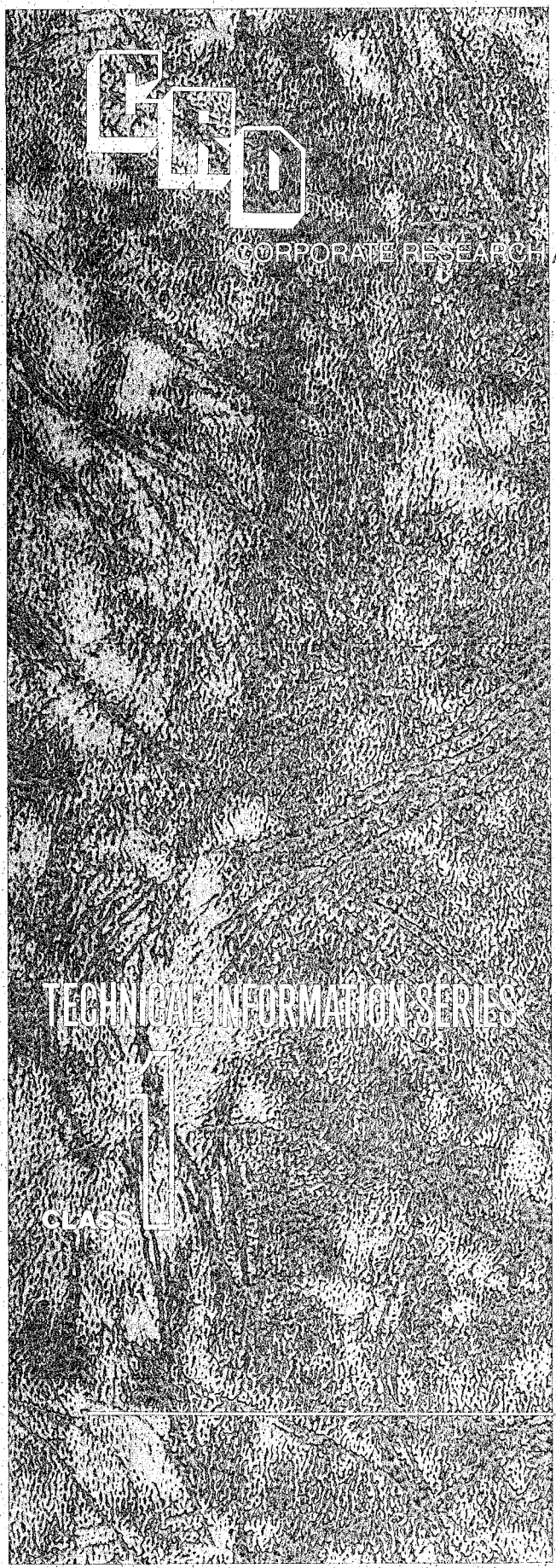

THE APPLICATION OF GAS ATOMIZED POWDER FOR IMPROVED THERMOELECTRIC DEVICES

by

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SUMMARY

The use of gas atomized powder is being explored as a means of improving both the quality and performance of thermoelectric devices.

Presently, the devices are prepared from powder produced by the comminution of small silicon germanium ingots. Comminution to powder is necessary because of the high level of segregation which occurs during solidification of the casting. The powder is then blended and hot pressed in order to provide a relatively homogeneous stock for fabrication of the thermoelectric components.

In this work, pre-alloyed powder of boron doped silicon germanium was prepared by gas atomization and the gas-liquid atomization-quenching process. The powder was then hot-pressed in a conventional manner.

The use of atomized powder, vs. the comminuted powder, has resulted in improved product homogeneity. It is believed that this improved homogeneity will result in increased manufacturing yields by reducing bonding failures of the components.

The figure of merit (Z) of a thermoelectric device is defined by:

$$Z = \frac{S^2}{\rho k_t}$$

where S, ρ, and k_t are the Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively. Because gas atomized powders are rapidly solidified, the use of these powders should result in a reduction of the thermal conductivity, and hence increase the thermoelectric efficiency. A reduction in the thermal conductivity is expected because of increased phonon scattering produced by the increased density of grain boundaries observed in the rapidly solidified material.

