Ceramic Fibers for Matrix Composites in High-Temperature Engine Applications

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High-temperature engine applications have been limited by the performance of metal alloys and carbide fiber composites at elevated temperatures. Random inorganic networks composed of silicon, boron, nitrogen, and carbon represent a novel class of ceramics with outstanding durability at elevated temperatures. $SiBN_3C$ was synthesized by pyrolysis of a preceramic *N*-methylpolyborosilazane made from the single-source precursor $Cl_3Si\text{-}NH\text{-}BCl_2$. The polymer can be processed to a green fiber by melt-spinning, which then undergoes an intermediate curing step and successive pyrolysis. The ceramic fibers, which are presently produced on a semitechnical scale, combine several desired properties relevant for an application in fiber-reinforced ceramic composites: thermal stability, mechanical strength, high-temperature creep resistivity, low density, and stability against oxidation or molten silicon.

The science and technology of improving the efficiencies of energy production, transformation, and storage have continued to be of special concern that promises high ecological and economic benefits.

In this context, the ready availability of better materials appears to be the main issue that determines the speed of progress. This limitation especially applies for any kind of heat engine, because its energy efficiency is directly coupled to the working temperature, and the working temperature is limited by the materials' properties. Although cost is always a factor in choosing a particular material, for high-temperature applications the main limitations are still physical and chemical: high strength, elasticity appropriate for the specific application, and resistance to creep as well as to corrosion, all at elevated temperatures for long periods of time. When considering applications in the field of air transportation, which is a competitive area undergoing rapid growth, low density is another major concern.

Metals and intermetallic compounds have been the main materials for gas and jet turbine engines. Performance has been steadily improved as nickel-based, polycrystalline superalloys have been superseded by single-crystal superalloys and later by NiAl- or $MoSi_2$-based composites (*1*). However, despite considerable recent achievements, there seems to exist an intrinsic, and not easily surmountable, limit for high-temperature applications of metallic materials. The mechanical and chemical requirements become insurmountable when attempting to push the operating temperature beyond 1200°C. Once an intermetallic compound is heated to about 80% of its melting temperature, the mechanical properties, such as creep resistance, typically decline sharply. Furthermore, the susceptibility to corrosion, which constitutes a major weakness of most metals, becomes nearly impossible to control under such drastic conditions.

Engineers nonetheless want to use higher working temperatures: The development of a new generation of gas turbines and jet propulsion engines for higher combustion temperatures requires new materials that can withstand temperatures of up to 1500°C for several thousand hours. Such a demand can only be fulfilled by the use of ceramic materials. Potential customers indicate that this thermal stability advantage over superalloys could reduce fuel consumption by 6 to 8% in aircraft engines and by 10 to 15% in gas turbines. However, the path toward large-scale commercial use of these materials is still obstructed by their inherent brittleness leading to unsatisfactory reliability for many applications. Microscopically, the brittleness originates from rapid and virtually unimpeded crack propagation through the bulk. Attempts to overcome this drawback have followed two paths. One approach is to try to improve the microstructure of the materials by reducing the number and size of the flaws that are crucial for failure under stress. A second, and often complementary approach, is to design composite structures such as fiber-reinforced ceramics. The use of ceramic fibers for reinforcement of ceramic matrix composites (CMCs) is well established in materials research (*2*) and, indeed, seems to be the most promising approach to fulfilling the ambitious demands of the jet propulsion turbine producers. Unfortunately, the presently available ceramic fibers do not survive long-term use under mechanical loads in an oxidizing atmosphere at 1200°C.

One route that has not been fully explored in the past, but can lead to major improvements, is the design of new materials at the atomic level by using chemical techniques. With this in mind, novel nonoxide materials were synthesized in the Si-B-N-C system by starting with a "single-source" precursor (*3*). In comparison to other ceramic materials, the $SiBN_3C$ composite exhibits superior thermophysical and chemical properties. It can be formed into ceramic fibers by melt-spinning the polymeric precursor *N*-methylpolyborosilazane (PBS-Me) and then being pyrolyzed. These new fibers, which bear the tradename Siboramic, show extremely promising properties for use as CMC materials in higher performance turbine engines.

