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Power Converter Nose Cone

Melvin Kolbert

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FOREWORD

This report was prepared by the Electronic Systems Center, Grumman Aerospace Corporation, Bethpage, New York 11714 under Contract No. F08635-72-C-0112 with the Air Force Armament Laboratory, Eglin Air Force Base, Florida. Lt. William H. McMillian (DLJF) managed the program for the Armament Laboratory. This effort was conducted during the period from 9 February to 29 December 1972.

This technical report has been reviewed and is approved.

FENDRICK R7, Colonal USAF Chief, Fuzes and Munition Control Systems Division

ABSTRACT

The report covers the application of aerodynamic heat as a means of generating usable electrical power for fuzing and arming circuits in a projectile. A 20mm projectile was chosen for sizing purposes. The program concludes that power sources of this type are inherently safer than and can be produced at prices competitive with batteries.

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SECTION I

INTRODUCTION

This report covers the Phase I program to study, refine, and characterize a power converter nose cone for use in fuzing and arming 20mm projectiles. The contractor wind tunnel and laboratory tests had previously established the capability of thermopiles to convert aerodynamic heat into usable electrical power by virtue of a significant temperature difference between internal and external components. This passive method of generating power could be used to fuze and arm a projectile after it is in flight and at safe distance from the firing crew. Thus, it holds significant promise for increased safety and shelf life.

This report describes the research and development required for feasibility studies, concept definition, and fabrication of ten breadboard units for test and evaluation.

SECTION II

BACKGROUND DATA AND GENERAL TASK REQUIREMENTS

2.1 BACKGROUND DATA

Sufficient data has been produced in the contractor wind tunnel and laboratory tests and model simulators to prove the feasibility of employing thermopiles as power sources for various ordnance devices. In addition, this data indicated that:

- Aerodynamic heat can produce at least 5 watts/square inch at Mach 2.0 and above.
- Bombs can be provided with a continuous supply of electrical power for arming and fuzing during the drop period if, prior to release, aircraft electrical power is used to:
 - Charge a heat sink in an electrically heated metallic block so that it can drive a thermopile power source.
 - Initiate chemical burning material which is mated to a thermoelectric power source.
- Mortar ignition (chemical burning) can produce sufficient heat to store in a metal block and drive a thermopile so that a mortar shell can be electrically armed and fuzed in flight.
- There is a possibility of obtaining milliwatt power continuously for implanted mines and/or surveillance devices using the temperature gradient developed between the air and ground.
- Air and water temperature gradients can be employed for powering ocean buoys and ocean surveillance devices.
- Thermopile devices offer greater safety than battery devices as well as unlimited shelf life.

2.2 GENERAL TASK REQUIREMENTS

Based on the background data obtained by the contractor, a three-phase program was proposed for developing a power source for a 20mm projectile. The general task requirements of these three phases are as follows: Phase 1

- Design and fabricate breadboard models of a power converter nose cone (PCNC) for use in 20mm HE projectiles.
- Perform metallurgical studies which will form the basis for selecting component materials.
- Insure size compatibility of the PCNCs with the proximity fuze for 20mm HE projectiles being developed under Contract FO8635-71-C-0154.
- Insure that aerodynamic heating of the PCNCs will generate sufficient electrical power for the proximity fuze.

Phase II

- Develop a pilot production facility for ogive 20mm power sources.
- Perform a material study.
- Produce deliverable, fireable samples.

Phase III

• Design a production facility for 20mm nose cone within a \$1.00 per unit cost criteria.

SECTION III

PHASE I EFFORT

The Phase I effort basically consisted of investigations of processes for fabricating thermoelectric power sources that could employ aerodynamic heat as the prime energy source for a 20mm projectile. The fabrication cost goal for final mass production was \$1.00 or less.

The thermopile was chosen to be the power source because it offers high reliability based on stable physical characteristics which will not change with shelf life or environment. In addition, previous contractor-funded wind tunnel tests had demonstrated that a thermopile could produce 5 watts per square inch at Mach numbers 2.0 through 5.0. Temperature rises due to aerodynamic heating were plotted and are shown in Figure 1.

3.1 THERMODYNAMIC STUDIES

Thermodynamic studies during Phase I indicated that the voltage rise time of the thermopiles is a function of their construction and material and the thickness of their surface conducting bars. The thicker the conducting bars, the longer the voltage rise time (see Figure 2). Therefore, by controlling this design parameter, it is possible to produce arming voltage and electrical power at predictable activation times after firing. (A projectile would be electrically dead until the thermopile develops . 707 of the B+ voltage.) Voltage rise times ranging from 100 to 400 milliseconds have been obtained during tests by merely changing the thickness of the conducting bars. For a 20mm projectile, these time delays correspond to gun separation distances of 260 feet and 1040 feet, respectively.