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KEY WORDS
thermoelectric, gas atomization, fine powder, thermal conductivity

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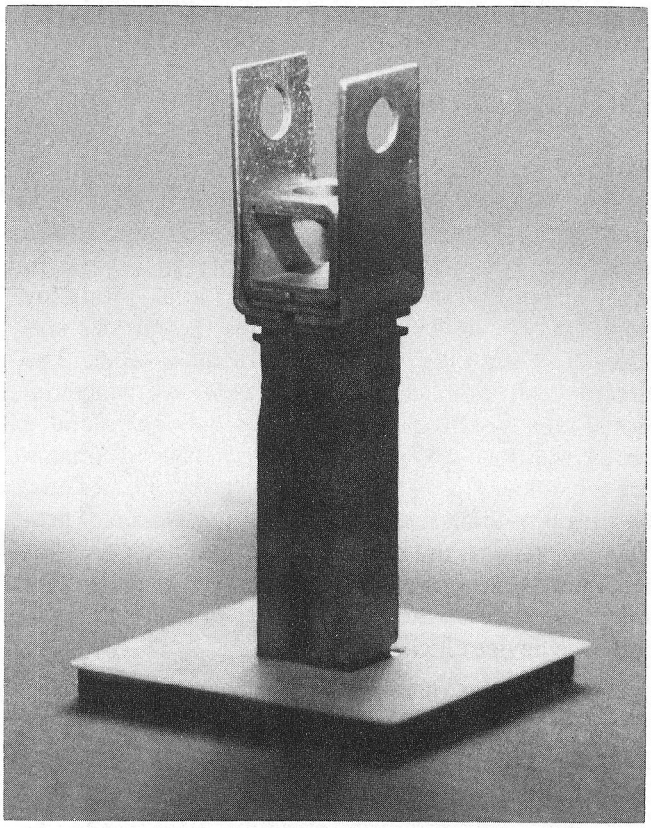
INTRODUCTION

Silicon germanium alloys are commonly employed in the fabrication of high temperature (500-1000°C) thermoelectric devices. Typical applications include deep space probes, where the devices are used to convert thermal energy into the electrical energy required to power the probe. Both P-type (boron doped alloy) and N-type (phosphorus doped alloy) materials are used in each device (Figure 1a).

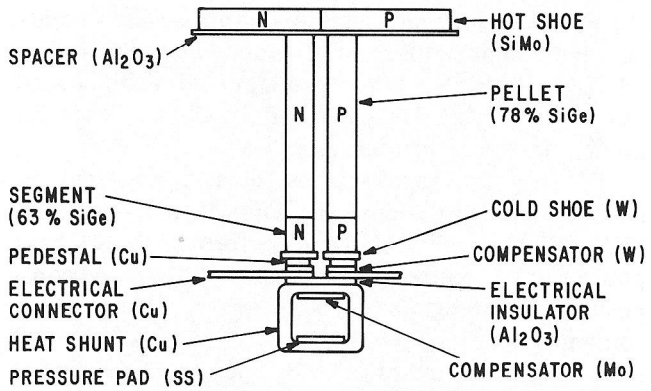
Silicon and germanium have 100% solid solubility in each other and hence form a single solid phase across the entire compositional range of the phase diagram. However, because of the extremely low rate of diffusion of germanium in the silicon-rich phase, a large amount of segregation occurs during solidification. In order to minimize segregation in the final product, present production practice is to chill cast the alloy into 600 gram ingots. The ingots are comminuted into −80 mesh powder, the powder blended and then hot pressed to form a dense compact. While comminuting the alloy into powder reduces the distance occurring between peak compositional differences in the final product, it does little to alter the magnitude of those differences. Additionally, the problem of variation in composition between the starting ingots is introduced.

The final remaining segregation can cause uncontrolled local melting during hot pressing and during the subsequent bonding (welding) of the different components of a complete device (Figure 1b). Additionally, the segregation causes a degradation in the operating efficiency of the device. Gas atomization to form the powder directly from the melt is a means to control the extent of segregation which can occur during solidification. The maximum scale of the inhomogeneity which can occur is limited to less than the size of the powder formed. Because of this inherent reduction in the extent of the inhomogeneity, large melts can be atomized at any one time eliminating the problem of composition variation between individual ingots.

The potential exists that the use of gas atomized powder will result in an increased device efficiency by providing a finer particle size. Further increases might also be attained by reducing the grain size and inhomogeneity of the powder.



(a)



(b)

Figure 1. (a) thermoelectric device for space applications and (b) schematic showing the materials employed.