Materials Development

The design concept is to generate a strongly bonded three-dimensional random network in a ternary or quaternary system of inorganic elements (that is, C is included as a carbide phase). The high degree of connectivity of the amorphous network, owing to the presence of N and C as network components, is expected to suppress rapid crack propagation within the bulk. Additionally, one gains the option of tuning the materials' properties by changing the compositions. A possible objection to this approach might be that amorphous solids are thermodynamically unstable (although not necessarily kinetically unstable) with respect to transformation into a crystalline state. However, an amorphous solid could meet the requirements of durability while resisting crystallization if it were based on strong covalent bonds, which would show negligibly small contributions to the enthalpy of formation from long-range bonding interactions that drive crystallization. These requirements seem to be best fulfilled by combinations of Si and B with N or C.

The diffusion coefficients of Si or B in compounds such as nitrides are extremely low, and binary components that are expected to form multinary carbonitridic ceramics do not melt without decomposition. Thus, there appears to be only one way to prepare the desired materials: synthesis through polymeric intermediates. In order to avoid spatial inhomogeneity, which might induce phase separation and even crystallization during pyrolysis, the polymers must show a homogeneous distribution of the components on the

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atomic level. Thus, molecular single-source precursors containing linkages that, in the most favorable case, would survive the processing into the final ceramic material, had to be synthesized. These preconditions are well met by Cl_3Si-NH-BCl_2 (trichlorosilylaminodichloroborane, or TADB) (*4*). This molecule contains a Si-N-B bridge that is reinforced by the well-known Si-N and B-N π-bond interactions (*5*), and is fully functionalized by chlorine, which allows for rapid polymerization by ammonolysis (or aminolysis) with subsequent polycondensation. This reaction sequence (Fig. 1A) has several favorable aspects when examined for use in large-scale production: (i) All starting materials are readily available and relatively cheap; (ii) all by-products can, in principle, be reused or recycled; (iii) the yield in each step is near 100%; and (iv) production on an industrial scale is technologically feasible. Polymerization is best achieved through ammonia or methylamine (Fig. 1B). In both cases, the ammonolysis or aminolysis reaction is followed immediately by polycondensation. The use of methylamine has the advantage that the oligomeric condensation products are liquid and can be separated from the salt by filtration. The polymer obtained by ammonolysis is principally unmeltable, whereas the viscoelastic properties of PBS-Me can be tailored by an appropriate heat treatment to be liquid, meltable, soluble, or unmeltable. Surprisingly, only three well-resolvable reaction stages occur during pyrolysis. From 200° to 600°C, the polycondensation is completed while methylamine is removed. At ~600°C, the largest weight loss occurs and is accompanied by the evolution of molecular fragments. Above 1000°C, H_2 and small amounts of N_2 are evolved. If ammonia is used as the reactive gas during pyrolysis, both types of polymers transform to a ternary nitride, $Si_3B_3N_7$, whereas in N_2 PBS-Me yields $SiBN_3C$.

Both $Si_3B_3N_7$ and $SiBN_3C$ are x-ray amorphous. Their exact compositions, $Si_3B_3N_7$ and $SiBN_{2.3}C_{0.8}$, respectively, have been determined by chemical analysis (*6*). Their thermal stabilities are impressively high. The onset of N_2 evolution in $Si_3B_3N_7$ begins at temperatures 160°C higher than that for crystalline (thermodynamically stable) silicon nitride. With respect to weight loss, $SiBN_3C$ is stable up to 1800°C, at which point it begins to decompose into Si, N_2, BN, and SiC. Remarkably, no changes in microstructure are detectable up to that temperature. The most critical drawback of nitride ceramics, compared with oxides, is their susceptibility to oxidation. In the area of oxidation resistance, an unforeseen feature makes $SiBN_3C$ superior to all known carbides and nitrides. Exposing this material to air at 1400°C results in the formation of a protective double-layer (SiO_2/BN). The outer layer, rich in Si and O but depleted with respect to B because of the evaporation of B_2O_3, acts as a diffusion barrier for oxygen. The inner layer, rich in N and B but with less Si because of diffusion of Si to the outside, suppresses cation diffusion. Thus, the maximum operating temperature for $SiBN_3C$ in air is 1500°C, which is significantly higher than that for all competing nonoxidic materials systems reported so far. Its hardness is comparable to that of sapphire, and the fiber density is 1.8 g/cm^3. Production has reached the pilot plant scale (batches of 150 kg).

