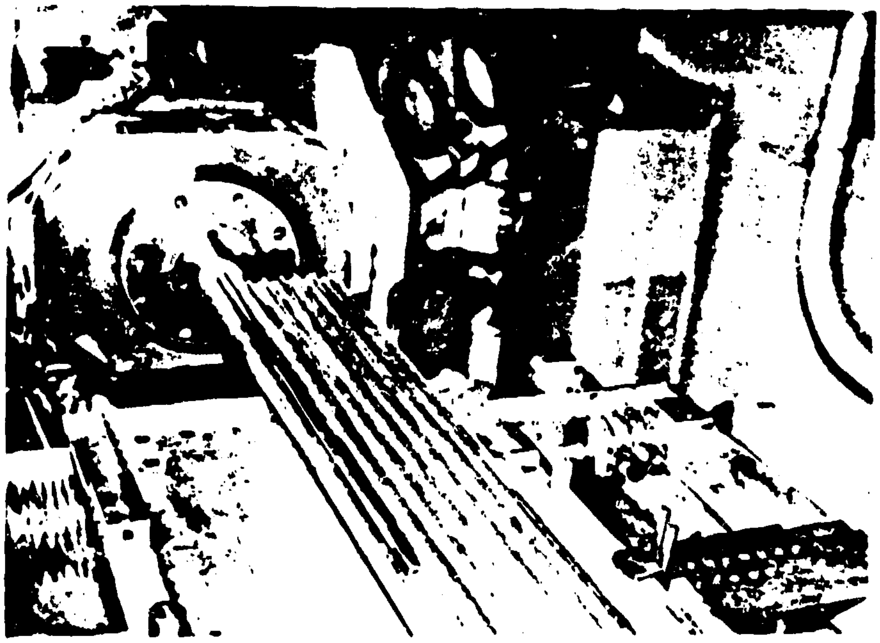

Fig. 5. Silicon Carbide - Carbon Extrusion Process.

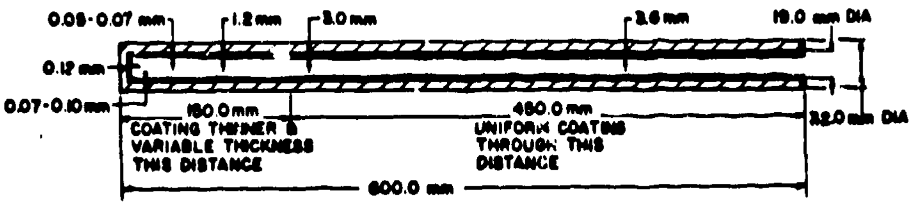

Fig. 6. CVD Tungsten Coating Distribution in SiC Tube--First Experiment with Computer Manifold Design.

tube of a silicon carbide with W deposited by the decomposition of WF_6. Figure 6 is a sketch showing the thickness of CVD-W in a typical heat pipe configuration. The manifold system used in this coating run was designed using a simple gas distribution code and the cross section shown was the result of the first coating trial. The results obtained in this first study suggest that a temperature distribution problem is affecting the deposition more than a flow problem. Previous experiments show that the coating rate is more sensitive to the temperature of the surface being coated and less sensitive to the effects of differences in mass diffusion of the coating gases. No serious problems are anticipated in this coating operation.

Figure 7 consists of photomicrographs of the structures developed in CVD-W deposited onto commercial CVD-SiC tubes. The as-deposited CVD-W has the typical columnar structure resulting from its epitaxial growth from the substrate. This condition is not ideal and it would be preferable to break up the columnar epitaxy and produce more fine grained equiaxed microstructure. The fine grained microstructure should give improved resistance to grain boundary migration of the alkali metal heat transfer fluid. At the same time, a "rough" surface for efficient capillary wicking on the inside surface is required. We believe that this can be effectively achieved by control of the deposition parameters. The lower figure shows a closeup of the interface layer between the CVD-W and the SiC. The composition of this layer has not been identified as yet, but we are concerned that it could be WSi_2. This phase has a coefficient of thermal expansion of 8.3 compared to 5.5 for W and SiC and this difference could lead to delamination of the bond. The SiC-C composite layer should be important in yielding a more effectively bonded layer at this interface.