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The efficiency of a thermoelectric device is defined by the figure of merit (Z)

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

where S, ρ and K are the Seebeck coefficient, electrical resistivity and the thermal conductivity, respectively. The thermal conductivity is the sum of the conductivity of the lattice and the conductivity due to the charge carrier concentration. In semiconductor material the lattice conductivity is significant, accounting for up to 85% of the total conductivity of a single crystal.[1] Theoretical work[2] predicts and experimental work[3] has shown that the lattice conductivity can be reduced by increasing the local disorder in the lattice, the degree of misalignment between neighboring lattices and the density of misaligned neighboring lattices. In practical terms this means maximizing the alloy homogeneity, and minimizing both the powder size used as well as the crystallite size of the powder. The first and third items are well documented characteristics of rapidly solidified materials[4,5] and the second, a reduction in particle size is a prime means of enhancing the quench rate of gas atomized powder.[6,7] Thus, besides providing a means of improving present production practice, the use of rapidly solidified gas atomized powder also offers the opportunity to control the microstructure of the final product in a way that will improve device efficiency.

EXPERIMENTAL

The powder was prepared by remelting prealloyed ingots of $Si_{78}Ge_{22}$ doped with 0.071 wt.% boron. The alloys were melted in boron nitride coated crucibles. The melts were atomized at approximately 1575°C. Two lots of powder were prepared by a vendor using argon gas atomization. Four lots of powder were prepared using an experimental atomizer incorporating the gas-liquid atomization-quenching process.[8] Of these four lots, three were atomized using argon, one was atomized using helium. In all four cases the liquid phase used was deaerated water.

Particle size distributions were determined by sieve and microtrac analysis. Optical metallography, SEM, XRD and EDAX were performed on the base powder to determine grain size, morphology and compositional homogeneity. 5 cm dia. × 1.3 cm thick compacts were prepared by vacuum hot pressing −400 mesh powder. The hot pressing operation was done at approximately 186 MPa, and 1250°C for a period of forty minutes. Densities of the compacts were determined by a liquid displacement technique. Specimens approximately 2.5 cm × 0.64 cm × 0.64 cm were cut from the compacts for electrical property measurement.

The electrical resistivity and Seebeck coefficient were measured from room temperature to 770°C in a flowing nitrogen atmosphere. The electrical resistivity was determined using a four probe ac technique. Instrumentation difficulties prevented accurate determination of this quantity above 550°C. The Seebeck coefficient was determined as the quotient of the thermal Emf produced across the sample and the temperature difference determined by two Chromel-Alumel thermocouples across the same region. As the temperature difference was small at the lowest temperatures, the accuracy of the results below 250°C is not good. The Seebeck coefficient and the electrical resistivity were also determined at room temperature with equipment calibrated against standards. All Seebeck coefficients have been corrected for the thermal Emf's produced in the leads and thus represent absolute values.

Optical metallography, SEM and EDAX were performed on the compacted alloy in order to determine the quality of the consolidation, grain size and extent of the segregation occurring in the final product.

DISCUSSION

The as-atomized powder yields are shown in Figure 2. In all cases high yields of usable alloy (−400 mesh) were attained. The particle size distributions were all log-normal and of similar slope with the exception of the helium atomized powder. The reason for the increased dispersion in particle sizes of the helium atomized alloy is thought to be due to the higher gas velocity and thermal transport properties of helium.

The comminuted powder presently used in production has little internal structure (Figure 3a) as the mean size of 45μm is less than the approximate 100μm repetition distance of the compositional variation in the original ingot. The atomized powder, how-