Production of $SiBN_3C$ Fibers

The combined properties of $SiBN_3C$ make it ideal for the production of ceramic fibers. Fortunately, the preceramic polymer PBS-Me can be processed through conventional polymer techniques, either by melt-spinning or by a dry-spin process. Melt-spinning is preferable because no solvent is required and, in general, the resulting "green" fibers (that is, before thermal processing) show better properties. The viscosity of the PBS-Me polymer can easily be adjusted to the desired working range of 80 to 260 Pa·s at shear rates between 400 and 1000 Pa·s. Under these conditions, ceramic fibers with diameters exceeding 15 μm can be produced by continuous melt-spinning through a spinneret with more than 300 holes at temperatures of ~150°C. Within this range of shear rates, the polymer behaves essentially like a Newtonian fluid. For production of fibers with diameters less than 15 μm, smaller capillary diameters and higher shear rates, up to 3200 Pa·s, are required.

Curing of the green (thermoplastic) polymer fibers can be achieved either thermally or chemically. Because thermal curing is slow for kinetic reasons (removal of methylamine), chemical curing with gaseous species is preferred. By applying, for example, $HSiCl_3$, curing of the polymer fibers with diameters of ~20 μm is completed within a few seconds.

The sufficiently cured polymer fibers are pyrolyzed by exposure to increasingly high temperatures, starting at ambient temperature and ending at about 1500°C. During this process, all organic species are removed and, in a yield of 55 weight %, pure inorganic $SiBN_3C$ fibers are obtained. The ceramic yield is of importance not only from an economic point of view. If released over a narrow temperature range, the gaseous by-products can cause damage (cracking) or even rupture of the ceramic part. Fortunately, during pyrolysis of cured PBS-Me fibers, the pyrolytic gases leave the system over the rather wide temperature range (from 300° to 800°C), and the integrity of the resulting fiber is kept. The fibers are dense, without any detectable porosity even under very high resolution transmission electron microscopy (better than 1 nm), and show a very smooth surface. The considerable mass loss during thermal treatment, which is usually regarded as unfavorable, causes a shrinkage of the fiber diameter by 40 to 30%, which can actually be an advantage for the production of ceramic fibers with extremely small diameters. Figure 2 shows the fiber on a reel as spun and pyrolized continuously at a speed of 130 to 140 m/min.

Properties of SiC and $SiBN_3C$ Fibers

Thus far, only a handful of ceramic fibers for use in CMCs have reached the market. Ube Industries and Nippon Carbon both produce a ceramic fiber made of silicon carbide, whereas 3M has developed an oxide ceramic fiber for this purpose. Dow Corning, which has been distributing the Nippon fiber, recently announced that it intends to enter the market with its own improved SiC fiber (Sylramic). Close behind are the nitridic ceramics, some of which, Siboramic among them, have by now reached the pilot stage. We present a brief comparison of the most important properties of these two classes of high-temperature ceramics.