3.1.1 Math Model

In the electrical analog of a thermopile shown in Figure 3, thermal coupling resistance (R_1) is a function of the method of applying heat energy to the conducting bar. For aerodynamic heating (transfer of kinetic energy), the value of R_1 decreases as velocity increases.

The temperature gradient $(T_1 - T_2)$ that can be developed across R_2 is time dependent, based on the values of T_2 and C_2 . The smaller the values of R_2 and C_2 , the more rapid must be the application of heat energy in order to develop a given gradient.



Figure 1. Mach Number Versus ΔT Due to Aerodynamic Heating



Figure 2. Thermopile Voltage Rise Times Due to Aerodynamic Heating

Thus, values can be selected for the thermal coupling resistance and temperature gradient so that a fuzing and arming voltage could be generated by aerodynamic heating during the 2-second ballistic life of a 20mm projectile, but conductive heating would be too slow, even in a fire.

3.1.2 Wind Tunnel Tests

Wind tunnel tests were conducted by the contractor at the General Applied Science Laboratory, Westbury, N. Y. Commercially available thermopiles were mounted in projectile simulators, as shown in Figure 4.

To obtain temperature recordings, five thermocouples were imbedded in various parts of each simulator. In addition, each simulator was painted with waxes calibrated to melt and change color at specific temperatures. Accurately timeframed, high-speed motion pictures documented flow and rise time, while the thermocouple outputs were recorded on chart recorders.

Separate runs made with various heat resistant and ablative coatings on the thermopile conduction bars confirmed that there was no problem in controlling or extending voltage rise time. This was equivalent to increasing activation time delay to obtain greater projectile-to-gun arming distance.

Outputs of 5 watts/square inch and 5.6 volts per square inch were reached at Mach 2.2 within 100 milliseconds. No effort was made to obtain this voltage in less time.

The commercially available cells used during these tests were 1/16-inch square. Freon tests were also performed on 1/20-inch square (50-mil) salami cut cells (Figure 5) made at the contractor plant. Smaller cells can now be made, but the minimum size has not been determined.

It was believed that the steady-state temperatures would be different due to the angle of attack of the model simulator. Tests at two different angles did not support this theory. Temperatures recovered by the thermal electric cells were very close to the total aerodynamic temperatures. (It is possible that the heat rise is a function of energy delivered and approaches total temperature as a saturation curve. It is believed that the saturation curve was approached at different rise rates. Thus, the blunter unit would rise faster than the high angle unit. This was not resolved by the tests, as insufficient data was obtained in this area of interest.)

3.2 FABRICATION CONSIDERATIONS

3.2 1 Mcterial Selection

In order to facilitate manufacturing and ensure homogeneity, a powdered metallurgical process was chosen as the method for fabricating thermopiles. The



Figure 3. Electrical Analog of Thermopile



Figure 4. Wind Tunnel Projectile Simulator Test Samples

materials most suited for this application are those semiconductor alloys that produce a high Seebeck voltage to give sufficient power to operate arming and fuzing devices.

A material used as an electrical power source should also have low electrical resistance. However, because of the low power requirements of a small electronic system, the resistance of semiconductor alloy cells generally is not significant. The voltage generated by a thermopile fabricated with cells of a given semiconductor material is a function of only the number of thermocouple pairs and their junction temperature differences, but the resistance is a function of the number of thermo-couple pairs, the thickness of the cell, and the junction surface area of each cell.

Thus, area and thickness of the thermopile must be considered not only from the physical standpoint but also from the standpoint of electrical characteristics. In addition, the amount of thermal energy available and the duration of its availability are important factors. The materials employed should have low thermal conductivity to limit the heat losses through each cell. Fortunately, some applications have considerably more thermal energy available than is required, and there is no need to design for thermal efficiency. Sufficient thermal energy can be obtained from the following sources:

- Aerodynamic heating generated by a cannon-fired projectile (see Figure 6).
- Chemical burning
 - Slow burning of fuel and oxidizer (see Figure 7).
 - Ignition of a mortar shell charge (see Figure 8).
- Remotely generated or stored electrical power (can be used to heat a heat sink) (see Figure 9).
- Air-to-water temperature differences.
- Air-to-ground temperature differences.

Fortunately, most of the developed units outlined in this report are designed for projectiles which have an excess of heat energy available.