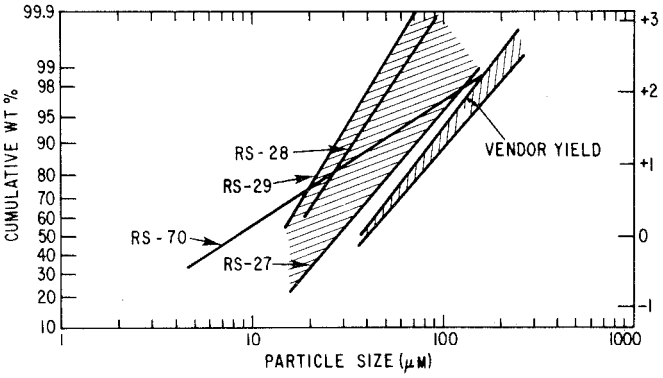
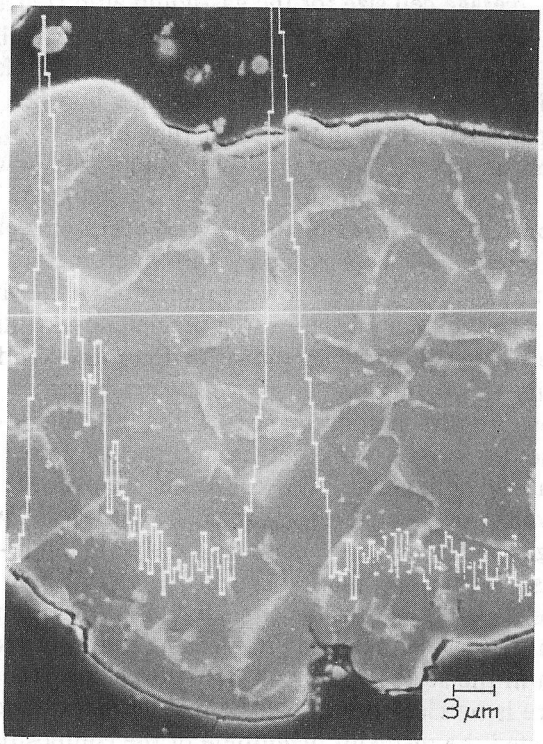


Figure 2. As-atomized powder yields for argon gas atomization (vendor), argon-water atomization quenching (RS-27 − RS-29) and helium-water atomization quenching (RS-70).

(a)



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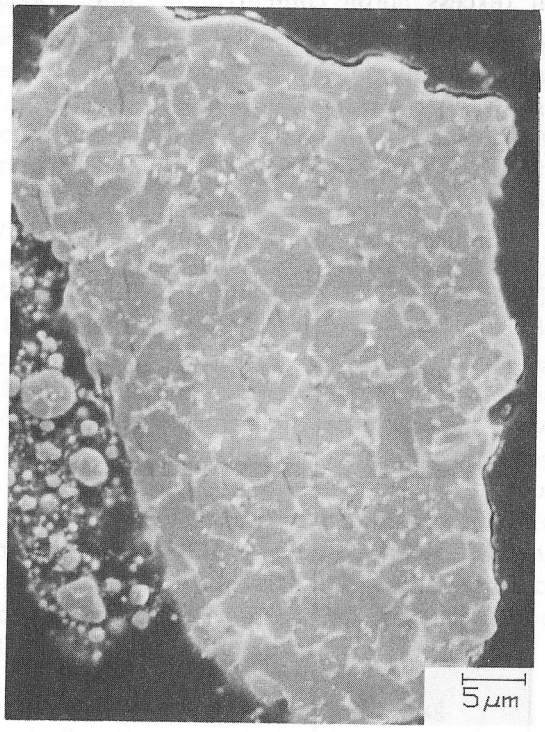
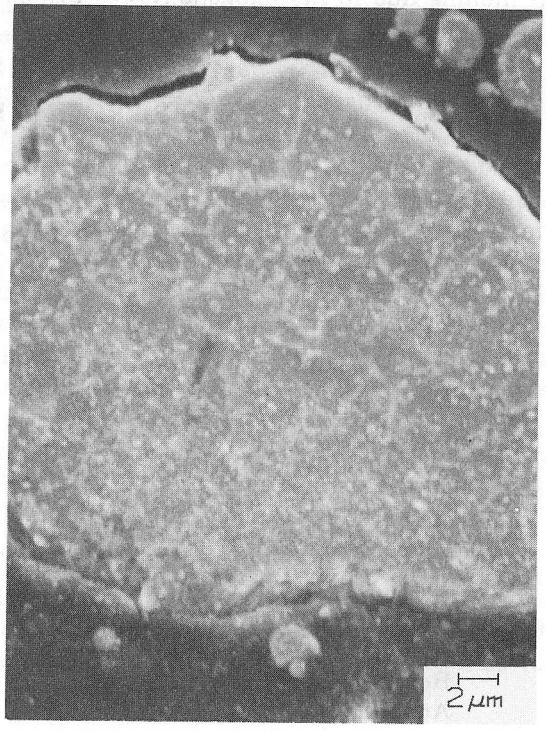


