

KAPL-P-000184

(K97078)

CONF-970701--

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July 1997

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THERMOPHOTOVOLTAIC EMITTER MATERIAL SELECTION AND DESIGN

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ABSTRACT

Thermophotovoltaics (TPV) is a potentially attractive direct energy conversion technology. It reduces the need for complex machinery with moving parts and maintenance. TPV generators can be run from a variety of heat sources including waste heat for smaller scale operations.

The United States Naval Academy's goal was to build a small experimental thermophotovoltaic generator powered by combustion gases from a General Electric T-58 helicopter gas turbine. The design of the generator imposes material limitations that directly affect emitter and structural materials selection. This paper details emitter material goals and requirements, and the methods used to select suitable candidate emitter materials for further testing.

OBJECTIVES

The objective was to select an emitter material based on an initial design that would withstand the environment, temperatures in excess 1300°C, and achieve an emissivity of at least 0.90. Additional material concerns included thermal shock resistance, thermal conductivity, and machinability.

METHODOLOGY

The objectives of this project were achieved through the following primary steps:

Background Research - A thorough review of previous thermophotovoltaic research and processes involved in TPV energy generation was conducted. Supporting research also included an involved study of materials and their associated material properties.

Experimentation - Candidate materials were tested for oxidation resistance, thermal shock resistance, and emissivity in cases where the information was not available in technical literature.

Material Selection - Final emitter material selection was based on TPV system requirements, data obtained through background research, and data from experimentation.

THE FUNDAMENTAL PROCESS

A TPV generator is composed of three main parts: a thermal radiator, a thermal radiation filter, and a semiconductor diode. In many instances, the thermal radiation filter is incorporated into the semiconductor diode, called a TPV cell (Borowsky and Dziendziel, 1994). In this project the TPV cells and filters (one unit) were supplied to the Naval Academy, hence two components of the generator are constant, leaving the emitter material as the final variable.

The choice of material to serve as the emitter dictates the characteristics of the emitted radiation. Planck's Law reveals how an ideal material radiates energy as a function of its temperature, but no material is ideal. Emissivity is the property used to quantify how closely a material models an ideal blackbody radiator. It is the material's emissivity that determines how the emitter will radiate its energy at a given temperature (DeWitt and Incropera, 1996). Additionally, emissivity directly influences the overall system efficiency.

INITIAL SYSTEM DESIGN

The design of the system determines the properties that are required of the material components that constitute the design. In a high temperature design project such as this, determining which portions of the design will experience elevated or cyclic temperatures is critical. Additionally, determining which materials will be exposed to combustion gases or heavy loading is important for determining the design life of the materials. The following is a brief overview of the United States Naval Academy's initial system design and the resulting material concerns.

INITIAL DESIGN

The TPV generator is to be powered by combustion gases from a General Electric T-58 helicopter gas turbine. Figure 1 is a diagram of the initial TPV system design:

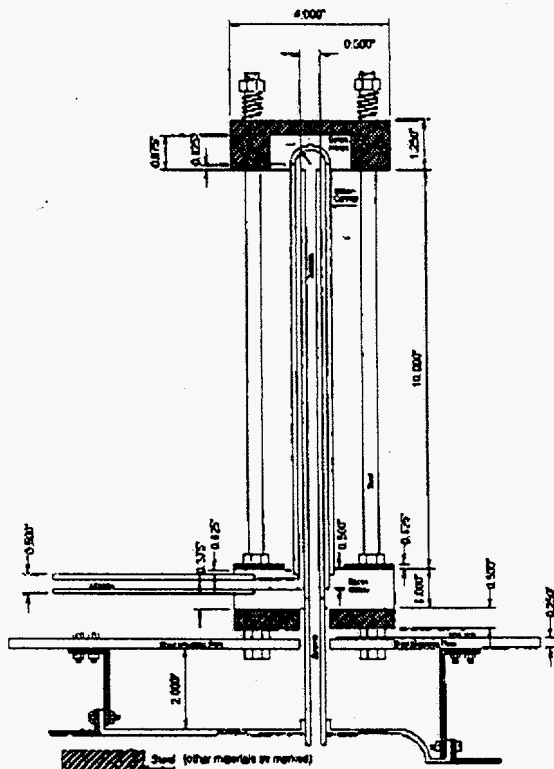


FIGURE 1. SCHEMATIC DIAGRAM OF THE ASSEMBLY

It can be seen that the combustion gases are extracted from the combustion chamber of the T-58 by way of an extraction tube. This tube extends from the inside of the combustion chamber to the inside of the emitter. The pressure inside of the combustion chamber is approximately 120psi, which is sufficient to force combustion gases up through the narrow opening of the extraction tube. The combustion gases pass through the tube and exit at the top. At this point, the gases are re-directed back down along the outside of the drawing tube within the confines of the cylindrical emitter. The gases then exit through an exhaust port at the base of the emitter, located in the base plate. The TPV cells (not shown) are located in close proximity to the outside surface of the emitter to absorb the emitted radiation. Water cooled channels are placed against the backside of the TPV cells to serve as heat sinks, because the cells are more efficient when cooled below 90°C.

EXHAUST GASES

The composition of the gases affects the corrosion mechanisms that may result from high temperatures. At increasingly high temperatures, corrosion rates accelerate, which makes accurate identification of potential corrosion hazards vital.

The exhaust gases from the gas turbine can be expected to contain the following (MSDS JP-5):

- Carbon monoxide
- Carbon dioxide
- Water
- Hydrocarbons
- Nitrous oxide

EMITTER MATERIAL PROPERTIES

The performance of the emitter is most directly linked to the material from which it is constructed. Thus the properties of that material influence the overall performance of the generator. Matching the emitter requirements to the properties of the material chosen is therefore critical. It is unlikely that one specific material will meet every single requirement for the emitter. It is more likely that the best material will require compromise; for example, one material may have a high melting temperature and emissivity but require a coating to provide for corrosion resistance. In any case, the important ideal emitter properties must first be identified and their significance weighted, before compromises can be made.

Melting Temperature

The material chosen must be able to withstand 1300°C without degrading. It is conceivable that the inside of the emitter may reach temperatures in excess of 1300°C during testing, so it is also important that there be some tolerance for even higher temperatures. Essentially, the higher the melting temperature the better. Some materials sublime rather than melt. This must also be avoided.

Emissivity

The objective of this research is to find a suitable emitter material that has an emissivity greater than 0.90. Unfortunately emissivity is not a property that is commonly known for most materials, especially for newly developed materials. It is important, therefore, to understand the fundamentals of emissivity in order to speculate as to which materials are worth investigating, since emissivity testing is both difficult and expensive.

The emission from a material is a direct result of the energy released by the oscillations or transitions of the electrons in that material. The oscillations of the electrons are dependent on the internal energy of the material, which in turn is dependent on its temperature. Radiation emerging from a finite volume of matter is the integrated effect of the local emission throughout the volume. In most solids though, radiation emitted from interior molecules is rapidly absorbed by adjoining molecules. Therefore, radiation that actually escapes the surface of the body originates from the molecules that are within approximately 1 μm from the exposed surface. Due to this effect, radiative emission is viewed as a surface phenomenon for solids.

Often, when high emissivities are required, materials must have their emissivities enhanced. Since the emissivity of a material is a function of the character of its surface, techniques for enhancing a material's emissivity focus on altering its surface. There are two main approaches to altering the surface of an emitting material: coating the surface and texturing the surface.

If a material has a low emissivity, its emissivity may be enhanced by applying a thin layer of another material that has a higher emissivity. The difficulty in this technique lies in matching the proper coating with the material. Just as in alloying

metals and joining materials, some materials respond favorably to coatings while others do not.