The Air Force contract covered in this report requires that the primary heat source be aerodynamic heat, as generated by the transfer of kinetic energy from air particles to a temperature rise on the surface of a projectile nose cone.



Figure 5. Salami-Cut Thermopile







Figure 7. Bomb Chemical Burn



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Figure 8. Mortar Ign¹tion as Prime Heat Source



Figure 9. Electrical Power as Prime Heat Source for Bomb

3.2.2 Production of N-Doped Bi₂Te₃

 $\operatorname{Bi}_2\operatorname{Te}_3$ and PbTe were acceptable candidate materials, but because the cost of PbTe proved to be prohibitive, it was rejected. Doped $\operatorname{Bi}_2\operatorname{Te}_3$ is commercially available at \$200 per pound, or a cost per unit of 50 cents. Because of this marginally acceptable cost (with respect to the mass production cost goal of \$1.00 per unit) and the foreign source which is considered unreliable, it was decided to produce doped $\operatorname{Bi}_9\operatorname{Te}_3$ at the contractor facility.

3.2.2.1 Experimental Procedure

A series of experiments was conducted to evaluate the feasibility of using commercially pure Bi and Te materials (99.9% and 99.5% purity, respectively) in manufacturing Bi_2Te_3 thermoelectric compounds. The compositions of Bi and Te powder mixtures and alloying (doping) agents used in these experiments were as follows:

	COMPOSITIONS	COMMENTS
•	5.3g Bi - 4.7g Te	Bi in excess of stoichiometric composition to yield "P"
•	5. 1g Bi – 4. 9g Te	Te in excess of stoichiometric composition to yield "N"
٠	5. 22g Bi - 4, 78g Te + 0. 015g CuBr ₂	CuBr ₂ doping agent added to yield "N"
•	5. 22g Bi - 4. 78g Te + 1. 0 Sb, Se,	Sb _g Se

The mixtures were mechanically homogenized and loaded in quartz tubes which were evacuated and sealed under vacuum. The tubes containing the charges were heated to 840° F for 4 days. (These parameters were based on data reported in the literature pertaining to manufacturing of $\operatorname{Bi}_2\operatorname{Te}_3$ intermetallic compounds.) The

sintered agglomerates were subsequently crushed to powder, compacted in a 1/2-inch-diameter die at 30 ksi, recompacted at 50 ksi in an isostatic chamber, and sintered in argon at 700° F for 2 hours. Test results of the thermoelectric characteristics of these specimens were inconsistent; considerable variations were detected even on individual specimens depending on the location of the test probe.

In the subsequent series of experiments, the temperature was increased to 1200°F; all other parameters were identical to those previously utilized. The evalua-

tion revealed that the thermoelectric properties of compacted and sintered 5.22 Bi - 4.78 Te - 1.00 Sb $_2$ Se alloy pellets were equivalent to those of commercial Bi $_2$ Te $_3$ "N" materials.

3.2.2.2 Results

The obtained data indicated the following:

- It is possible to reduce the cost of doped Bi₂Te₃ material from \$200/pound to approximately \$20/pound by utilizing commercially pure (rather than ultra-pure)constituents.
- Commercially available doped $\operatorname{Bi}_2\operatorname{Te}_3$ materials may be rather complex alloys containing appreciable amounts of the doping agent. These preliminary studies did not include a complete evaluation of the various alloys in the Bi_2 - Te_3 - Sb_2 - Se_3 system, and the processing parameters were not optimized. Further studies aimed at a reduction of the initial cost of thermoelectric materials are definitely warranted.
- Seebeck voltages of contractor-produced material were tested and found to be equivalent to, or better than, the commercial material (\$200/lb), but no quantitative measurements were taken on the resistivity or physical parameters of strength. Qualitative tests indicated reasonable similarity.

3.2.3 Structural Consideration (See Figure 10)

Stratum or nose cone structural material must withstand shock and high temperatures. In normal ordnance use, heat is developed for such a short duration that only high surface temperatures are developed. However, during fabrication, $Bi_{2}Te_{3}$

must be sintered in the stratum for 2 hours at temperatures which would deteriorate most plastics quite rapidly. For this reason, the following high-temperature stratums were considered:

- Fiberglass with polyimide bonding
- Vespel
- Teflon
- Coated metal (polyimide)
- Ceramics

- Rigid silicon
- Modified polyester

Initially, polyimide looked like the long-range choice, but the processes for developed mass production techniques would have required study and development beyond the scope of the present effort. (The contractor is presently studying the techniques employed in developing polyimide tooling for fabrication of aircraft parts under another program. This effort is being watched very closely for fallout applicable to this program.)