(c)



(d)

Figure 3. (a) Comminuted powder, helium-water atomized quenched powder showing the transition in structure with decreased particle size; (b) 45 μm diameter; (c) 40 μm diameter; and (d) 35 μm diameter.

ever, contains a definite cellular structure (Figure 3b). The average cell size for the gas-liquid atomized alloy is less than that for the conventionally atomized alloy, as a result of an increased solidification rate (Table I). While there is no significant difference between the average cell size of the different runs of argon-water atomized powder, the helium-water atomized powder had a cell size approximately 25% smaller than the argon-water atomized material. With decreasing particle size below approximately 40 micrometers the helium-water atomized powder undergoes a transition from the cellular structure to a precipitate-like structure. This transition is shown in Figures 3c and 3d. While the definition of the cell walls becomes less clear and the predominance of the precipitate-like structure grows with decreasing particle size (increased cooling rate) the cell walls were never observed to completely vanish. The cell walls (Figure 3b) and the precipitates are a germanium-rich phase, while the matrix is silicon rich. While the differences in the various quench rates of the atomization processes employed produced a significant reduction in the scale over which the segregation occurred there is no clear trend that the quench rates imposed affected the resultant magnitude of the compositional variation (Table I).

The pressing conditions and the properties of the vacuum hot pressed compacts are shown in Table II. Local melting due to inhomogeneity was evident in three of the six compacts. Because of this, the hot pressing temperature was reduced to approximately 1175°C for the RS-29 compact. The compact prepared from argon atomized powder was rejected for low density and the compacts prepared from the RS-27 and RS-29 powder had insufficient Seebeck coefficients. The low Seebeck values are probably due to excess boron picked up during the melting operation.

Figure 4 shows the microstructure of the hot pressed compacts. The refinement of the microstructure due to the use of decreased powder particle sizes is evident. EDAX analysis of compacts prepared from standard material (Figure 5a) and from the helium-water atomized powder (Figure 5b) reveal the difference in structure and segregation of the atomized material. The light zones correspond to germanium-rich alloy, the dark zones are silicon-rich alloy. The segregation in the melt atomized alloy is reduced both in magnitude and scale when compared to the production material. As Figure 6 shows, the level of segregation shown in Figure 5a is common in the production material. The electrical resistivities and Seebeck coefficients are plotted in Figures 7 and 8 as a function of temperature for the gas atomized material and production material. The somewhat lower electrical resistivity of the gas atomized material compared to the production material indicates a somewhat higher carrier concentration in the gas atomized material (excess boron content). The lower Seebeck

Table I

POWDER PROPERTIES PRIOR TO HOT PRESSING

Powder Production Process	Mean Particle Size Consolidated (μm)	Mean Cell Size ~30μm Powder (μm)	Si Concentration Si Rich Phase (atomic %)	Si Concentration Si Depleted Phase (atomic %)
Comminuted	45	45*	–	–
Argon Atomized (vendor)	23	5.3	87.6	7.6
Argon-Water Atomized (RS-27)	20	4	88.5	3.3
Argon-Water Atomized (RS-28)	15	3.6	90.3	1.9
Argon-Water Atomized (RS-29)	13	3.9	92.6	3.6
Helium-Water Atomized (RS-70)	6.5	2.9	88.6	11.4

*repetition distance in the starting ingots is approximately 100μ m and is therefore limited in the powder by the powder size.

Table II

HOT PRESSING PARAMETERS AND ROOM TEMPERATURE PROPERTIES OF THE COMPACTS

Powder Production Process	Hot Pressing Conditions Time (min.)	Temp. °C	Density (g/cc)	Room Temp. Seebeck Coefficient (μV/°C)	Observations
Comminuted	40	1250	3.040	112	Local Melting Non Homogenous (EDAX)
Argon Atomized (Vendor)	40	1220	2.96	125	Homogenous (XRD) Compact cracked
Argon-Water Atomized (RS-27)	40	1240	3.046	99	
Argon-Water Atomized (RS-28)	40	1240	-	-	Compact Melted
Argon-Water Atomized (RS-29)	40	1175	3.062	76	Local Melting Reduced inhomogeneity (EDAX)
Helium-Water Atomized (RS-70)	40	1250	3.098	107	Reduced inhomogeneity (EDAX)

coefficient, above 300°C , of the gas atomized material is also consistent with a higher carrier concentration in the melt atomized material.

