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THEORETICAL-DENSITY
INTEGRALLY-BONDED
THERMOELEMENTS

Contract No. AT (30-1)-3605

Summary Report
for the period covering
September 1, 1965 to August 31, 1966

AEC Research & Development Report

by

N. Hemmat and M. Weinstein

for

United States Atomic Energy Commission
Sandia Area Office
Box 5400
Albuquerque, N. M.

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ABSTRACT

A technique utilizing ultrasonic agitation of a solidifying melt has been developed for the preparation of thermoelectric materials. Specifically, n-type PbI_2 doped PbTe and p-type $\text{Pb}_{0.7}\text{Sn}_{0.3}\text{Te}$, which exhibit high electrical efficiencies along with exceptional mechanical stabilities have been prepared. To accomplish this, a carbon concentrator crucible assembly has been designed which greatly facilitates materials preparation. Over 200 experimental casting runs have been carried out during this period. A new 2000 watt ultrasonic casting setup capable of producing ingots up to 2-3/4" in diameter and 2" long has been constructed and made operational. The n-type material exhibits a higher integrated α^2/ρ factor than commercially available material for the temperature range ($25^\circ\text{C} - 500^\circ\text{C}$). The p-type material exhibits an integrated α^2/ρ factor comparable to that of the commercially available material over the temperature range of interest. Thermoelements with uniform dimensions were prepared from these fine-grained ingots by conventional machining operations. In particular, it was shown that cylindrical shapes could be produced to tolerances of ± 0.0005 " using conventional hole saws, and the material could be turned on a lathe using normal hardened carbon steel tools. Bonding of ultrasonically prepared fine-grained thermoelectric materials to pure Fe electrodes was accomplished by a diffusion bonding process. Typical contact resistivities of $30 \mu\Omega \text{ cm}^2$ for n-type and $50 \mu\Omega \text{ cm}^2$ for p-type were produced. Specific runs indicated that it should be possible to obtain resistivities of less than $10 \mu\Omega \text{ cm}^2$ for both p- and n-type material by the diffusion process.

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SUMMARY

1. An ultrasonic casting system and technique has been developed for the preparation of fine-grained, chemically homogeneous n-type PbTe and p-type $\text{Pb}_{0.7}\text{Sn}_{0.3}\text{Te}$. The system consists of a 700 watt ultrasonic generator and matching magnetostrictive transducer coupled to a specially designed carbon concentrator-crucible assembly. Utilizing this approach, homogeneous grain refinement has been accomplished in thermoelectric ingots up to 1.5" long.

2. A newly designed 2000 watt ultrasonic generator with matching magnetostrictive transducer and carbon concentrator was constructed and made operational. The 2000 watt unit is capable of producing ultrasonically grain refined ingots up to 2 3/4" in diameter and 2" long.

3. A quench casting process was developed to obtain homogeneous thermoelectric charge material for use in the ultrasonic casting process.

4. A new stationary temperature programming ultrasonic casting technique was developed which produced improved grain refinement. This technique has allowed a considerable reduction in process time.

5. The thermoelectric and mechanical properties of n- and p-type elements machined from the ultrasonically grain refined ingots were evaluated and compared with the commercially available cold-pressed and sintered thermoelectric elements. The ultrasonically prepared n-type material exhibits a higher electrical efficiency factor (α^2/ρ) over the entire temperature range (25°C - 500°C) than does commercially available material. The ultrasonically prepared p-type material exhibits an integrated α^2/ρ factor comparable to that of the commercially available material over the temperature range of interest.

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6. The thermoelectric material prepared by the ultrasonic casting technique exhibits excellent machinability. Thermoelements with uniform dimensions were prepared from the fine-grained ingots by conventional machining operations. The material can be drilled, tapped, and turned to specific dimensions on a standard metal working lathe. Thermoelements have been machined to a tolerance of $\pm .0005''$ (for elements 0.5 inches in diameter) utilizing a conventional hole saw.

7. Bonding of ultrasonically prepared fine grained n- and p-type thermoelectric elements to pure Fe electrodes was accomplished by a diffusion process. Typical specific contact resistivities were $30 \mu\Omega\text{-cm}^2$ for n-type and $50 \mu\Omega\text{-cm}^2$ for p-type by this process. Optimum diffusion bonding with Fe electrodes can lead to contact resistivities less than $10 \mu\Omega\text{-cm}^2$ for both p- and n-type material.

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I. INTRODUCTION

In many respects thermoelectricity poses considerably more formidable materials problems than other electronic phenomena, since thermoelectric structures must display chemical, electronic, and structural stability at high temperatures and under large temperature gradients. A thermoelectric generator during temperature cycling is subjected to the forces of differential thermal expansion and contraction. Moreover, the generator is a high heat flux device. In order to obtain high over-all efficiency, the thermoelectric element must be either placed in compressive engagement (in which case the element is subjected to a mechanical stress) or bonded metallurgically to metallic electrodes (in which case factors such as thermal expansion and chemical compatibility must be considered).

Since the majority of useful thermoelectric materials such as PbTe and PbTe alloys are isotropic, there is no need to employ single crystal material. In fact, the presence of grain boundaries in these materials has been shown to be desirable, since it renders the thermoelement more resistant to creep and low load plastic flow. Brittleness is also an extremely undesirable property for materials subjected to mechanical stress. In thermoelectric materials in particular, the preferential cleavage so frequently encountered during handling can be catastrophic in operational devices. The material must be resistant to operational mechanical and thermal shocks. It is also desirable if the material can be machined by conventional tooling to high dimensional tolerances.

A fine-grained casting of chemically homogeneous materials makes them mechanically isotropic, relatively ductile, and readily machinable. This report describes work carried out under the subject contract for (a) producing fine-grained PbTe based thermoelements by ultrasonic irradiation of a solidifying melt, (b) optimizing the thermoelectric and mechanical properties of these thermoelements, and (c) preparing and evaluating metallurgical bonded n- and p-type thermoelements.

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II. MECHANISM OF GRAIN REFINEMENT

When a liquid composition is solidified in a mold, the ingot may assume one of the three cast structures illustrated in Fig. 1, depending upon the heat transfer conditions. Figure 1(a) shows a cast structure produced when surface of the liquid adjacent to the mold wall is cooled rapidly to the liquidus temperature by heat conduction through the mold wall and beings to supercool. At some degree of supercooling, nuclei of solid are formed with a random orientation. Because of anisotropy of growth rate, crystals whose direction of maximum linear growth is parallel to that of heat flow grow faster and crowd out crystals of less favorable orientation.

Thus, a second zone – called the columnar zone – with a preferred orientation forms adjacent to the chill layer. Depending on the heat transfer conditions, the columnar zone may extend to the center of the casting or, more frequently, be followed by another zone of equiaxed, randomly oriented grains in the center position of the casting, as shown in Fig. 1(b). The as-cast structures described are considered undesirable since (a) there will be a tendency for planes of weakness to develop where columnar grains growing from the different mold faces meet, (b) the materials will exhibit strength anisotropy due to preferred orientation of the columnar grains, and (c) there will exist a bulk inhomogeneity due to segregation at dendritic boundaries within the columnar grains and at the columnar grain boundaries.

The type of ingot structure in which the mentioned effects are minimized is a fine-grained, equiaxed structure, shown in Fig. 1(c). The fine-grained equiaxed structure is the most desirable type since:

- (1) It reduces segregation of alloy constituents.
- (2) It provides better dispersion of any non-metallics that might be present.

(a)

(b)

(c)

Fig. 1 Three main types of ingot structure

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- (3) It reduces the possibility of hot tearing (separations of grains due to the melting of a low melting point constituent in the grain boundaries).
- (4) It imparts a somewhat higher strength.

Various techniques have been employed to produce fine-grained materials. These include inoculation, casting with various superheats, vibration or stirring, and irradiation with ultrasonic energy^(1, 2, 3, 4). The latter technique was previously applied to the preparation of fine-grained ingots of thermoelectric materials^(5, 6).

Basically, there are two theories on the effects of vibration on solidifying metals. The first one postulates that fragmentation of primary crystals or dendrites acts as an artificial source of stable nuclei^(7, 8, 9). The second hypothesis explains the effect as an increased rate of nucleation produced by the alternate pressure and rarefaction waves in the metal^(10, 11). The following mechanisms may be operating according to the second hypothesis:

- 1. Permitting sub-critical nuclei to agglomerate and thus form nuclei of sufficient size to cause crystallization.
- 2. Changing the state of surface adsorption of various catalysts found in the liquid melt.
- 3. Causing temperature fluctuations to occur in certain parts of the melt, thereby increasing the supercooling at specific points in the liquid.
- 4. Decreasing the critical nucleus size by increasing the pressure at specific points in the melt.