Teflon[®] was rejected because it will plasticize and distort under the temperature required for sintering.

Metal nose cones could be sprayed with polymide and set. Unless coated evenly, however, problems may develop when the powdered metal is placed in nonuniform holes.

Both the rigid silicon and modified polyester plastic can be injection molded and can withstand the required sintering temperature for the period of time required. As the injection molding process is inexpensive, this method and the materials appear desirable.

3.2.4 Mass Production Techniques

The thermoelectric materials are compounded alloys and mixtures which must be uniformly dispersed. Unfortunately, this uniform dispersion is obtained by processes that are difficult to perform, and any melting of the material or excessive heating can drive off, either by evaporation or oxidation, components in the alloy and mix which would reduce the Seebeck efficiency. Thermoelectric materials have been made at the contractor facility by melting, whereby the same ingot had N and P properties because of this alloy separation. This fabrication technique required rapid heating and cooling in certain sections of the ingot to develop different concentration of materials. In the normal procedure (powdered metallurgy) uniform dispersion of components is maintained by locking-in the powders to render them immobile. This fabrication technique was employed in developing thermopile units. Particles were locked in after initial preparation and never unlocked during fabrication. Even during the sintering, which is required to strengthen the material, the lock is kept intact. Sintering, which must be accomplished in an oxygen-free, inert environment, was performed in an argon furnace (Figure 11).

The $Bi_2 Te_3$ formed by powdered metallurgy was tested for compression fabrication. The material was placed in a die and pressed at 60,000 pounds/square inch (see Figure 12a). The same material was pressed at 10,000 pounds/square inch and



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Figure 11. Argon Furnace





then isostatically pressed, as shown in Figure 12b. The first unit showed stratification, while the isostatically pressed unit indicated high density and limited stratification. Upon sintering, this stratification was removed (see Figure 13).

3.3 THERMOPILE FABRICATION METHODS

Two methods of fabricating thermopiles were explored, namely:

- Salami Cut Method
- Bumps and Grinds Method

3.3.1 Salami Cut Method

3.3.1.1 Assembly

The first step in assembling a salami thermopile was to coat a pressed or cut square (0.050 x 1 x 1 inch) of Bi_2Te_3 with a thin, insulating, high-temperature plastic. Talc was mixed with a resin to produce a plastic material that could be spread to an ultra-thin coat without beading. After the insulation set, N and P Bi_2Te_3

squares were alternately stacked and glued together with similar talc-filled plastic binder. The assembled unit was then cut by the diamond saw shown in Figure 14. The cuts were then insulated and glued alternately to produce the salami shown in Figure 15a. Cutting the salami as shown in Figure 15b resulted in the thermopile structure shown in Figure 15c.

3.3.1.2 Adding Conduction Bars

To provide the proper electrical path, the N and P cells must be connected in series. Direct printing (silk screening) of metal bars between the cells would require sintering of the conduction bars to the cells at temperatures above the melting point of the thermoelectric material. Bars of metal suspended in epoxy would have good flake-to-flake conductivity, but during the bonding process the epoxy which develops between the cell and the flake offers high resistivity. Thus, instead of printing conductive materials, a non-water soluble anti-bond mask is printed where metal is not required (see Figure 16). After printing, the unit is either hot-metal sprayed (see Figure 17a) or plated (see Figure 17b). Electroplating will not provide a uniform plating bar because of the insulation and bonding material. Electroless plating does provide a uniform coating (see Figure 18). Figure 19 shows a 0.002-inch-thick electroless plating completely bridging the bonding and insulation material. After electroless plating, the anti-bond mask was washed in a solvent and the thermoelectric unit is completed. Unfortunately, the electroless precleaner







A EMPLOYING ACID B RESISTING ANTI-BOND

ELECTROLESS PLATING EMPLOYING ACID RESISTING ANTI-BOND

Figure 17. Conduction Bars



Figure 18. Uniformity of Electroless Plating



Figure 19. Cross-Section of Electroless Plating

used on one unit dissolved the bonding plastic in the assembly. Since there was insufficient time to assemble new units with acceptable plastic material, the remaining units were hot-metal sprayed with a manually operated torch. The appearance of these units would have been much better if a smaller automatically controlled torch had been used. A dual process that employs hot spray and then a finishing plate may provide an even better finish.

Soldering and locking electrical connections to the pile proved difficult. The wires were stress relieved by epoxy bonding to the plastic. An actual bond into the plastic margin would have provided better stress relief for the connecting or output wires and contact bar (see Figure 20).