The somewhat higher Seebeck coefficient of the gas atomized material below 250°C may in part be due to systematic measurement error as discussed in the experimental section. This is supported by the room temperature value of the Seebeck coefficient as determined in a different, calibrated device, of 107 microvolts/°C (Table II).

While the electrical resistivity and Seebeck coefficient are somewhat different for the two materials, it is not clear at this time that the difference is significant, as the two properties are partially offsetting in the figure of merit $Z = S^2/\rho K$. Additionally, some deterioration of the electrical properties due to the use of fine powder is reported in the literature.[9,10] The benefit of the gas atomized powder is expected to appear in a reduction of the thermal conductivity and a corresponding increase in the figure of merit. Evaluation of the thermal conductivity of the compact prepared from atomized alloy has not been completed and will be reported in future work.

CONCLUSION

Present thermoelectric theory predicts that increased device efficiencies will be attained by the use of smaller powder sizes, smaller crystallite sizes, and reduced inhomogeneity. Gas atomization is a means of producing fine powder. The gas-liquid atomization quenching process has been employed to make rapidly solidified powder for thermoelectric components. The compacted material has a reduced grain size and reduced inhomogeneity when compared to production material. These microstructural changes are expected to improve device performance.

Gas atomization is superior to comminution as a production technique able to produce large lots of uniform powder (of the boron-doped material) at one time. Confirmation of improved thermoelectric efficiency via fine rapidly solidified powders will not be attained until the evaluation of the thermal conductivity is completed. Application of gas atomization as a technique to produce the phosphorus-doped powder is yet to be evaluated. It is expected to be more difficult a problem due to the high vapor pressure of phosphorus at the temperatures required for atomization.

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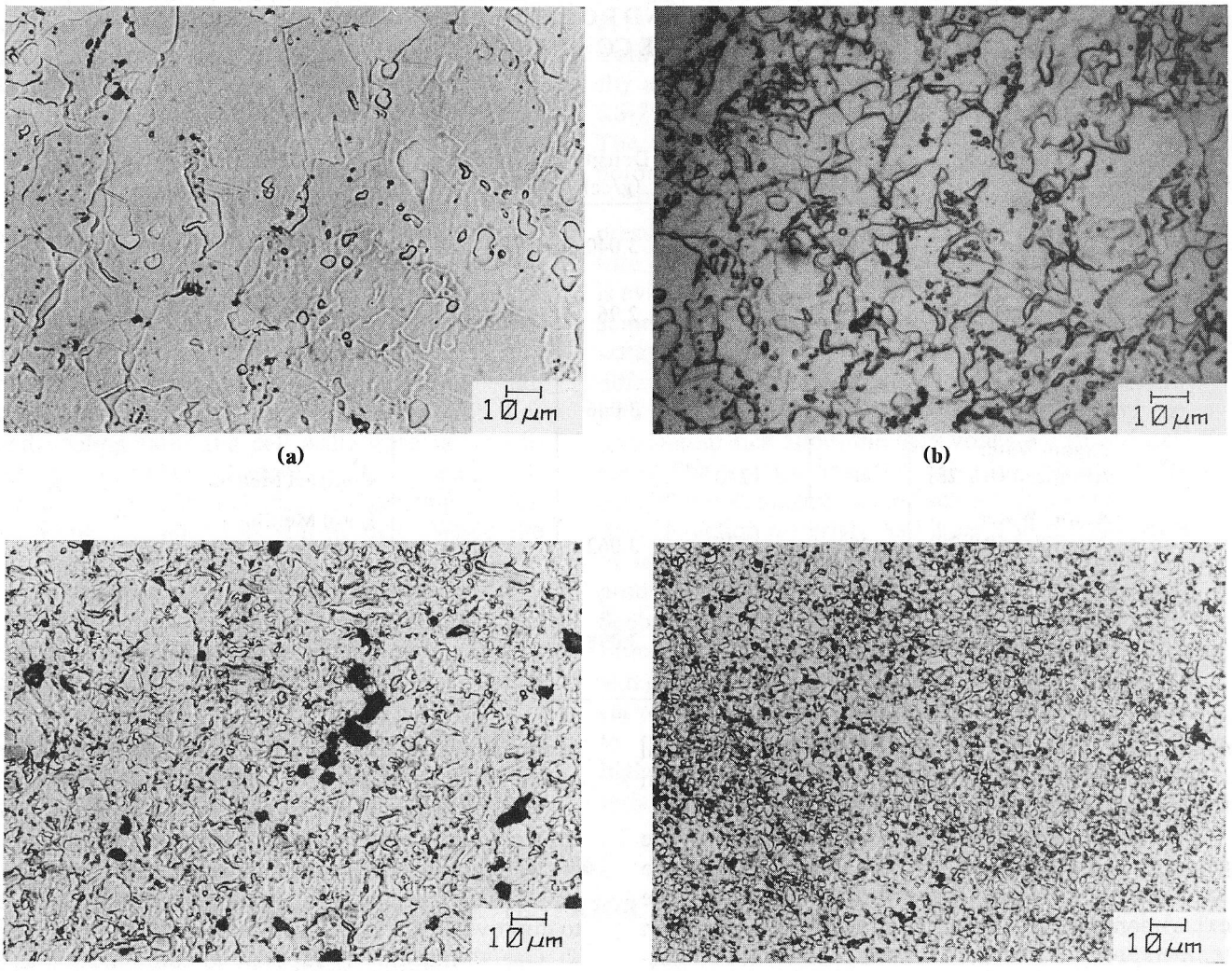