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In any case, ultrasonic waves in a liquid produce cavitation and it appears that grain refinement is intimately related to cavitation effects in the melt. The most familiar example of cavitation occurs in boiling of a liquid. In all cases, a nucleus is required for cavitation. This may be a very small (10^{-6} inch diameter) bubble already existing in the liquid, or a small pocket of gas trapped in a surface irregularity at a wall. Nuclei remain in a quiescent state until some thermal, mechanical, or chemical change occurs which upsets their equilibrium. Ultrasonic waves provide a mechanical disturbance consisting of pressure fluctuations above and below the pressure of the liquid in which they are traveling. A high pressure will disrupt bubble growth or cause the collapse of one that has started to grow. It is the sudden collapse of bubbles which have started to grow that produces the characteristic effects associated with cavitation.

The factors affecting cavitation intensity are numerous and in many cases interrelated. They include:

1. Temperature of the liquid
2. The static pressure in the liquid
3. The size and number of bubble nuclei
4. The frequency and intensity of the applied sound field
5. The surface tension of the liquid
6. The vapor pressure of the liquid
7. The cohesion strength of the liquid
8. The viscosity of the liquid
9. The density of the liquid
10. The heat transfer rate in the liquid

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Whatever the mechanism or combination of mechanisms for altering the nucleation characteristics of a solidifying melt by ultrasonic energy, there should exist for each material a set of interdependent process parameters for which the flux of ultrasonic energy is most effective in producing a grain-refined, equiaxed material.

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III. ULTRASONIC CASTING EQUIPMENT AND PROCEDURE

A. Design, Construction, and Optimization of Ultrasonic Casting Equipment

1. Ultrasonic Power Generator and PZT Crystal Transducer

A special 500-watt power oscillator to be used in conjunction with a PZT crystal transducer was initially designed and constructed. Figure 2 indicates a block diagram from the ultrasonic generator employed. In this system, a manually variable oscillator was followed by a buffer amplifier which is in turn followed by a power amplifier. The power output was monitored by a Tektronics Oscilloscope, Model 545, with a type CA plug-in amplifier. The generator was later modified by rebuilding the vacuum tube generator into a single tube power oscillator of the electron-coupled type, with the power control in the screen grid. Also, a small choke was introduced in series with the crystal transducer to maintain an impedance match between the resonance circuit and the PZT crystal.

This ultrasonic generator was used in conjunction with a Clevite PZT-4 (40500) crystal transducer, $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_2$. Crystal transducers 1.5" and 2.5" in diameter and 0.5" thick with natural frequencies of 36 kc were used. In order to couple the ultrasonic vibrations into the liquid melt, a solid quartz concentrator (horn) was used. Various concentrator designs were employed to improve the transfer of ultrasonic energy to the solid-liquid interface. Figure 3 shows a schematic drawing of some of them. Figure 4 is a specific design which consists of a lower quarter wave cylinder 1.5" long (the lower quarter wave cylinder includes the crystal length) by 2 1/2" in diameter and a cone shaped quarter wave section terminating in a diameter of 20 mm. The velocity of sound in quartz ($c = 545 \text{ mm/sec}$) was assumed to be constant for all the quartz rods obtained from the same manufacturer.

Fig. 2 Block diagram of the power oscillator

Fig. 3 Various concentrator designs employed with PZT crystal transducer

Fig. 4 Piezoelectric transducer, quartz concentrator, and crucible assembly

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To a first approximation, amplification of the amplitude of the oscillations of the concentrator is equal to the ratio of the diameter of its end faces⁽¹²⁾.

$$n = \frac{2.5 \times 25.4}{20} = 3.12$$

That is, the amplitude of the vibration at the solid-liquid melt interface is approximately 3.12 times as large as the amplitude at the PZT-crystal quartz interface. The 3" long concentrator was machined from a quartz ingot.

The quartz concentrator was attached to the PZT transducer with a silver-epoxy mixture, Eccobond Solder 56c (Emerson & Cuming, Inc., Canton, Mass.). The solid quartz structure acted as an extremely good heat insulator, thereby allowing efficient operation of the piezoelectric transducer.

Before each ultrasonic-casting run, a clear quartz tube (20 mm OD, 18 mm ID) to be used as the metal container was fused to the end of the quartz concentrator. The thermoelectric material was placed in the tube and sealed under vacuum (10^{-6} mm Hg). This procedure removed excess moisture and eliminated problems of contamination and volatilization during the run. The PZT transducer quartz concentrator crucible assembly was then placed on a polyfoam support. The furnace was lowered and carefully positioned around the container tube, and heating of the system was initiated.

In general, the ingots obtained by employing the PZT transducer and quartz concentrator did not exhibit uniform grain refinement. The most effective grain refinement occurred within the first 0.25" portion of the ingot to solidify. Contributing to the limited extent of grain refinement were (a) insufficient ultrasonic power output (the amount of power introduced to the solid-liquid interface decreases as the amount of solidified ingot increases), (b) impedance mismatch between the generator and the crystal transducer (if impedances are not

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matched, power is dissipated in the oscillator circuit before reaching the transducer), and (c) lack of effective frequency tuning during the run, to accommodate changes in resonant frequency as the liquid-solid interface receded in the growth direction.

2. Ultrasonic Generator with Nickel-Laminate Stack Magnetostrictive Transducer

A second ultrasonic casting system consisting of a generator and magnetostrictive type transducer was subsequently put into operation. In this system the driver unit consisted of a Raytheon ultrasonic power generator, Model 2-332-1, which supplied 700 watts of ultrasonic power at a frequency of 25 kc. The generator had a frequency range between 17 and 27 kc, although most efficient operation occurred between 23 ± 2 kc. The frequency of the tuning circuit could be manually adjusted to the load frequency. The unit was also equipped with a so-called "resonance frequency indicator meter" and a manual power level adjusting knob. The matching transducer consisted of a Raytheon Nickel-Laminate Stack Magnetostrictive Head unit model 2-33-2-40. Figure 5 shows various designs of quartz concentrators, initially used with the magnetostrictive transducer. Figure 6 shows the optimized concentrator design employed with magnetostrictive system.

In general, the ingots obtained using this equipment exhibited considerable improvement in grain refinement in comparison to the piezoelectric transducer system. However, again the grain refinement was mainly restricted to the bottom half of the ingot. Also, the use of higher irradiation energies was limited by the fracture strength of the quartz concentrator. Figure 7 shows the extent of grain refinement obtained by use of the magnetostrictive transducer and quartz concentrator.

B. Concentrator Material and Design

1. Choice of Concentrator-Crucible Material

In the previous sections it was noted that the use of clear quartz material as concentrator and crucible necessitated an

Fig. 5 Various concentrator designs employed with the magnetostrictive transducer head.

Fig. 6 Schematic diagram of the optimized quartz-Monel concentrator used with the magnetostrictive transducer at 24.8 kc.

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(b)

(a)

Fig. 7 Cross-sectional views of an ultrasonically cast ingot (etched), prepared in the quartz concentrator-crucible used with the magnetostrictive transducer.
a) cross-sectional area of the first section of the ingot to solidify.
b) the last section of the ingot to solidify.

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experimental procedure in which quartz tubing was initially fused onto the quartz concentrator before each run, the charge placed in the tube, and the tube then evacuated and sealed. After each ultrasonic casting run it was necessary to cut away the quartz tubing (which contained the cast ingot) from the quartz concentrator, with a carborundum cutting wheel. Also after each run the end of the quartz concentrator had to be ground flat prior to fusing the next quartz tube onto the concentrator. This consumed considerable time and involved an excessive number of steps for a process of this sort. In addition, the power input to the quartz concentrator was limited due to fracture of quartz at previously micro-cracked regions.