The other technique for improving a material's emissivity is surface texturing. NASA Lewis Research Center in Cleveland, Ohio has developed three techniques for enhancing surface emissivity that were being considered for this project. All of these techniques involve ion sputtering. The three principle techniques are sputter etching, sputter deposition, and sputter texturing. Sputter etching is the process of removing material from a surface by bombarding it with a stream of high energy ions or neutral particles. Surface atoms and molecules are ejected from the surface of the target material due to interactions with the bombarding particles. The end result is a highly pitted surface, which enhances emissivity. Sputter deposition is the process by which material that is sputter etched from a target is accumulated on the surface of another material. Essentially, sputter deposition is similar to sputter etching except that the goal is to use the ejected atoms and molecules from the sputter etching process rather than to actually etch the material. The fundamental idea behind sputter texturing is that the surface material have distinct spatial variations in its sputter yield, meaning that different regions of the target material will eject more atoms when exposed to the ion beam. Ultimately, this creates the texture as areas of the surface will in time have ejected significantly more atoms than neighboring regions. Ideally, the emitter material will be a material that does not require surface texturing or coating (Banks, B. A., 1981)

Corrosion Resistance

At 1300°C, most materials degrade quickly and easily. Few materials, in fact, can withstand these temperatures by themselves and not corrode in some manner. An additional concern in this application is the possibility of corrosion products depositing on the TPV cells.

If absolute corrosion resistance cannot be provided, then it may be necessary to compare each potential material's corrosion rate. In this scenario, the goal would be to choose the emitter material that will last the longest. This would at least enable the overall design to be tested until an improved emitter is discovered.

Thermal Expansion

The ideal emitter would have a low coefficient of thermal expansion. Thermal expansion will not directly effect the performance of the emitter, but it will influence the design of the overall TPV generator. At 1300°C, thermal expansion can be considerable. If steps are not taken to allow for this expansion, considerable stresses could develop in the emitter material, potentially causing catastrophic failure. In the initial design, springs are located at the top of the generator to account for the thermal expansion of the emitter. Ideally, if thermal expansion cannot be minimized, thermal expansion coefficients of neighboring materials should match, allowing for the entire structure to expand in unison. This is particularly critical in regions where materials are tightly fitted together, such as the end caps that are used to seal the emitter tube.

Thermal Shock

When the T-58 gas turbine is ignited, combustion gases immediately impinge on the extraction tube and emitter assembly.

This sudden surge from room temperature to 1600°C in a gaseous environment can cause catastrophic failure in many materials due to rapid thermal expansion which can induce extreme stress. A material's crystal structure alters at high temperatures, thus if the temperature change is sudden, a rapid structural change can induce material failure. Typically, materials with low coefficients of thermal expansion are more resistant to thermal shock (Richerson, 1992).

Thermal Conductivity

The thermal conductivity of the emitter directly affects the efficiency of the TPV generator. It is very difficult to heat the emitter up to 1300°C with the combustion gases of the T-58 generator due to the low convection coefficient of most gases. If the emitter is a poor thermal conductor, it is difficult for the outside of the emitter to reach 1300°C, due to the large temperature difference between the inside and outside of the emitter. The emissive power of the emitter is a direct function of the emitter's outside surface temperature, therefore the overall generator's efficiency can be drastically reduced if a large temperature gradient exists between the inside and outside walls of the emitter.

Machinability

Although machinability is difficult to quantify, the perfect theoretical design is worthless if it cannot be built. Many of the emitter candidate materials are ceramics and ceramic composites, and therefore are difficult to machine. This inherently limits the geometry of the emitter. Since most materials can be manufactured cylindrically, a cylindrical emitter seems most practical. Depending on the material however, shaping and sizing the cylindrical emitter may prove difficult.

INITIAL MATERIAL SELECTION

Initial material selection represents the first attempt at limiting the number of samples to be tested for the critical emitter properties. The approach that was used was to first list a large number of materials and gather published data on those materials. From that listing, the candidate materials to be further tested were chosen. Once the candidate materials were determined, they were ordered from manufacturers and suppliers.