Joining of Liners and Ceramic Material

One of the problems that must be overcome in order to demonstrate the feasibility of quantity production of ceramic heat pipes is in the general area of heat pipe component joining. The liner material must be joined using a process that guarantees a good vacuum. This vacuum is necessary to ensure purity of the working fluid and to minimize noncondensable gas effects. Vacuum tight seals to the liner material have been made using a Pd-Co brazing alloy process. For production, welded closures would be preferable. Figure 8 shows some typical configurations that have been welded to date. The weld joint shown in the top of the sketch is clearly preferable from a mechanical point of view. The difficulty lies in the back machining of the SiC component required to expose the weld. Some problems have been encountered with this welding scheme from the standpoint of cracking the SiC layer and also in the CVD W itself. The bottom figure is a suggested cross section that presents problems with regard to residual stress in the weld. Welds that have been produced

CVD Tungsten on SiC Cross-Section 100X

CVD Tungsten-SiC Interface Cross-Section 500X

Fig. 7. Photomicrographs of CVD-W.

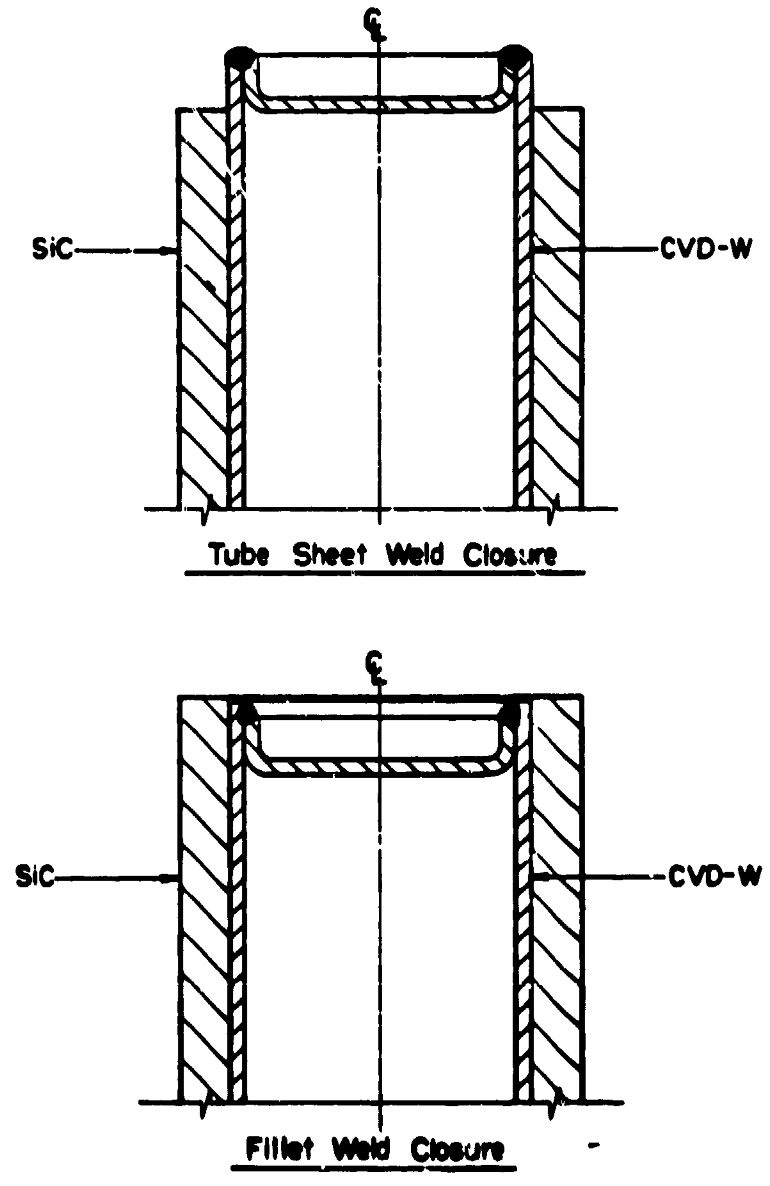

Fig. 8. Typical Weld Joint Configurations.

using this joint design show some stress cracking. This is an area of continuing development.