3.3.1.3 Test Results and Conclusions

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The finished 8 x 8-cell (64-cell) thermopile has an area of about 1/6 square inch with a high ratio of active to inactive material for maximum efficiency and minimum resistivity. It has a nominal resistivity of 4 ohms. At a ΔT of 100^oF produced by Freon, it produces in excess of 0.5 volt or 3 volts/square inch. At Mach 2.2 it would develop about 15 volts and about 9.5 watts/square inch. To expedite testing and obtain qualitative data, the units were sprayed with 100^oF Freon and oscillographs recorded time constants well within 300 milliseconds (see Figure 21). This indicates that a risetime of 100 milliseconds is possible with aerodynamic heating.

Unfortumately, the thermopile has no structural members other than that of the voltage producing material, which is brittle. This structure does not permit construction of other than a flat pile. Thus, salami-cut thermopiles cannot be used in applications involving shock, vibration, or curved surfaces as in a nose cone. Nevertheless, where electrical and thermal efficiency is the main criteria, this method may be optimum.

3, 3. 2 Bumps and Grinds Method

The bumps and grinds method of thermopile fabrication is simpler than the salami method and resulted in stronger less expensive samples. Although not as efficient as the salami units, they have sufficient power density to provide the required power and voltage for projectiles 20mm and up.

3.3.2.1 Assembly

The bumps and grinds method was developed around a precast high-temperature nose cone or stratum. Holes were provided for each cell and precast grooves were provided where electrical conduction bars were desired (see Figure 22). The thermoelectric powdered N material was selectively placed in half the holes and P material in the other half. The materials can be placed by a vacuum system, as shown in







Figure 21. Voltage Rise Times of Salami-Cut Thermopiles Using Freon to Develop 100⁰F ΔT





Figure 22. Bumps and Grinds Thermopile Design

Figure 23, or by other mechanical means that have been developed. After prepacking the material, the unit was placed in a PVC liquid and the liquid was set in an oven to form a self-constructed sealed bag. The assembly was then placed in an isostatic press (Figure 24) and subjected to a pressure of 60,000 pounds/square inch. After removal of the processed unit from the bag, the assembly was placed in an argon sintering furnace (Figure 11) and baked at 700°F for 2 hours to densify, strengthen, and increase the electrical conductivity of the material. The unit was then coated by a hot metal spray or electroless nickel, covering all exposed surfaces. After plating, the surface was ground down slightly deeper than the plating surface to remove all nickel except that which was deposited on the surface of the cell and the grooves linking each cell. This formed the electrical conduction bars. Test samples of electroless plating of the plastics and Bi₂Te₃ are shown in Figure 25.

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In order to prepack a thermoelectric nose conc, a prepacker (Figure 26) was developed. Since P had to be masked while filling N holes, it was decided to employ only one thermoelectric material and fill all the holes. The alternate thermoelectric material would be replaced by plated-through holes of nickel. One unit built in this way is shown in Figure 27. The plated-through holes should be made small compared to the thermoelectric material because the impedance of the nickel is very low. The use of a single material did not reduce the output voltage. The only loss was due to the space required for the plate-through holes, which is small, because the voltage output of N and P differ in magnitude as well as direction. The loss of voltage due to the plate-through hole can be made up by choosing the material (N Gr P) having the greater Seebeck coefficient. In lieu of plating-through, it is possible to initially cast a wire in the nose cone stratum.

3.3.2.2 Adding Conduction Bars

Initially, various metal salts were considered. However, these salts required a sintering temperature above the melting point of Bi_pTe_q .

Flaked metal held in an epoxy suspension was then investigated. When set, the flakes set up a conductive chain. Initial tests indicated high resistivity (point-topoint). Although some samples were found to have marginally acceptable linear resistivity, the epoxy tended to get under the flake and produce unacceptably high and unstable resistance into the base. As the set of the epoxy changed, so did the resistance into the base metal.

An anti-bond was then screened in a negative manner. The screen was made to cover the areas not requiring conduction bars. After the unit was so screened, metal could be applied by electroplating, electroless plating, or hot-metal spraying.

Hot-metal spraying has been used by the contractor for many years. Powdered metal or wire is blown into a gas-developed flame where it is melted and then



.....etc

Figure 23. Vacuum Pre-Press System



Figure 24. Isostatic Press







Figure 26. Rotary Prepacker

thrown at high velocity onto the material being coated, where it bonds to the stratum material. Samples of Bi_2Te_3 wafers were coated with Ni, Al, Cu, and an alloy of Ni-Al by this method. The copper appeared to alloy with the Bi_2Te_3 . The Ni-Al

alloy provided a low electrical resistance as well as an excellent bond without detrimental alloying. The hot-metal spray was also tried on various plastics with equal success. An anti-bond which had an asphalt base was sufficiently stable to provide masking of the hot spray and at the same time was easily removable by a solvent (see Figure 17). The Ni-Al alloy appeared to have the best adherence capability but was difficult to soft solder. Plain Ni wire without the Al did not have the soldering problem, but it did not adhere to the Bi₂Te₃ as well as the Ni-Al alloy. Both were tried and found acceptable.