Figure 4. Hot pressed compact microstructures: (a) comminuted powder; (b) argon atomized powder; (c) argon water atomized powder; and (d) helium water atomized powder.

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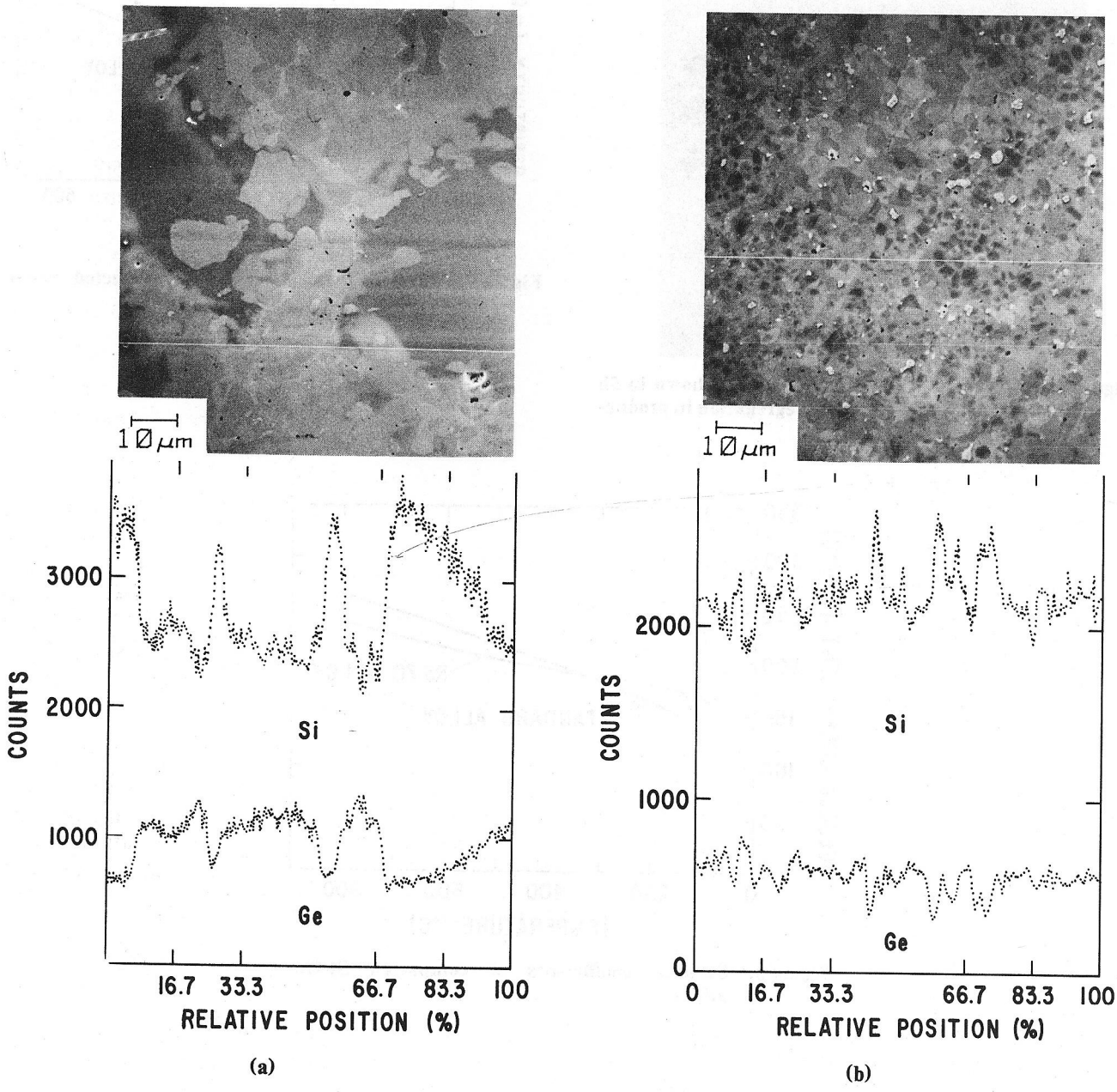