The results of evaluation of sealing materials for sealing the unmetallized silicon bonded silicon carbide material are summarized in Table 5. These results were produced on samples using simple butt joints, a difficult geometry to bond. The use of pure Si joining material was suggested by Carborundum Company and the Corning Glass was suggested by Norton. A method that has been used to successfully join carbide-carbon composites at Los Alamos consists of a butt joint that is bonded using a transition metal foil. This joining technique has been used with great success in joining thousands of carbide-carbon composite parts for a reactor built at Los Alamos in the late 60's and early 70's. In the reactor case,high volume percentage carbide materials were being joined.

A final step in the production of a heat pipe that uses the composite material design is to overcoat the finished subassembly with SiC. This can be done through chemical vapor deposition of SiC. This deposition can be readily achieved by decomposition of trichloromethyl silane at about 1200-1300°C. Figure 9 is a photomicrograph of a first attempt at CVD coating a SiC-C composite tube.

In conclusion, there is at present a strong interest in the development of high performance ceramic heat pipes for use in industrial processes. Proof of concept has been demonstrated. The development of practical and economic components is the subject of continuing efforts.

Table 5. Sealants Evaluated for Unmetallized Ceramics.

Seal Material	Temperature °K	Atmosphere	He Leak Rate cm^3(STP)/S
34 Al_2O_3 - 16 MgO - 50 SiO_2	1673	Air	$\sim 10^{-[illegible]}$
37.5 CaO - 6.5 MgO - 56 SiO_2	1673	Air	$\sim 10^{-[illegible]}$
91 Feldspar K - 8 Kaolin - 1 Bentonite	1673	Air	Gross
Trioxide (Al_2O_3 - SiO_2 - MnO)	1673	Air	$\sim 10^{-[illegible]}$
Honeywell No. 7377	1533	Air	$\sim 10^{-[illegible]}$
Corning 7052	1523	Air	$\leq 10^{-[illegible]}$
Corning 1720	1373	Air	Gross
Nicrobraze LM	1311	Air	Gross
68.8 Ag - 26.7 Cu - 4.5 Ti	1173	Air	Gross
70 Ti - 15 Cu - 15 Ni	1233	Air	Gross
Aluminum	1073	Air	Gross
Silicon	1733	N_2	$<10^{-[illegible]}$
Silicon	1733	VACUUM	Gross

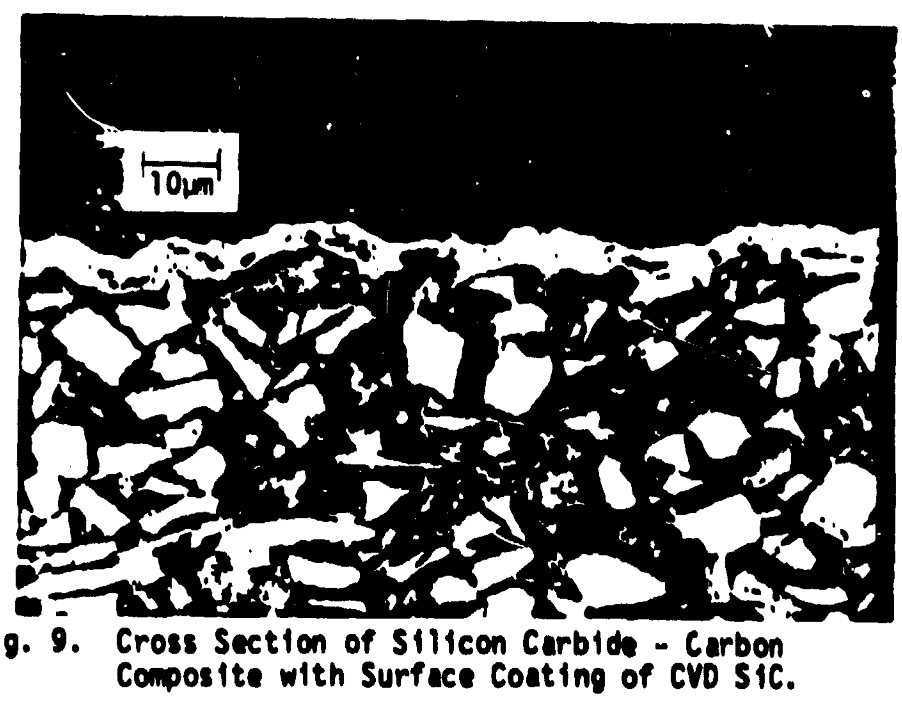

Fig. 9. Cross Section of Silicon Carbide - Carbon Composite with Surface Coating of CVD SiC.