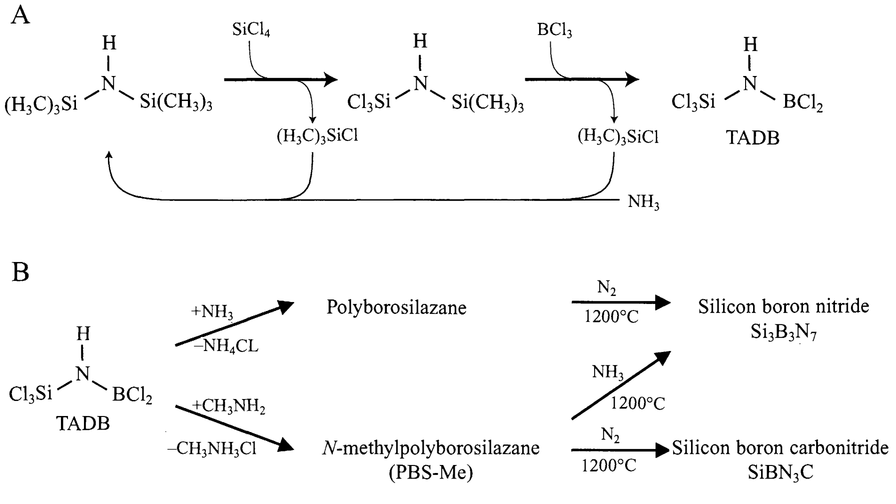

Fig. 1. (**A**) Synthesis of the precursor molecule TADB. (**B**) Pyrolysis and polymerization of TADB.

SiC fibers. The second-generation crystalline SiC fibers such as HiNicalon, the Dow Corning SiC fiber Sylramic, and the recently developed Ube SA fiber can easily withstand temperatures up to 1800°C for long periods in nonoxidizing atmospheres, which is about 150°C higher than those reported for the standard Nicalon SiC fibers. However, the SiC fibers already lose a large part of their mechanical strength below 1400°C, as measured by creep resistance (*7–9*). Similar to the case of intermetallic compounds, there appears to exist a temperature limit, above which it becomes very difficult to fulfill all of the desired mechanical requirements. SiC fibers that retain sufficient strength above about 1300°C exhibit unacceptably high creep rates, whereas those SiC fibers having a sufficient creep resistance have tensile strengths that are too low for reinforcement applications (*7*).

The creep behavior of the SiC fiber types (Fig. 3) is dominated mainly by grain boundary sliding (surface diffusion), which depends on the SiC grain size and the O content of the respective fibers (*10*). Thus, the fiber with the coarsest microstructure, the Ube SA fiber, exhibits the best creep behavior of all SiC fiber types. A total fiber creep strain of 1% during service life is expected to be sufficient for high-temperature CMC applications (*11*). However, because of their crystalline nature, stoichiometric SiC fibers are intrinsically prone to subcritical crack growth that significantly limits their service life under load at high temperatures.

Regarding the corrosion resistance at high temperatures, the primary concern is stability with respect to oxidation. A scanning electron micrograph (SEM) of a HiNicalon SiC fiber after thermal aging in air at 1500°C for 15 hours (Fig. 4A) reveals a crystalline oxide layer that contains several cracks and shows debonding from the fiber core. Furthermore, all SiC fiber types appear to exhibit grain growth when in contact with liquid Si, which leads to a significant loss of strength. From the point of view of processing technology, such growth essentially prevents the use of liquid Si infiltration during materials processing.

Fig. 2. A $SiBN_3C$ fiber as produced by continuous melt-spinning and pyrolysis of a preceramic polymer.

$SiBN_3C$ fibers. The second-generation crystalline SiC fibers represent a significant step forward from the traditional intermetallic compounds, but it has not been clear whether the improvements achieved are sufficient to justify substituting SiC-based CMCs for the metallic systems. One class of more promising compounds are the nitridic ceramics, and we discuss $SiBN_3C$ fibers as a leading representative of this family.

As discussed above, $SiBN_3C$ fibers can easily withstand temperatures of up to 1800°C in nonoxidizing atmospheres and up to 1500°C under oxidizing conditions for long periods, while retaining almost all of their mechanical strength. A SEM micrograph of a $SiBN_3C$ fiber after temperature cycling in air (from 20° to 1500°C, five cycles of 10 hours each) (Fig. 4B) demonstrates that the oxide layer of the oxidized $SiBN_3C$ fiber is crack-free and shows good adhesion to the fiber core. The tensile strength of the oxidized fiber is as high as that of the unoxidized one. Even after temperature cycling, ceramic fibers made of $SiBN_3C$ remain absolutely amorphous both in the bulk material and in the oxide layer.