Because of these difficulties, the feasibility of high-purity, high-density graphite as a concentrator and crucible was explored. The advantages of carbon over quartz can be summarized as follows:

- (a) Carbon is considerably more economical from the standpoint of the material and machining costs. The carbon system can also be more easily scaled-up.
- (b) Individual carbon crucibles can be machined to conform to the end of the carbon concentrator, in which case the crucibles are reusable.
- (c) Specialized glassblowing is eliminated and the processing time considerably shortened.
- (d) The ultrasonically cast ingots can be easily removed from the carbon crucible, thus eliminating the cutting away of the crucible and ingot from the concentrator avoiding a possible source of mechanical damage to the ingots.

2. Design of Resonant Structure

The amount of ultrasonic energy transferred to the melt interface depends critically on the amplitude of vibration at the loading end of the concentrator. Since the amplitude of vibration at the transducer head is comparatively low, it was necessary to design an appropriate

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resonator (amplifier) specifically for the 25 kc magnetostrictive ultrasonic generator. Three types of designs commonly used for concentrators are straight, tapered, and exponential. In this work a combination of the straight and tapered designs was used to achieve maximum amplification with minimum mass. A small mass is desirable since it minimizes energy losses due to attenuation in the concentrator material and reduces heat transfer through the concentrator by conduction.

Since the resonant frequency of the concentrator must be matched to the transducer resonance, its length, l , is determined by the fundamental relation $l = n \left(\frac{v}{2f} \right)$, where f = resonance frequency, and v = velocity of propagation of ultrasonic waves in the material.

Figure 8 is a schematic drawing of the concentrator assembly. The first section of the concentrator consists of a half wavelength of straight R-Monel, 2" in diameter, 3.61" long, ($v_{\text{monel}} = 1.804 \times 10^5$ inch/ sec, $f = 25$ kc). Since the carbon horn cannot be attached directly to the transducer (top surface diameter 3/4") by a mechanical coupling, the monel section provides a rigid coupling between the transducer and the carbon concentrator. Carbon was fastened to monel with an epoxy-bonded joint. The second section of the concentrator consists of a tapered, 2" $\rightarrow$ 1" diameter cross section. The propagation velocity (with the grain) of ultrasonic waves at 25 kc, (for the type of carbon used) was determined to be 125×10^3 inch/ sec. The tapered portion consisted of two half-wave sections of carbon, (~ 5 " long). The transition from the tapered to straight section was placed at an anti-node of the standing wave in the graphite in order to minimize the stress concentration in the graphite. The third section of the concentrator was again a straight rod, 1" in diameter, 7.5" long (equivalent to 3 half-wave sections). The total of the 5 half-wave sections of carbon was the allowable minimum length for preventing overheating of the epoxy joint. (The present epoxy is rated at 140°C).

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Fig. 8 Schematic drawing of monel-carbon assembly used with the magnetostrictive transducer (dimensions not to scale)

3. Concentrator Cooling System

In the quartz concentrator system the quartz provided excellent thermal insulation between the melt (920°C) and the bond region between the quartz concentrator and base metal (Fig. 5). Carbon concentrator caused overheating the epoxy bond between the carbon and the base metal because of their higher thermal conductivity. In order to avoid overheating, a series of water cooling systems were designed and successively improved upon. Figure 9 shows a schematic drawing of the cooling system presently being used. The basic design specifications of this assembly were:

- (a) To provide sufficient cooling at the base of the carbon concentrator to prevent the epoxy bond region from overheating.
- (b) To impose the least possible load on the vibrating parts of the ultrasonic assembly.
- (c) To act as the seal base plate for the vacuum enclosure.

It is to be noted that in this system (Fig. 9) two silicone "O" rings provide the only physical contact between the vibrating concentrator and the stationary parts. Excellent water and vacuum seals were obtained in this system: Prior to each ultrasonic casting run, it was necessary only to remove the quartz bell-jar from the rest of the assembly in order to charge the crucible. An electric water flow switch automatically assured flow of water in the transducer and the water jacket before the ultrasonic power could be turned on.

C. Maintaining Resonance During Ultrasonic Casting

A basic problem in introducing ultrasonic energy into a melt is that of maintaining a resonant condition in the coupling system between the transducer, concentrator, and the load during a run. Temperature changes in the concentrator assembly change the velocity of sound in the

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Fig. 9 Schematic diagram of the carbon concentrator-crucible assembly and the water cooling system (dimensions not to scale)

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materials and in turn, the resonant frequency. The resonant frequency also depends on the length of the solidified ingot. High-power ultrasonic generators presently available are not provided with even moderately accurate resonance indicators.

In order to maintain resonant frequency during the ultrasonic casting run, we developed an amplitude monitor consisting of a magnetized pin attached to the base of the concentrator and positioned freely inside an accelerometer coil. The mV output of the coil is fed into a sensitive AC electronic voltmeter, (Ballantine Model 310-A). This provides an excellent measure of the relative amplitude of the vibration of the concentrator. The resonant frequency can be maintained during the entire casting run by manual adjustment of the frequency to obtain maximum deflection of the mV indicator.

Figure 10 shows the variation of frequency required to maintain the solid-liquid interface at resonance during an ultrasonic casting run. The resonant frequency remains constant before the start of solidification and after the entire melt is solidified, but it decreases steadily during the solidification process. The frequency was decreased gradually during solidification to maintain resonance.

D. Traveling Mechanism and Furnace

The moveable heater assembly used for melting the charge consisted of a 1-kw vertical resistance furnace with super kanthal winding. The winding configuration was designed to produce a reasonably flat temperature zone along 2/3 of the length of the furnace, with a sharp temperature drop at one end. The cylindrical furnace was 12" long, 8" OD, and 2 1/2" ID. A platinum-platinum 13% Rh thermocouple was used in conjunction with a Honeywell Precision Set-Point Temperature Controller, Model #6870781. The controller was capable of maintaining the furnace

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Fig. 10 The variation of input frequency with time in order to maintain the solid-liquid interface at resonance during an ultrasonic casting run

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temperature within $\pm 0.5^{\circ}\text{C}$. The furnace was mounted vertically on a carriage plate which is worm driven by a 1/15 horsepower variable speed DC motor and controller (Fig. 11). The motor is connected to a proper gear reducing system to produce a range of travel rates of between 1/2" and 12" per hour.

E. Ultrasonic Casting Procedure and Effects

Initially, a number of directionally solidified (without ultrasonic agitation) PbTe ingots with varying PbI_2 doping concentrations were prepared in order to obtain control data for use in evaluating both the electrical properties and the effectiveness of ultrasonic agitation. The directionally solidified ingots prepared in a carbon crucible normally consisted of a few large grains, as shown in Fig. 12. This type of ingot typically develops fractures along the major grain boundaries upon cooling and is extremely susceptible to cleavage fracture during machining.

Figure 13 shows the Seebeck-voltage as a function of temperature for a directionally solidified ingot with 0.01 mole pct PbI_2 , and Fig. 14, for an ingot with 0.03 mole pct PbI_2 .

It is to be noted that in these unagitated castings the carrier type changes along the length of the ingot. Figure 15 shows the resistivity profile of an ingot (doped with 0.03 mole pct PbI_2) in the growth direction. These results are similar to the results obtained by other investigations on Bridgman-grown single crystals. The resistivity peak at the midsection of the ingot indicates a combined effect of doping and the tendency for the stoichiometric liquid to initially reject the tellurium rich composition.

Figure 9 shows a schematic drawing of the over-all ultrasonic system assembly of graphite concentrator and crucible presently used. The concentrator is machined from high purity, high density graphite with a guaranteed average ash content of less than 0.03%, maximum grain size 0.016 mm, bulk density 1.68 g/cc, and flexural strength (with grain) of 2100 lbs/in² (National Carbon Co., New York, N. Y.). The energy transfer for this type of carbon concentrator is considerably more than for the quartz concentrators described in previous sections.

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Fig. 11 Photograph of the 700 watt ultrasonic generator and casting unit

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(a)

(b)

Fig. 12 PbTe ingot directionally solidified in graphite crucible at 1" per hour.
a) longitudinal section, etched,
b) cross-section, etched.

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Fig. 13 Seebeck-voltage as a function of temperature for a directionally solidified PbTe ingot with 0.01 mole pct PbI_2 (unagitated)

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Fig. 14 Seebeck-voltage as a function of temperature for a directionally solidified PbTe ingot with 0.03 mole pct PbI_2 (unagitated): (a) first section of ingot to solidify, (b) last section to solidify

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Fig. 15 Resistivity profile along the length of the ingot, (Run #5, $\text{PbTe} - .03\% \text{PbI}_2$).