Initially, hot-metal spraying of the bumps and grinds units produced conduction bars of uncontrolled thickness; this was subsequently corrected by controlled grinding. Finished units were well within strength and electrical resistance requirements (see Figure 28).

The hot spray technique can also be used to spray ceramics. (If the contractor had not found a proper plastic for the bumps and grinds unit, the nose cone stratum would have been die-casted and coated with hot-ceramic spray. However, a few plastics capable of withstanding the required environments were found.)

Electroless nickel plating, developed at the Bureau of Standards, employs an unstable metal compound in solution. This solution uses nickel, palladium, iron, or aluminum as a catalyst seed. Once the process is initiated, the plated nickel then provides the catalyst and the process continues.

Palladium chloride was used to start the process. (The process can be made selective by placement of the palladium chloride or by coating all over.) After initial plating, the high spots were wiped and then the process continued. A semishine material with good adherence, weathering, and soldering characteristics was chosen. (Besides the nickel plating materials others have been developed to plate tin, gold, platinum, copper, etc.) The material was plated on Vespel plastic and $\operatorname{Bi}_2\operatorname{Te}_3$ (see Figure 25) and found to provide good adherence and low resistivity.

3.3.2.3 Thermoelectric Material Pre-Press Compaction (Bumps and Grinds)

The initial compaction process was intended to hold the N and P powdered material in the selected holes during processing. Further densification was to occur later. The first compaction method employed was a manual process of placing and pressing the materials. Holes were selected by an indexed mask. The method was successful but time-consuming and could never be accomplished within cost criteria. The second sequences with easily as automated, applaye war usin and the second s



Figure 27. Single Material Experimental Thermopile



Figure 28. Hot-Spray Bumps and Grinds Thermopile

∿⊴ 25 The second method, which could easily be automated, employed vacuum and pressure to drive the powdered $\operatorname{Bi}_2\operatorname{Te}_3$ into preformed holes. This method provided the compaction needed, but the density left much to be desired. Placing the powdered $\operatorname{Bi}_2\operatorname{Te}_3$ into a carrier of alcohol, which was then vacuumed and air pressed, improved the technique. When further densification was developed, the amount of material in the hole shrank and had to be refilled at a later point.

The third method employed a powdered slurry of alcohol that was pumped through the selected holes. A backup acreen was used to pass the alcohol but not the powdered Bi_2Te_3 . This resulted in the screen filling up before the hole filled (see Figure 29).

The final method employed a grinding technique. The powder was rotated and pressed into holes in a nose cone. The combination of rotation and pressing was highly successful but not selective. Though a mask could be constructed to aid in the process, the single material $\operatorname{Bi}_2\operatorname{Te}_3$ (N or P) seemed like a better method of construction.

Though all samples submitted except one were delivered with N and P material, the single material appeared to be most promising. The odd sample submitted is of the single material type and operates as expected. The plated-through holes were the holes lacking the second material. No attempt was made to employ small platedthrough holes, since this would cause delay in delivery of the contracted samples.

3.3.2.4 Isostatic Press

The isostatic press developed employs a steel block with a round cavity chamber. A piston with an O-ring seal is used to provide the pressure element. The cavity was filled with water and a file cut made so that, when the piston was pressed, air and water would leak through the cut until the O-ring passed the bottom of the cut. This permitted proper alignment of the piston and removed compressible air. Pressures of 60,000 pounds/square inch were easily obtainable from a standard hydraulic press. It was noted that, after continuous operation, the piston would grind the surface of the cavity. An undercut, slightly below the O-ring on the piston, provided the seal strength and eliminated operation wear.

In production, the piston would be employed as a holding fixture for the nose cone for most of the processes besides being the piston seal for isostatic pressing.