The list of initial materials represents an attempt to sample materials from a broad range of possible high temperature candidates: monolithic ceramics, composite ceramics, and refractory metals. The initial materials included:

Boron Nitride	Tungsten-40%Rhenium
Nb based C-103	Niobium-1%Zirconium
Ni based MA758	Silicon Nitride
Fe based MA956	SiC/Si

EXPERIMENTATION

Once the candidate emitter materials were selected, initial testing was needed to narrow the candidates. Further testing was conducted on those materials deemed worthy. This was necessary because some of the testing could not be done at the U.S. Naval Academy and had to be contracted out to other laboratories. Costs were controlled by limiting the number of samples that were tested outside of the Academy.

Initial tests were either pass or fail. In the process of testing for potential emitter materials, consideration was given to whether a material might also function as a structural material. Materials that were completely ruled out were those materials that could not be used for either the emitter or the structural components of the TPV assembly.

Initial Oxidation Experiment

The objective of the experiment was to evaluate how samples of different materials responded to a 1300°C free air environment. The initial candidate materials were placed in a Thermolyne furnace at 1315°C.

Several materials were eliminated from consideration based on the results of this experiment. Specifically, tungsten-rhenium and C-103 demonstrated tendencies to corrode in the furnace. Tungsten-rhenium vaporized and left a yellow rhenium residue. A heavy, brittle, white oxide formed on the C-103 sample causing significant degradation.

Follow-up Oxidation Experiment

A second round of oxidation testing was conducted also using the Thermolyne furnace. The objective of this test was to produce quantitative results that compare mass changes due to oxidation for the different candidate materials. In some cases, the materials that had been eliminated in the initial testing were re-tested in order to generate data on them.

The quantitative results follow:

Material	Mass Change
Boron Nitride	- 2.42%
C-103	+ 15.54%
MA956	+ 1.09%
Nb-1%Zr	+ 1.77%
Silicon Nitride	+ 0.10%
Tungsten-rhenium	- 100.00%
Zirconia	- 0.04%

BN, C-103, MA956, Nb-1%Zr, and WRe all demonstrated significant mass changes that eliminate them as emitter candidate materials. Silicon nitride and zirconia demonstrated a resistance to oxidation.

Thermal Shock Testing

Thermal shock testing was conducted at Technology Assessment & Transfer, Inc. in Maryland. The objective of the test was to determine which candidate materials withstood the thermal shock that results when the combustion gases of the T-58 gas turbine first enter the emitter assembly.

The individual candidate materials were exposed to a flame from an acetylene torch and heated until they reached 1300°C. An optical pyrometer was used to measure the temperature of the samples to determine when they had reached 1300°C. Two samples of each material were heated with the torch, so that one could be air quenched and the other water quenched. Thermal shock on heat-up is the greatest concern for the emitter, but quenching was performed to develop an understanding of how the emitter material would perform once the T-58 gas turbine was extinguished and the emitter was allowed to cool.

Zirconia was the only material that catastrophically failed upon heating. C-103, MA956, and Nb-1%Zr all generated oxides that cracked from air quenching and shattered from water quenching. Tungsten-rhenium left a yellow rhenium residue after being removed following heating. These materials were eliminated from consideration since they are likely to fail after repeated start-ups of the gas turbine.

Emissivity Testing

Emissivity testing was conducted at NASA Lewis Research Center in Cleveland, OH. This testing was the most critical part of the research, since few materials exhibit emissivities greater than 0.90.

In all, eleven materials were tested for their emissivity. The materials tested ranged from ceramic composites to refractory metals. At this point, many of the materials had been eliminated from consideration because of oxidation or thermal shock problems, but they were still tested to provide general data and to serve as a basis for comparison.

Additional materials were included for testing because initial emissivity data on silicon carbide indicated that ceramic composites typically have higher emissivities. A variety of carbon and silicon carbide composite samples were gathered from various manufacturers for screening. These materials will be tested for other properties in the near future since emissivity testing confirmed the initial data.

The testing procedure follows. A series of lamps and filters were used to selectively radiate the samples with light of a specific wavelength. A system of mirrors was then used to capture the light that was reflected from the samples surface. This light was then directed to an integrator that calculated the reflectivity of the material's surface. The emissivity of the sample was then extrapolated from the reflectivity. A plot of the sample's reflectivity versus wavelength was then displayed on a nearby monitor that was connected to the system. The data used to generate the plots was saved. Correction factors were applied to account for the fact that the atmosphere within the test chamber was not a vacuum and that the test was conducted at room temperature. The material's emittance was extrapolated and plotted as a function of the incident wavelength and corresponding temperature, as shown in Figure 2-12.