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In practice, a carbon crucible 1-1/2" OD, 1" ID, and 3" long is fitted in the top of the carbon concentrator and is charged with approximately 100 grams of precast thermoelectric material. Then the carbon cap is fitted on top of the crucible, and the quartz bell jar is placed in position on a flat rubber gasket and is tightened down to the water jacket assembly. The quartz chamber is alternately evacuated and flushed a number of times prior to establishing in the quartz chamber a slight positive pressure of prepurified Argon. The furnace is lowered to a predetermined position and it encloses the charge and a portion of the concentrator. The furnace is turned on to reach a predetermined temperature. The temperature of the interface (bottom of the melt) is read and recorded during the entire ultrasonic casting run. The charge is normally kept under a fixed temperature (50°C superheat) for 20 minutes before the ultrasonic generator is turned on. The generator, tuned to resonant frequency, agitates the melt in order to mix and homogenize the charge prior to solidification. It has been found that for the same amount of charge the n-type material requires 25% higher energy density to produce grain refinement compared to p-type material. This effect is thought to be related to the difference in sound velocity in the two types of material. After 2 minutes at the resonant frequency, the charge is automatically withdrawn from the furnace at a rate of between 1/2 - 1"/hr., while resonance is maintained during the entire solidification process by manually varying the frequency. The frequency is continuously monitored with a digital frequency readout, Berkeley Scientific Corp., Model 554.

A series of experiments were conducted to relate the effect of casting variables (initial melt temperature, input energy density, and rate of solidification) on the extent of grain refinement. Figure 16 shows the extent of grain refinement as the ultrasonic power is successively increased.

In one experiment commercially available cold-pressed and sintered, n-type PbTe elements were used as charge and ultrasonically agitated. All other experimental variables were kept constant. After agitation, a large quantity of oxides and other impurity

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Fig. 16 The effect of a) 60%, b) 75%, and c) 100% nominal power setting on grain size (1 inch diameter ingot).

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particles were found at the top surface of the ingot (Fig. 17). This was in contrast to the ingots prepared from our precast charge which were prepared directly from the high purity elements. In the latter case, the entire ingot shows a clean metallic luster.

In the course of ultrasonic casting experiments, it was noted that a more uniform and finer grain structure could be obtained if directional solidification were accomplished by gradual change in the temperature profile imposed on the entire charge instead of by withdrawal of the charge from a constant temperature zone. Since the carbon concentrator basically constitutes a heat sink for the molten charge during solidification, directional solidification initially takes place from the bottom of the crucible. To date the best results have been obtained by utilizing a relatively fast rate of cooling ($10-15^{\circ}\text{C}/\text{minute}$) under ultrasonic agitation.

This type of ultrasonic casting technique requires the charge to be positioned inside the furnace and the furnace temperature to be automatically programmed down while agitation is in progress. The start and completion of the charge solidification are detected by sudden changes in amplitude. Figure 18 shows two cross-sectional views of a p-type ingot grain refined by the "stationary charge-temperature programming" technique.

This technique represents an important step towards the scaling-up of the casting process since it decreases considerably both the complexity of the equipment and process operation and the time necessary for solidification.

F. Design and Construction of 2000 Watt Ultrasonic Casting Unit

A new 2000 watt ultrasonic generator was designed and made operational during this period. A photograph of the entire system is shown in Fig. 19. The generator specifications are given below:

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Fig. 17 Top surface of an ingot ultrasonically prepared from a charge of commercially available n-type PbTe thermoelectric elements.

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(a)

(b)

Fig. 18 Photomicrograph of a p-type ingot (1" in diameter) ultrasonically cast by the "stationary charge-temperature programming" technique.

- a) cross-section view of the ingot (etched) 5X.
- b) longitudinal section, (etched, same magnification).

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Fig. 19 Photograph of the 2000 watt ultrasonic generator, casting equipment, and controls.

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Line input 220 volts, 60 cps, 3 phase

Power output 2000 watts (100% duty cycle) into 15 ohm inductive load, 0-25 amps DC adjustable for magnetic polarization.

Frequency output 20 K cps (nominal); manually adjustable frequency range: 19.5 K cps to 21.5 K cps.

Output impedance is variable through a tapped transformer for 9, 12 and 15 ohms.

The specifications of the matching magnetostrictive transducer are as follows:

Input power 2000 watts at 100% duty cycle, input impedance 15 ohms (nominal)

Operating frequency 20 K cps (nominal)

Vibration amplitude 0.0011 inches peak to peak (maximum)

Water cooled 1/2 gallon per minute at 15 psi.

The carbon-monel concentrator being used with this generator is an improved version of the previously designed concentrator now being used with the 700 watt generator. The monel section of the concentrator is 2.5" in diameter and 3.27" long (corresponding to half a wave length at 19.2 KC). The monel base section is followed by a tapered carbon section which is reduced to 1" diameter cross section (tapered section 1/2 wavelength). The third section of the carbon concentrator consists of a one wavelength straight 1" diameter rod. The last half wavelength of the concentrator is part tapered and part straight, terminating at a 2" diameter radiating surface.

The magnetostrictive transducer and concentrator are mounted on a vertical frame. The vertical frame also includes a movable carriage which supports a 3.5 KW vertical resistance furnace. The furnace is 3.5" ID, 24" long, and is controlled by a Honeywell set-point temperature controller, Model 6870781. This concentrator specifically designed for the 2000 watt generator, has the capability of ultrasonically casting ingots 2- 3/4" in diameter and up to 2" long.

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Preliminary tests have shown the system to be both efficient and reliable. Optimization of the casting variables such as the temperature, rate of solidification, energy input, etc., is presently being carried out.

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IV. PbTe and PbTe BASED THERMOELECTRIC MATERIAL

A. Thermoelectric Material Selection

PbTe is an intermetallic compound crystallizing in the rock salt structure (face centered cubic) and melting at 922°C. It is known that PbTe has a range of stoichiometry -- that is, excess Pb or Te can be incorporated into the lattice along with the formation of the appropriate vacancies. In the PbTe compound lead behaves as a divalent ion; thus, PbTe could be classed as a group II-VI semiconductor. The solubility of excess Pb or Te increases with temperature; however, the limit is only a few hundredths of a percent, which is equivalent to 10^{17} atoms/cm³. In order to increase the concentration of donors or acceptors above this level, doping techniques can be used.

In PbTe the substituted impurity can be placed in either the anion or cation lattice. The donor dopants may be incorporated in the form of PbI₂, PbBr₂, Bi₂Te₃, Cr₂Te₃, etc. Common acceptor dopants are Na₂Te and K₂Te.

The role of substitutional impurities in such semiconducting elements as silicon and germanium has been explained by a number of investigators. In the case of semiconducting compounds, the question of substitution by impurities becomes more complex since two types of lattice sites exist where substitutions can occur. Also, an excess of one component must be considered as an impurity; one example of this is shown in the following: The addition of lead chloride, iodide, or bromide to pure PbTe which has p-type conduction at the stoichiometric composition does not alter the type unless sufficient excess lead is also added⁽¹³⁾.

Optimally-doped PbTe, because of its low thermal conductivity, high Seebeck coefficient, and high electrical conductivity, has been used extensively as the active element in thermoelectric generators. However, because of the propensity for doping elements in PbTe to segregate on normal freezing and also of the inevitable columnar-structure formation on normal freezing, thus far all commercially available PbTe thermoelectric elements have been prepared by cold pressing and sintering and by extrusion of powder charges. The mechanical instability of the material

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prepared by the latter two techniques has in many cases complicated the mechanical design of thermoelectric generators.

Also, it is well known that standard solidification techniques using stoichiometric melts will result in a solid with non-stoichiometric composition^(14, 15). However, homogeneous alloys of stoichiometric PbTe can be prepared by solidification of a liquid of 0.41 at. percent excess lead using a technique in which the liquid composition is held constant⁽¹⁶⁾.

Casting under ultrasonic agitation appears to constitute a condition in which the entire melt is constantly being stirred and abrupt nucleation takes place. Thus, the liquid composition is also invariant during solidification.