Through the compaction provided by the isostatic press was adequate, the use of an ac pressure wave could permit higher densification. This ac pressure wave could be provided by employing a crystal transducer, a solenoid, or the contractor Wave Transducer. To develop the pressure in the isostatic press, the unit to be pressed was sealed in a watertight bag. If the bag was not employed, the water would wet the Bi₂Te₃ and force its way into the material, causing little or no pressure to go into the densification. The bags initially employed were commercial isostatic bags. Unfortunately, these bags were thick walled, and the forces applied did not provide pressure around the wall of the small holes. Thus, rubber and plastic balloons were used. These provided the pressure uniformly in the hole; however, if the initial compaction was not of reasonable density, the rubber would stretch under high clamping forces and break. Either higher strength bags and high pre-densification should be used, or a lubricant should be used in the bag to permit sliding, thereby preventing clamping action. Normal lubricants would pollute the Bi₂Te₃ which, in turn, would provide a poor plating surface. Thus, a thick lubricating alcohol having a low boiling

point was used to prevent residue after heating. Stronger bags of PVC were made at the contractor facility. The bags were made by dipping a test tube in PVC liquid, setting with heat, and then rolling it off the tube (see Figure 30). The bag could be sealed by using a taffy-like substance or by hot sealing. Hot sealing appeared to be the better method.

Since placing the sample in the bag and sealing the bag would increase the cost of the process facility as well as the cost of fabrication of the unit, the whole sample was dipped in the PVC, spun, and set in an oven. This provided a self-made sealed bag. This unit was tested and found to be feasible for mass production. In production, the bag would be cut with a "V" knife cutter after isostatic pressing by spinning the sample while on the mandrel. The modification would be to the ogive shape of the nose cone. At present, the cutting is done manually.

3.3.2.5 Sintering Argon Furnace

After the removal of the PVC bag, the units are placed in a tube that is run through a 700° F furnace. An argon atmosphere is bubbled through the tube to prevent oxygen from combining with the Bi₂Te₃. Initial sintering was performed in the furnace without the argon. The Bi₂Te₃ oxidizes and provides a material having high electrical resistance and low strength. The Bi₂Te₃ resistance and strength is much improved by the argon sintering. The injection of a reducing gas, such as hydrogen, may further improve the material since the hydrogen would remove the oxides previously formed. This addition of hydrogen has not been tried yet.

3.3.2.6 Stratum of Nose Cone

The period of the sintering is two hours at a temperature of 700° F which is required to be developed in the stratum as well as the Bi₂Te₃. The stratum must withstand the 700° F for two hours without deteriorating. Only a few plastics are



- 23.4

capable of these temperatures for continuous life. Most, if not all, high-temperature plastics as well as ceramics are transfer molded, a process which is quite costly. Further, most of these high-temperature plastics are also brittle.

Vespel⁽¹⁾, a Dupont plastic, is capable of 1300[°]F continuous but must also be transfer molded.

Some plastics are set at high temperatures but cannot sustain their properties at these temperatures over prolonged periods. Dow Corning and Carborundum Corporation claim that their high temperature plastics can be injection molded and withstand the 2-hour 700° F cycle without deteriorating. This short duration would have the effect of a tempering cycle. The capability of these plastics should be studied in an injection molder and under accelerated life test.

Another possibility is where the stratum can take the form of a metal casting that is hot sprayed with ceramic or dipped in a high temperature coating. Though the material would be strong, it could short to the base or form non-uniform coatings which would negate its usefulness.

For injection molding, the nose cone stratum would be cast with the conduction bar grooves for subsequent plating and grinding. The grooves would be inside as well as outside.

3.3.2.7 Single Material Bumps and Grinds (see Figure 27)

Various techniques have been developed whereby metal inserts can be molded into plastics in the injection process. If this is found possible, cost will be one of the basic tradeoffs to determine the possibility of employing wire inserts as a substitution for the second thermoelectric material.

It is desirable that the plate-through holes take up a minimum of space. By making the hole smaller, the slenderness ratio of the hole increases, thereby making the development of plate-through holes difficult. It is anticipated that, to minimize the hole size, a positive pressure system would be employed that causes the electroless plate liquid to flow through the plate-through holes. This plating can take place before or after final sintering of the total nose cone.

3.4 FUTURE EFFORT REQUIRED

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The test processes described have demonstrated the capability of producing thermopiles in quantity. All processes noted have been tested, and appraisal of the data indicates feasibility. Samples have been produced under contract with the Air Force Armament Laboratory, Eglin AFB, Florida. Pilot production facilities to be built will be a serial augmentation of the processes already developed. The optimization of these processes have not yet been achieved, but by the application of automation it is believed that the cost per unit can be made compatible with the cost of batteries presently employed.