The results of the testing were as follows:

Material	Emissivity at 1500K
Woven C/SiC	0.86
CVD SiC	0.90
SiC/Si	0.88
SiC/Si (oxidized)	0.93
CVD SiC/C	0.88
ZrB ₂ /SiC	0.78
CVD HfC	0.67
HfC w/ 10% TaC	0.70
BN	0.26
Nb-1%Zr	0.33
WRe	0.22
SiN	0.87

Emittance as a Function of Temperature for Selected Materials

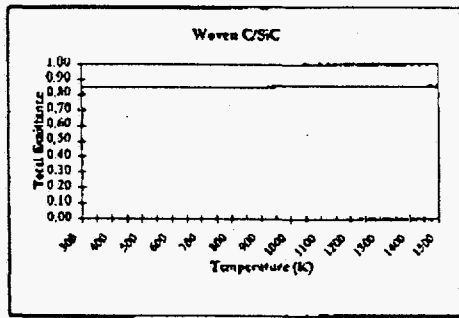


FIGURE 2. EMITTANCE OF WOVEN C/SiC

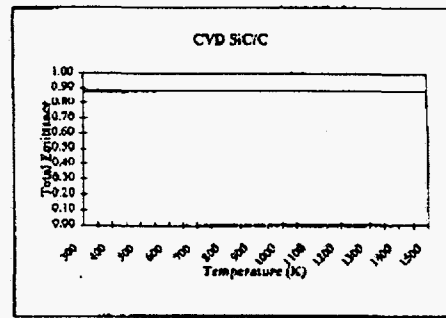


FIGURE 6. EMITTANCE OF CVD SiC/C

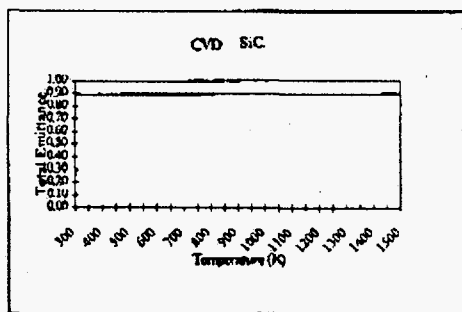


FIGURE 3. EMITTANCE OF CVD SiC

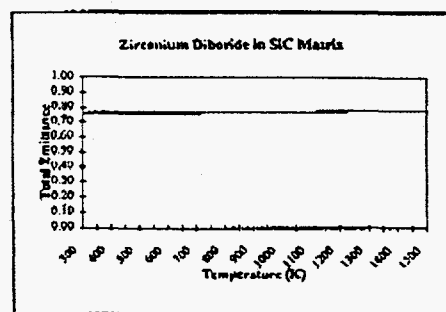


FIGURE 7. EMITTANCE OF ZrB₂IN SiC

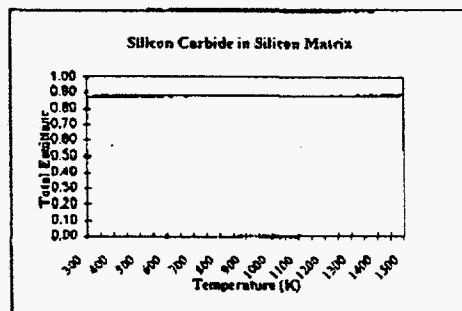


FIGURE 4. EMITTANCE OF SiC/Si

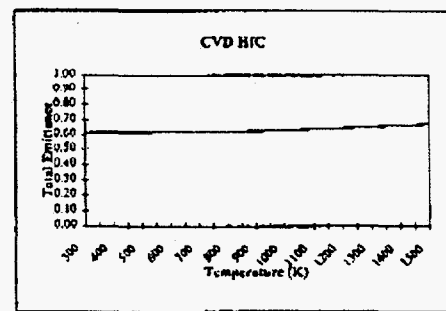


FIGURE 8. EMITTANCE OF CVD HfC

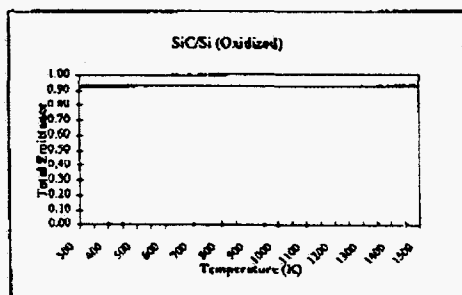


FIGURE 5. EMITTANCE OF OXIDIZED SiC/Si

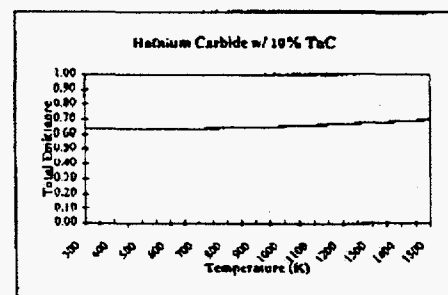


FIGURE 9. EMITTANCE OF HfC w/ 10% TaC

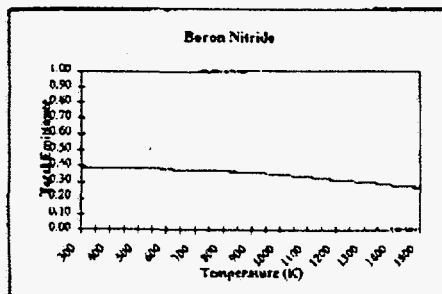


FIGURE 10. EMITTANCE OF BORON NITRIDE

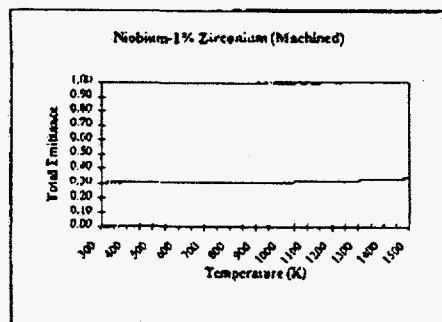


FIGURE 11. EMITTANCE OF Nb-1% Zr

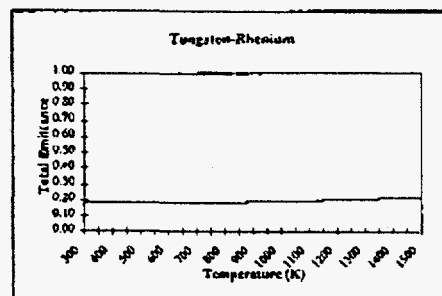


FIGURE 12. EMITTANCE OF WRe

An oxidized sample of SiC/Si had the highest emissivity, and in fact had an emissivity 0.05 greater than non-oxidized SiC/Si. This indicates that the performance of this material improves as it oxidizes during TPV generator operation. A one inch diameter tube of SiC/Si has been ordered for additional testing.

CVD SiC had the second highest emissivity at 0.90. CVD SiC is a typical oxidation resistant coating applied to carbon composites. This high emissivity indicates that ceramic composites with a SiC overcoat are a promising option.

A silicon-carbide fiber composite has been ordered for additional testing. This composite will undergo a reverse thermal gradient chemical vapor infiltration process by which carbon will be infiltrated into the fiber weave. A silicon carbide overcoat will then be applied to the surface of the infiltrated fiber weave.

CONCLUSIONS

Oxidation, thermal shock, and emissivity testing demonstrated that monolithic ceramics and refractory metals cannot withstand the environment of this TPV generator. Ceramic composites were the only materials that possessed emissivities equaling or exceeding the goal of 0.90.

Two materials were found that met the requirements of the thermophotovoltaic generator: lightly oxidized SiC/Si and the CVD SiC overcoat that is typically applied to composite ceramics to provide oxidation protection. Larger samples of these materials have been ordered in one inch diameter tubes to closely model the actual emitter.

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