For n-type PbTe, carrier concentrations of about $3 \times 10^{17}/\text{cm}^3$ can be induced by introducing excess lead into stoichiometric PbTe. However, in order to obtain a high figure of merit, PbTe carrier densities about an order of magnitude higher are required. These excess carrier densities can be attained by further addition of impurity doping. Based on the analysis of resistivity, thermal conductivity, and Seebeck coefficient as a function of temperature for a range of doping concentrations, it is apparent that 0.01 to 0.10 mole % PbI_2 produces elements with the highest average figure of merit at temperatures up to 500°C . In our study, for n-type material 0.4 at. % excess Pb + 0.03 mole % PbI_2 has been found to give satisfactory electrical properties. However, it is expected that a slightly higher concentration of PbI_2 doping should prove to be more desirable in order to obtain the maximum efficiency at higher temperatures.

In the case of p-type thermoelectric material, the PbTe-SnTe system has been confirmed to have a higher figure of merit than p-type doped PbTe compound, since these pseudo-binary solid solutions generally have a more favorable ratio of electrical conductivity to thermal conductivity than either of the components⁽¹⁷⁾. In our study thus far the $(\text{Pb}_{50}\text{Te}_{50})_{0.7}(\text{Sn}_{49.2}\text{Te}_{50.8})_{0.3}$ composition has shown near satisfactory electrical properties. It is conceivable that further optimization of this ratio would yield a higher figure of merit, particularly at higher temperatures.

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B. Preparation of Homogeneous Material for Ultrasonic Casting

In order to obtain large quantities of well-defined thermoelectric charge material for the ultrasonic casting, it was essential to develop a procedure for the preparation of charge material with homogeneous and reproducible electrical properties. This is particularly important since it has been experienced that the magnitude of dopant segregation depends critically upon the degree of superheat, the temperature gradient, and the rate of cooling.

A number of experiments were conducted to ascertain the effect of casting variables on the bulk homogeneity of the cast material. Figure 20 shows the voltage output as a function of temperature for the two end sections of a casting when the melt is cooled at the rate of 16°C per minute or slower. It is seen (Fig. 20) that the distribution of carriers is not uniform throughout the casting. It was determined that by agitating and quenching the melt to room temperature from 1000°C , a uniform carrier distribution could be maintained in the bulk of the casting. Figure 21 shows the voltage output as a function of temperature for the two end sections of an n-type casting and Fig. 22, for p-type. It is to be noted that this type of casting exhibits a uniform conductivity throughout its bulk and that the voltage output as a function of temperature is independent of the direction of applied thermal gradient.

Based on a number of casting experiments, it was ascertained that chemical homogeneity could be retained in the cast ingot by agitating and quenching a melt with $40 - 60^{\circ}\text{C}$ superheat to room temperature. N-type PbTe with approximately 0.4 at % excess Pb + 0.03 mole % PbI_2 and p-type material $(\text{PbTe})_{.7}(\text{SnTe})_{.3}$, where SnTe is non-stoichiometric (see above), have been found to give satisfactory electrical properties after quench casting. In practice, the appropriate quantities of high-purity (99.999^{+}) elemental constituents and dopant are weighed with an accuracy of ± 0.1 mg, placed in a 2.5 cm diameter, clear quartz ampoule, evacuated to 10^{-6} mm-Hg, and sealed. The ampoule is then placed in a 3 kw resistance furnace with an 8" long flat temperature zone at 1000°C . The melt, while in the furnace, is kept under agitation for 20 minutes, taken out, and quenched in water at room temperature. The cast charge is kept in the sealed quartz ampoule until it is used.

Fig. 20 Voltage output as a function of temperature for n-type cast-charge cooled to room temperature at a rate of $16^{\circ}\text{C}/\text{minute}$: (a) top section of casting, (b) bottom section

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Fig. 21 Seebeck voltage as a function of temperature for n-type cast-charge quenched to room temperature: (a) bottom section of casting, (b) top section (superimposed)

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Fig. 22 Seebeck voltage as a function of temperature for p-type cast-charge quenched to room temperature: (a) section from bottom of the casting, (b) section from top

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V. EVALUATION OF THERMOELECTRIC PROPERTIES

A. Test Equipment

Figure 23 shows a schematic diagram of the fixture used for room temperature resistivity measurements and the block diagram of the test equipment arrangement. In this fixture one of the voltage probes is movable and is positioned by a micrometer vernier for incremental readings. Pure indium plates are positioned between the thermoelement and the current contact probes to minimize the contact resistance. A constant current is passed through the material at 400 cps and the voltmeter tuned to this frequency measures the IR drop across the voltage probes. In each measurement the potential drop is compared with the potential drop across a known precision resistor. This type of arrangement tends to nullify the effect of nonohmic contacts and rectification in the measuring circuit.

Figure 24 shows the schematic diagram of a lava-fixture used for measurements of resistivity as a function of temperature. In practice, the room temperature resistance of the element is measured as above and then the element is placed in the lava-fixture, and the current contacts are carefully positioned (on the two end faces of the element) to obtain the same value for the total, room temperature resistance. This technique minimizes the effect of contact resistance during the resistivity vs. temperature measurements. The same electronic test equipment is used for room temperature and high temperature resistivity measurements.

The resistivity as a function of temperature is measured on both heating and cooling. It has been found that for a specific element the ratio of resistivity at 500°C to resistivity at room temperature is nearly constant for a range of starting-room temperature values. A range of room temperature resistivities on one sample can be obtained by varying the contact pressure between the current electrodes and the element. For this reason, utmost care is taken in each measurement to minimize the effect of contact resistance prior to the resistivity vs. temperature measurement.

Figure 25 is a schematic representation of the Seebeck-voltage measuring equipment. The hot and cold junction temperatures are monitored with Chromel-Alumel thermocouples. The Alumel legs of the two thermocouples provide the voltage output leads. The Seebeck-voltage output as a function of hot junction temperature is recorded on an x-y recorder during the measurement. Since $\int_0^T \frac{dV}{dT}$ is a closed integral, it is mathematically

Fig. 23 (a) Schematic diagram of the fixture used for room temperature resistivity measurements
(b) Block diagram of test equipment used for resistivity measurements

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(a) TOP VIEW

(b) CROSS-SECTIONAL VIEW

Fig. 24 Schematic diagram of the lava-fixture used for resistivity vs. temperature measurements

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Fig. 25 Schematic drawing of the Seebeck voltage measuring equipment

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Description of the Parts

Part No.

1	Hot stage
2	Hot stage insulation (Top)
3	Hot stage insulation (Bottom)
4	Heat sink
5A	Hot stage bracket (Top)
5B	Hot stage bracket (Bottom)
6	Thermocouple lead hose
7	Bell-jar clamp ring
8	Bell jar
9	Bell jar clamp bolt
10	Hot stage T. C. spring
11	Thermocouple spring insulator
12	Spring bolt
13	Retainer nut
14	Collar
15	Cold T. C. spring
16	Compression rod bracket
17	Compression rod
18	Spring retainer
19	Cap screw
20	Hot stage
21	Bell jar gasket
22	1/ 4" NPT to 1/ 4" Ferrule sitting

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correct merely to determine the slope of the Seebeck voltage-temperature function at a specific temperature to obtain the Seebeck coefficient at each temperature. The determination of the slope is made using a Derivimeter. Care must be taken to refer the Seebeck voltage to a specific standard state. It has become somewhat general practice to refer all Seebeck-voltage information to Cu. The direct temperature gradient allows the determination of the Seebeck voltage and Seebeck coefficient as a function of temperature for a specific thermoelectric element in less than 15 minutes. This makes it a much more useful measurement technique than the small temperature difference approach.

B. Homogeneity of Ultrasonically Prepared Elements

In order to assess the homogeneity of the ultrasonically prepared elements, the room temperature resistance of a number of p- and n-type elements were measured as a function of distance. Figure 26 shows a typical plot of room temperature resistance as a function of distance for an ultrasonically prepared p-type element. It is to be noted that the individual measurements do not deviate significantly from the average value.

Figure 27 is a plot of resistivity as a function of temperature as measured on opposite sides of an ultrasonically prepared p-type element. The distance between voltage probes was also varied during these measurements. Again note that (considering the initial variation of resistivity values at room temperature) the individual measurements do not deviate more than a few percent during the resistivity vs. temperature measurements. This is within the experimentally determined error for these measurements.

C. Thermoelectric Property Measurements

The optimum performance characteristics of a thermoelectric device can be predicted theoretically if the figure of merit of the material is known. The figure of merit is defined by the relationship:

$$Z = \frac{\alpha^2}{K\rho}$$

where α = Seebeck coefficient, volt/K°; ρ = specific electrical resistivity, ohm-cm; and K = specific thermal conductivity, watts cm⁻¹deg⁻¹ (where the quantities described represent the average values over the appropriate temperature range).