This program has demonstrated feasibility, but further work must be accomplished to develop the low cost units. Future efforts must include:

- Development to improve thermoelectric devices employing commercial grade materials (Bi₉Te₃ - PbTe, etc.).
- Development of an ogive fireable thermoelectric nose cone for a 20mm projectile.
- Study of thermopile parameters
- Pilot laboratory production facility for producing 1000 units/month.
- Incorporation of thermopiles in ordnance other than 20mm.
- Development of a single thermoelectric material thermopile.
- Tests to determine the thermopile's resistance to weathering, shock, vibration, abrasion, thermal extremes, and thermal shock.

3.4.1 Development of Improved Thermoelectrical Material

Development of N-type $\operatorname{Bi}_2\operatorname{Te}_3$ has shown that commercial grade materials can be employed as thermoelectric materials. Although it is feasible to produce the material within cost requirements, further optimization is necessary. P-type $\operatorname{Bi}_2\operatorname{Te}_3$ must be developed and conductivity can be improved through refining techniques such as sintering in a reducing gas. Material improvement means using PbTe which may have the advantage of higher power densities since it can tolerate higher surface temperatures while providing greater structural strength. Additionally, various dopants have been employed indicating the possibility of higher Seebeck voltages and higher conductivity. High cost initially precluded the use of PbTe; however, low-cost fabrication techniques presently being developed at the contractor facility may permit re-evaluation of PbTe. Since the thermoelectric material represents a significant portion of the total unit cost, a material improvement effort is extremely important.

3.4.2 Development of an Ogive Unit

Materials have been tested which indicate compatibility for use as a fireable nose cone, one of which is DuPont Vespel⁽¹⁾. This poses problems similar to that

experienced with the Doped Bi_2 Te₃, i.e., available only from a single source, high cost, and no control over delivery schedules. Cost reduction appears possible by making a metal structural nose cone coated with a high-temperature polyimide. The contractor has studied and produced polyimide and glass structures for aircraft. The techniques should be examined for application to production of small nose cone units.

3.4.3 Thermopile Parameter Study

In the initial program, the temperature rise time desired was 100 milliseconds. This is a realistic number but, for various reasons, other time constants should also be developed. A study of the thickness of material and conducting bars is indicated. Given the short exposure time, the amount of Bi₉Te₉ now employed is ex-

cessive. Since the amount of material is based on structural considerations, it may be possible to reduce cell thickness to the point where silk screen or other type printing of the total unit may be practical. This would result in a laminar thermopile. Because the flight time of a nose cone is rarely greater than two seconds, the thickness of the thermoelectric material can be limited to that sufficient to prevent the flow of high heat to the cold junction. The thin cells also permit low resistivity of the pile and higher current capability. This study may provide a basis for developing high-power inexpensive units that are operable for very short periods.

3.4.4 Development of Other Ordnance Devices

Development so far has indicated feasibility of a thermoelectric converter for 20mm shells but has not included shock and other environmental considerations. As was previously discussed, these environmental problems do not exist in many of the other applications, such as thermoelectric power sources for bombs and mortars. In the case of the bomb, the missing element is the heat source. In the case of the mortar it would be limited only by the heat sink. Thus, the present technology will permit a parallel development of application to other ordnance devices in the immediate future.

3.4.5 Test Program

Tests to be conducted include:

• <u>Tests of Various Ordnance Systems</u>. The lowering of cost of the thermoelectric power source opens the field to the incorporation of this device into other ordnance systems. Power units can be developed for other larger cannon-delivered projectiles as well as bombs, mortars, etc. This effort can be included in a general program or as an off-shot program. • <u>Test of Materials</u>. Selection of materials based on strength, cost, and ease of fabrication must be traded off to provide the most optimum system. PbTe must be considered and developed as it has more strength and higher temperature capability. Its original rejection was based on cost of procurement. With the breakthrough of producing Bi₉Te₃ at a reduced price, PbTe

might also be developed at a low cost.

- Test of Equipment Efficiencies. As explained in this report, to obtain firesafe devices, certain construction features must be considered. A parametric study should include time constants of rise and drop-off voltage. This should be developed with strength and reliability as an additional feature.
- Environmental Tests. To provide an indication of reliability, tests should include weathering, shock, vibration, abrasion, thermal extremes, and thermal shock. These parameters can go far in defining plating methods and materials.

3.4.6 Pilot Production Facilities

Pilot production facilities should be evaluated employing techniques outlined previously for semi-automatic production capable of at least 1000 units per month (tooling, processing, handling, etc.). This pilot production facility should be capable of producing sufficient quantities of power converter nose cones to provide units for field evaluation. The facility, while producing units, will provide a realistic base to permit final definition of a mass production facility and assessment of costs. A concept of this pilot production unit is defined in Figure 31.



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