Figure 5. Micrographs and EDAX traces for compacts prepared from
(a) comminuted and
(b) helium-water atomized powder.

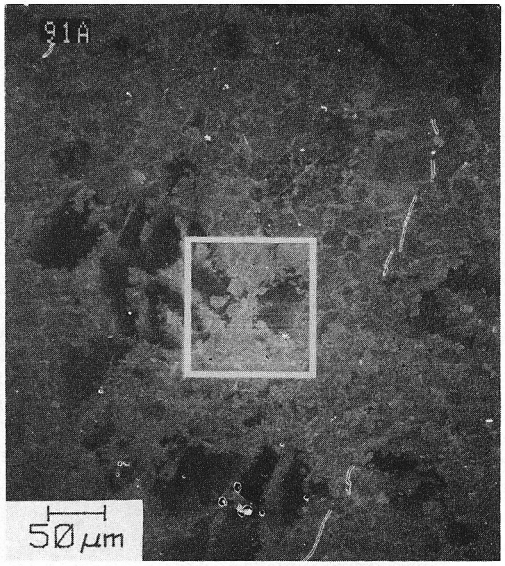

Figure 6. Micrograph including the region shown in 5b to indicate the extent of segregation in production compacts.

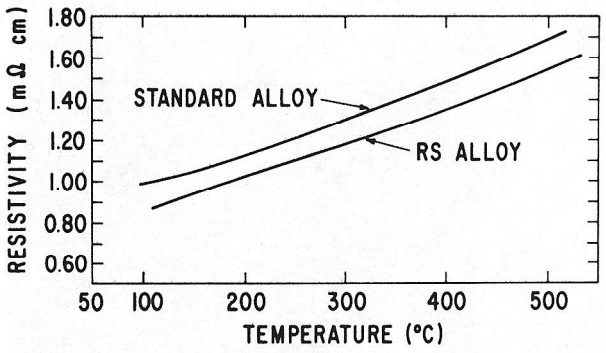

Figure 7. Electrical resistivities of compacted Si-Ge alloys.

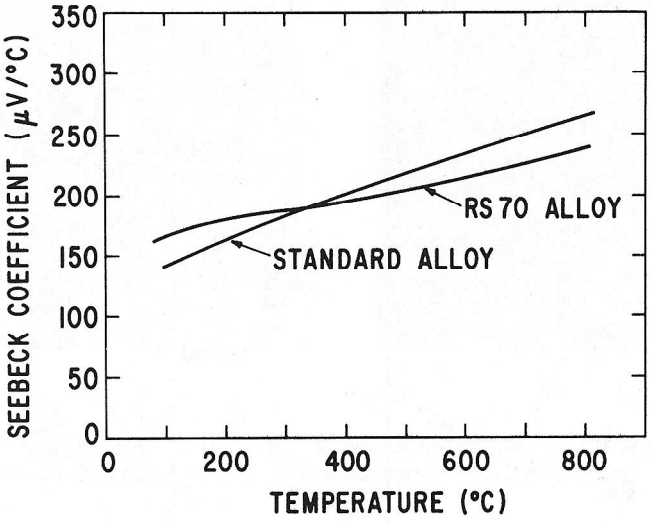

Figure 8. Seebeck coefficients of compacted Si-Ge alloys.