Fig. 26 Typical plot of room temperature resistance as a function of distance along the length of an ultrasonically prepared thermoelement

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1. Resistivity as a Function of Temperature

The resistivity as a function of temperature for n- and p-type material is given in Figs. 28 and 29 for commercially available cold-pressed and sintered elements and ultrasonically prepared material. The ultrasonically prepared n-type PbTe contained 0.03 mole percent PbI_2 and 0.4 at % excess lead. The ultrasonically prepared p-type material consisted of $(\text{PbTe})_{0.7}(\text{SnTe})_{0.3}$ molar composition, with consideration being made for the deviation of SnTe from stoichiometry, $(\text{Sn}_{49.2}\text{Te}_{50.8})$.

2. Seebeck-Coefficient as a Function of Temperature*

It should be noted that Chromel-Alumel thermocouples are used in all our temperature measurements, and the two Alumel leads from the cold and hot junction thermocouples are used as the Seebeck-voltage output leads. In order to compare the electrical properties of ultrasonically prepared material and the cold-pressed and sintered elements, the Seebeck-voltage values obtained on our material is extrapolated from Alumel reference to copper reference. (The voltage output of the 3-M elements are measured with reference to copper.) For the sake of clarity, the extrapolation procedure is described in the following paragraph.

In order to convert the Seebeck-voltage, and Seebeck coefficient, from Alumel to copper reference the thermoelectric potential of Alumel relative to copper must be considered (ref. Thermoelectricity, Robert R. Heikes and Roland W. Ure, Jr., Interscience Publication, New York, 1961). The following table lists the values of Seebeck-voltage potential for Alumel relative to copper for the 0° to 500°C temperature range. In order to convert the Seebeck-voltage values measured with Alumel to the copper reference, the correction term is added in case of n-type material and it is subtracted in the case of p-type material.

* Previously reported values (Second Quarterly Report) of Seebeck-voltage, Seebeck-coefficient, and electrical efficiency were based on Alumel as reference.

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Fig. 28 Resistivity as a function of temperature for (a) ultrasonically prepared n-type thermoelectric elements and for (b) cold pressed and sintered n-type elements

Fig. 29 Resistivity as a function of temperature for (a) ultrasonically prepared p-type thermoelements and for (b) cold-pressed and sintered p-type thermoelements.

Table I

Correction Factors for Reference from Alumel to Copper

<u>Temperature</u>	<u>Conversion Term (mv)</u>
50	1.02
100	2.06
150	2.98
200	3.92
250	5.14
300	6.42
350	7.94
400	9.52
450	11.30
500	13.15

In Figs. 28 through 33 corresponding values of commercially available cold-pressed and sintered elements (from 3 M Company) are superimposed for the sake of comparison. The values of the resistivity and Seebeck-coefficient for the 3 M thermoelectric material are obtained directly from 3 M's data sheet (received in May 1966)*. The values of the Seebeck-voltage for the 3 M thermoelectric material are not given in their data sheet. The values of Seebeck-coefficient of the ultrasonically prepared elements were determined from the slope of the voltage vs. temperature curve at the temperature in question.

Figure 30 shows the Seebeck-coefficient for ultrasonically prepared, and cold-pressed and sintered n-type thermoelectric elements. It is to be noted that the ultrasonically prepared n-type material exhibits a higher value of Seebeck-coefficient than that of cold-pressed and sintered elements for all temperatures.

- * The electrical properties of the 3 M material reported previously (Second Quarterly Report) were based on measurements made on a single purchased lot. Since the properties in any lot may vary as much as 10% from the 3 M supplied data, the previously reported values are not considered sufficiently reliable for proper comparison.

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Fig. 30 Seebeck coefficient as a function of temperature for (a) ultrasonically prepared n-type thermoelectric elements and for (b) cold-pressed and sintered n-type elements.

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Figure 31 shows the Seebeck coefficient for ultrasonically prepared and cold-pressed and sintered p-type thermoelectric elements. It is to be noted that the ultrasonically prepared p-type material exhibits a comparable Seebeck coefficient up to 400°C.

3. Electrical Efficiency (α^2/ρ)

The average values of α^2/ρ as a function of temperature are given in Fig. 32 for n-type and Fig. 33 for p-type material. It is to be noted that the values of α^2/ρ are higher for ultrasonically prepared n-type elements than for those of cold-pressed and sintered elements, and comparable in the case of p-type material. Further work will be carried out on the p-type composition in order to raise the material efficiency above 450°C. Work on doping with Ag showed some promise. Initial Ag doping experiments utilizing exact stoichiometric $\text{Pb}_{0.7}\text{Sn}_{0.3}\text{Te}$ produced material with an excessively high resistivity and an improved Seebeck coefficient. Recent work, however, employing excess Te to fill the Te vacancy sites has yielded material with lower electrical resistivity. Further detailed work on the optimization of composition (variation in Pb and Sn composition) and Ag doping is being contemplated.

4. Ultrasonic Casting of 3M's Thermoelectric Powder

A number of ultrasonically cast n- and p-type ingots were produced from charge of 3M's thermoelectric powder. Figures 34 and 36 show the resistivity and Seebeck voltage as a function of temperature for ultrasonically cast material from charge of 3M's (TEGS - 3P) thermoelectric powder. Figures 35 and 37 show the resistivity and Seebeck voltage as a function of temperature for ultrasonically cast material from charge of 3M's (TEGS - 3N) thermoelectric powder. For the sake of comparison, the corresponding values (given by 3M's property sheet) for the thermoelectric elements TEGS - 3P and 3N are superimposed in Figs. 34 through 37. It is to be noted that (a) the Seebeck voltage of the ultrasonically cast material is in fair agreement with the values given by 3M's property sheet (maximum deviation - 5.5%) and (b) the resistivities at 500°C are within 10% deviation.

The ingots cast ultrasonically from 3M's thermoelectric powder exhibited equiax-grain structure comparable to the ingots cast from charge of castings made from the elemental constituent. Figure 38 shows a photomicrograph (50X) of the ultrasonically prepared material from 3M's (TEGS -

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Fig. 31 Seebeck coefficient as a function of temperature for (a) ultrasonically prepared p-type thermoelectric elements and for (b) cold-pressed and sintered p-type elements.

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Fig. 32

Electrical efficiency (α^2/ρ) as a function of temperature for (a) ultrasonically prepared n-type thermoelements and for (b) cold-pressed and sintered n-type thermoelements.

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Fig. 33 Electrical efficiency (α^2/ρ) as a function of temperature for (a) ultrasonically prepared p-type thermoelements and for (b) cold-pressed and sintered p-type thermoelements.

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Fig. 36

Seebeck voltage as a function of temperature
(a) 3M's cold pressed and sintered p-type elements
(TEGS-3p property sheet)
(b) Ultrasonically cast material from charge of 3M's
p-type thermoelectric powder

Fig. 37 Seebeck voltage as a function of temperature
(a) 3M's cold pressed and sintered n-type elements (TEGS-3n property)
(b) Ultrasonically cast material from charge of 3M's n-type thermoelectric powder

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Fig. 38 Photomicrograph of ultrasonically cast material from charge of 3M's n-type thermoelectric powder (TEGS-3n) 50X

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3N) thermoelectric powder. The second phase inclusions are noted in the structure. The constitution of the second phase leads to the conclusion that they may be metallic lead. The large amount of the second phase suggests that an excess of one of the matrix constituents has been introduced to adjust the thermoelectric properties to desired levels.

5. Isothermal Life-Test Procedure and Results

A 2 kw resistance furnace 12" O.D., 2 1/2" I.D., 30" long was constructed for isothermal life testing of the thermoelectric elements and bonded thermoelements. The furnace has been designed with a 6" long isothermal section (500 - 600°C) which could accommodate up to twenty bonded thermoelements. The furnace is controlled by a Wheelco temperature controller Model 204.

Seebeck voltage and resistivity as a function of temperature were measured initially on ten ultrasonically prepared thermoelectric elements. These samples were sealed individually in a sealed quartz ampoule under a pressure of 0.5 atm of Argon. The quartz ampoules were positioned in the furnace, at the 500°C temperature zone. The samples were taken out after 500 and 1000 hrs at temperature and Seebeck voltage and resistivity vs. temperature was again measured. No significant change could be detected in either measurements after 500 and 1000 hrs at 500°C.

D. Mechanical Properties

Figures 39 and 40 show the stress as a function of strain for cold-pressed and sintered material and ultrasonically prepared material. The compressive fracture strengths were measured using 0.25" diameter by 0.25" long cylindrical elements. Average maximum fracture strengths for cold-pressed and sintered n- and p-type PbTe were 12,800 psi with a total deformation of 12%, and 12,550 psi with 2.5% deformation, respectively.

These results are in good agreement with measurements made previously (under Contract No. 65-861015, Bureau of Ships, Department of the Navy): n-type 14,500 psi at 13%; p-type 11,550 psi at 3%. The values published by the manufacturer are also in general agreement with our findings. The compressive fracture strength of the ultrasonically prepared materials were found to be 19,200 psi at 30% deformation and 16,400 psi at 34% for n- and p-type material, respectively.

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The cold-pressed and sintered material fractured by what appeared to be complete collapse of particle cohesion. The extremely low cleavage strength exhibited by the cold-pressed and sintered material is obviously a consequence of the excessive number of pores and foreign particles found in this structure. In the case of fine-grained material prepared by the ultrasonic technique, fracture occurs by a transcrystalline cleavage mechanism. The increase in cleavage strength with decreasing grain size had been explained^(18, 19) simply in terms of a mechanism which involves the propagation of initially present microcracks through the polycrystalline aggregate. Obviously, the finer the grain size, the greater the resistance to transcrystalline microcrack propagation along the energetically favorable cleavage plane. Figures 41 and 42 show the structures of ultrasonically prepared and cold-pressed and sintered materials.

The improved workability and strength of ultrasonically prepared material was demonstrated by cutting ingots into rectangular blocks on a diamond saw and further shaping the blocks into cylindrical elements 1/4" in diameter by 1/2" long, on a lathe using an ordinary carbon-steel tool. Figure 43 shows a uniformly fine-grained ultrasonically prepared ingot and several rectangular blocks machined from the ingot.

The fine-grained material can also be drilled and threaded by conventional techniques. A number of thermoelectric elements 0.5" in diameter and up to 3/4" long were cut from ultrasonically prepared ingots. Figure 44 shows a group of 0.5" diameter thermoelements machined from ultrasonically grain refined ingots. Although the elements were cut by use of a coarse tooth hole saw, the variation in diameter for each element and between elements was determined to be less than ± 0.0005 ". The capability of maintaining such close dimensional tolerances should be most useful in the preparation of elements for sophisticated thermoelectric modules. The smaller diameter ($< 3/8$ ") cylindrical elements have been prepared by use of a fine diamond core-drill. Currently, the feasibility of continuous batch shaping of ultrasonically prepared elements by centerless grinding is being evaluated.

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(a)

(b)

Fig. 41 Photomicrographs of ultrasonically prepared thermoelectric material:
a) p-type, and b) n-type 50X.

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(a)

(b)

Fig. 42 Photomicrographs of cold-pressed and sintered thermoelectric material:

a) p-type, and b) n-type 50X.

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Fig. 43 Photomicrographs of (a) a fine grained ultrasonically prepared ingot, and (b) several rectangular blocks machined from the ingot.

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Fig. 44 Photomicrograph of seven 0.5" diameter thermoelements machined from ultrasonically grain refined ingots.

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E. Outline of Total Evaluation Procedure

The following chart outlines the successive processes and measurements required in evaluation of bulk material and bonded elements.

a. Procedure Before Bonding

<u>Starting Form of Material</u>	<u>Process</u>	<u>Measurement</u>	<u>Information to be Obtained</u>
ultrasonic ingot	1) Grind top, bottom, and one side of the ingot; polish and etch.		Evaluate physical structure and extent of grain refinement.
ultrasonic ingot	2) Cut ingot into blocks of 5/16" x 5/16" cross section and greatest lengths. Select and identify 4 blocks for further processing and measurement.	a) Seebeck voltage vs. temp. (2 samples) b) Room temp. resistivity (2 samples) c) Resistivity vs. temp. (2 samples)	a), b), c): Determine values and consistency of the bulk material thermoelectric properties.
5/16" x 5/16" blocks (ultrasonic)	3) Grind 1/4" diameter elements.	a) Room temp. resistivity with standard voltage probe spacing b) Room temp. resistance with largest voltage probe spacing Specify element length c) Resistance vs. temp. with largest voltage probe spacing	a) Compare to resistivity measured on blocks. b) Determine total element resistance at room temperature. c) Determine total element resistance vs. temp. prior to bonding. Calculate resistivity.
1/16" diameter ultrasonic elements	4) No further preparation	Stress-strain test in compression-to-fracture (2 unmeasured samples)	Determine yield point, ultimate strength, and percent deformation.

b. Procedure After Bonding

<u>Starting Form of Material</u>	<u>Process</u>	<u>Measurement</u>	<u>Information to be Obtained</u>
$\frac{1}{4}$ " diameter bonded ultrasonic elements	5) No treatment	a) Seebeck voltage vs. temp. b) Room temp. contact resistance of each bond c) Determine total resistance of the bonded element (voltage probes on the electrodes) d) Resistance vs. temp. for the bonded elements (voltage probes on the electrodes) e) Resistivity vs. temp. of the element (voltage probes on the element with standard spacing)	a) Compare with unbonded element. b) Evaluate individual contact resistance. c) Compare with the total resistance of the unbonded element; item (b) should constitute the difference. d) Determine contact resistance vs. temp. e) Compare to resistivity before bonding and of bulk material.
$\frac{1}{4}$ " diameter bonded ultrasonic elements	6) a) Cycle 10-15 times between room temp. and 500°C b) Hold in temp. gradient (room temp to 500°C) for extended period.	a) Seebeck voltage vs. temp. and resistivity vs. temp. after cycling. b) Seebeck voltage and resistivity while elements are under test.	a) Determine effect of temp. cycling on Seebeck voltage and resistivity. b) Determine effect of long term temp. -gradient on Seebeck voltage and resistivity of bonded elements.
$\frac{1}{4}$ " diameter bonded ultrasonic elements	7) No treatment.	Tensile strength test for bonds-to-fracture.	Determine strength of bond between element and electrodes

VI. BONDING OF ULTRASONICALLY PREPARED THERMOELECTRIC ELEMENTS TO IRON ELECTRODES

A. Bonding of Metal Electrodes to Thermoelectric Elements

One of the major limiting factors in the efficiency of thermoelectric generators employing PbTe alloys is the high contact resistance at the thermoelement-metal electrode interface. The thermoelement-metal contact should not only have a low resistance but it should also exhibit long term stability under wide ranges of environmental conditions such as high temperatures, rapid temperature fluctuations, and severe vibration. The following properties are desirable in bonding elements to metal electrodes:

1. The electrodes must provide the principal mechanical support for the thermoelements.
2. The thermoelement and electrodes should possess reasonable ductility and/or matching thermal expansion coefficients to avoid mechanical stress leading to fracture.
3. The electrode and thermoelement should be chemically compatible under operating conditions.
4. The electrodes must not introduce any significant resistive component compared with the total resistance of the element.
5. The junction should have a high thermal conductivity and low electrical resistance coupled with good mechanical strength.

Our work on bonding was initiated with full consideration of the present state of the art. Our aim was to develop the most appropriate system and technique for the fabrication of bonded, PbTe-based thermoelements. The initial work was based on the results of

investigations conducted in this laboratory on metallurgical bonding of PbTe systems*. Satisfactory low resistance bonds were produced by interdiffusion of n-type PbTe and an iron (Armco) electrode below the Fe-PbTe eutectic temperature (874°C) and by braze bonding with SnTe of p-type PbTe base alloys to iron electrodes.

It should be noted that the major portion of the previous study was conducted on commercially available cold-pressed and sintered thermoelectric elements. In the present study ultrasonically prepared thermoelectric elements were used exclusively.

B. Design and Construction of the Bonding Equipment

A 2.5 kw resistance furnace with a 6" constant temperature zone was designed specifically for the bonding study. A Leeds and Northrup D-C null detector temperature controller model 9834-2 was used in conjunction with the resistance furnace. Figure 45 shows the graphite assembly designed for constant pressure loading of the elements during bonding. Dead weight and axial loading was employed. Separate graphite assemblies were used for the two types of material (n and p) to avoid contamination of the elements during bonding. The graphite fixture was cleaned prior to each bonding run by heating to 1000°C for one hour.

C. Outline of the Preparation Procedures Prior to Bonding

The following procedure was carefully followed in the brazing of Fe electrodes to the thermoelectric elements:

1. Preparation of Elements Prior to Bonding

a. The ultrasonically prepared ingots were mounted on ceramic plates and diced to $5/16 \times 5/16 \times 1/2$ " individual blocks.

* M. Weinstein and A.I. Mlavsky, Rev. Sci. Inst. 33, 1119 (1962).

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Fig. 45 Schematic diagram of the graphite assembly designed for constant pressure loading of the elements during bonding

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b. Blocks were removed from the ceramic plate and cleaned in n-propanol to remove wax (Dennison 14A) used to fasten ingot to block

c. Blocks were then ground individually into 1/4" diameter, 1/2" long elements.

d. Element faces were lapped flat and parallel using a fixture designed for this purpose. The faces were finished to 1800 grit Al_2O_3 lap.

e. Elements were degreased in boiling n-propanol, washed in Alconox, and rinsed ultrasonically in de-ionized water.

f. Prepared elements were then stored in methanol until immediately prior to loading into the bonding fixture.

2. Preparation of Electrodes Prior to Bonding

a. Fe electrodes were ground flat on a glass plate to 5 μ Al_2O_3 by lapping successively with progressively finer alumina powders.

b. Electrodes were washed and rinsed ultrasonically in methanol to remove any traces of lapping compound.

c. Prepared electrodes were stored in methanol until immediately prior to loading into the carbon fixture.

3. Preparation of SnTe-brazed Electrodes

a. SnTe braze was prepared from high purity elements in a sealed, evacuated, quartz ampoule.

b. The cast SnTe was carefully broken (by mortar and pestle) into small chunks.

c. Iron electrodes were positioned in the carbon fixture and approximately 1 gr of SnTe was positioned on the surface of each electrode.

d. The loaded carbon fixture was positioned in a quartz tube inside the resistance furnace.

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- e. The quartz tube was evacuated and flushed three times and finally held under vacuum.
- f. The furnace was heated to approximately 150°C; then argon was introduced into the system and maintained at a slight positive pressure.
- g. Temperature of the furnace was raised to 820°C, and it is held for 10 minutes.
- h. The furnace was cooled gradually to room temperature at a rate of about 3-5°C per minute to avoid thermal stress at the interface.
- i. The SnTe brazed electrodes were ground and lapped, leaving a layer of approximately 4 mils of SnTe braze on the Fe electrodes.
- j. Prepared electrodes were cleaned and stored in methanol until immediately prior to use.

D. Bonding Procedures and Evaluation of Bonded Elements

1. SnTe-Braze Bonding of Thermoelectric Elements to Iron Electrodes

The braze bonding of p- and n-type elements was accomplished by first preparing the elements and electrodes as outlined in the previous section, followed by braze-bonding in a carbon fixture of the type shown in Fig. 45. Dead weight-axial loading of 50 gr/cm² at 820°C for 10 minutes was employed. A typical curve of resistivity as a function of temperature for a p-type braze bonded thermoelement is shown in Fig. 46. Curve (a) represents the resistivity as a function of temperature measured on the element prior to bonding. Curve (b) represents the resistivity values measured on the same element after braze-bonding. Curve (c) shows the total resistivity (including the contact resistance) of the braze-bonded element.

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It is to be noted that the resistivity of ultrasonically prepared p-type thermoelements remains virtually unchanged after SnTe-braze bonding, and thus the contact resistance is very small relative to the resistance of the element.

The following procedure was used to obtain accurate, room-temperature contact resistance measurements with bonded elements. Voltage probe (1) was positioned on one of the electrodes; the other probe (2) was positioned on the second electrode. Resistance measurements were made while moving probe (2) toward probe (1). The contact resistance was determined from the difference in resistance measured when the movable probe traversed the contact. The same procedure was then repeated with probe (2) as the stationary probe.

The measured room-temperature contact resistances on braze-bonded contacts ranged from 50 to 100 $\mu\Omega$. If these values are expressed in terms of cross-sectional area of the contact (.316 cm²), the specific contact resistivity is 16 to 32 $\mu\Omega$ -cm². The contact resistance contributed approximately 3% of the total thermoelement resistance (for an element 1.2 cm long x 0.63 cm diameter). The effect of braze-bonding on the Seebeck voltage output is shown in Fig. 47. The slight decrease in output (10%) is not associated with deterioration but is merely an effect produced by the decreased thermal gradient across the element.

Three p-type braze-bonded thermoelectric elements are shown in Fig. 48.

2. Diffusion Bonding of Thermoelectric Elements to Iron Electrodes

Although the results obtained on the braze bonding of p-type thermoelements were considered satisfactory, further attempts were made to evaluate the possibility of direct diffusion bonding of Fe to both n- and p-type thermoelements.

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Fig. 47

Seebeck voltage as a function of temperature
for (a) p-type element prior to bonding,
(b) same element after braze bonding.

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Fig. 48 Photomicrograph of three p-type braze-bonded thermoelectric elements.

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A direct diffusion bond is preferable because it eliminates any possible effect by SnTe on the thermoelectric material (long term effects on brazed contacts have not been thoroughly evaluated). Diffusion bonding is also simpler than brazing.

Over fifty diffusion bonding experiments were conducted using ultrasonically prepared n- and p-type elements. Axial dead-weight loading of 70 to 180 gr/cm² was used. The effect of time-temperature cycles on the bond properties was also studied. P-type thermoelements were diffusion-bonded to iron electrodes at 845°C for 45 minutes; N-type elements were diffusion-bonded at 855°C for 30 minutes.

Figures 49 and 50 show typical plots of Seebeck voltage as a function of temperature for p- and n-type elements, prior to and after diffusion bonding. The slight (~ 7 mV) decrease in Seebeck voltage of the bonded elements is caused by a decrease of the effective temperature gradient across the thermoelectric material caused by the introduction of the iron electrodes. The applied temperature gradient (30 to 500°C) is determined from the temperatures which are measured at the outer surfaces of the iron. Since the iron electrodes themselves support a thermal gradient, the actual temperature gradient across the thermoelectric element is less than the measured value.

In order to determine the effect of iron electrodes on the Seebeck measurements, the following experiment was performed. Initially, the Seebeck voltage was determined on a number of n-type elements. Then two 1/8" long iron electrodes were positioned on each element, and the Seebeck voltage was again measured. An average drop of 8 mV (at 500°C) in Seebeck voltage was noted. Thus, the drop in Seebeck voltage of the bonded elements is associated directly with the reduced thermal gradient across the thermoelectric material.

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Fig. 49 Seebeck voltage as a function of temperature for a p-type thermoelement (a) prior to bonding and (b) after diffusion bonding.

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Fig. 50 Seebeck voltage as a function of temperature for an n-type thermoelement (a) prior to bonding and (b) after diffusion bonding.

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Figures 51 and 52 show typical plots of resistivity vs. temperature for p- and n-type thermoelectric elements before and after diffusion bonding. It is to be noted that the deviation in resistivity is within experimental error. Thus it is concluded that the resistivity of the element is unaffected by the diffusion bonding.

Diffusion bonding of n-type thermoelements to iron electrodes produced an average contact resistance of less than 0.10 m-ohm, or, in terms of the contact area, an average specific contact resistivity of less than $32 \mu\Omega\text{-cm}^2$. Individual contact resistivities of less than $10 \mu\Omega\text{-cm}^2$ were not unusual for n-type diffusion bonded elements.

Diffusion bonding of p-type elements to iron electrodes produced an average value of contact resistance of 0.15 m-ohm. This corresponds to a specific contact resistivity of $50 \mu\Omega\text{-cm}^2$. Figure 53 shows a photograph typical of diffusion-bonded n- and p-type thermoelements. The intimate contact of the iron electrode with the thermoelement at the bond region is shown in the photomicrograph of Fig. 54. The surface was coarsely ground to delineate the bond region; a finely ground surface yields a distorted bond region because of the difference in hardness between PbTe and Fe.

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Fig. 53 Photomicrograph of typical diffusion-bonded n- and p-type thermoelements.

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(a)

(b)

Fig. 54 Photomicrograph of a coarse-ground surface of the diffusion bonded region between an n-type element (a) and iron electrode (b) 50X.

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