The existence of a protective double layer and the stability of the random network are the most likely reasons for the high degree of resistance to corrosion by liquid metals, such as copper and Si (Fig. 5). In particular, $SiBN_3C$ is corrosion resistant to liquid Si, which would enable CMC producers to use the low-cost production method of liquid Si infiltration. In this context, it should be noted that for such a composite to be useful, the bonding strength between the fiber and the surrounding matrix material has to be carefully adjusted. It must be strong enough to guarantee sufficient adhesion, while being weak enough to ensure that cracks will be deflected around the fiber and stopped. Serendipitously, in the case of $SiBN_3C$, the SiO_2/BN double-layer that is formed during an oxidative curing step appears to provide the proper bonding requirements. This curing step is easily performed in a continuous process at 1500°C in air and directly follows the pyrolysis and sintering steps. For such a $SiBN_3C$-glass composite, deflection and absorption (by energy dissipation) of a crack by the fiber-matrix interfaces is shown in Fig. 6.

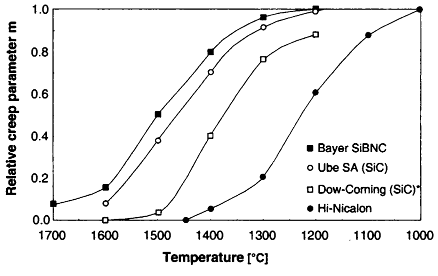

Fig. 3. Comparison of the creep resistance of various ceramics. End-user specification: Relative creep parameter $m > 0.5$ at operational temperature.

We present the thermomechanical data for $SiBN_3C$ fibers in Table 1, along with the corresponding data for various SiC fibers.

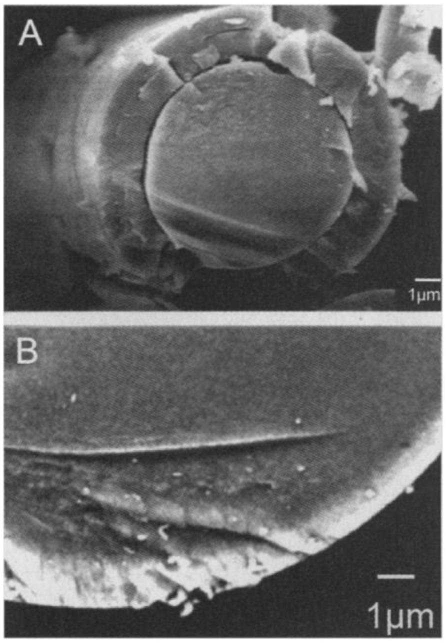

Fig. 4. Oxidation resistance of *Siboramic* compared with HiNicalon fibers (Nippon Carbon) (SEM). **(A)** Fracture surface of HiNicalon fibers after exposure to air (15 hours, 1500°C). **(B)** Fracture surface of $SiBN_3C$ fibers after exposure to air (50 hours, 1500°C).

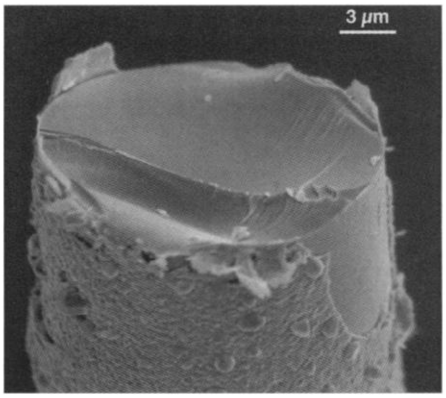

Fig. 5. $SiBN_3C$ fiber treated with molten Si (1600°C, 35 min) (SEM).

Table 1. Mechanical data of SiBN$_3$C fibers (reported in this article) compared with the requirements of potential users (European turbine producers) and to various SiC-fiber types (*12–16*). RT, room temperature.

Property	End-user specification	Siboramic (*16*) (Bayer)	Sylramic (*7, 11, 13*) (Dow Corning)	HiNicalon (*7, 11, 13–15*) (Nippon Carbon)	Ube SA (*12,13*) (Ube Industries)
O content (weight %)	–	1.0	0.2	0.8	0.3
Tensile strength					
At RT (GPa)	3.0	4.0	2.8	3.0	2.5
At 1400°C in air (% RT value)	83 (1500°C)	95	95	70	95
E-modulus					
At RT (GPa)	300	290	420	280	300
At 1400°C in air (% RT value)	83	90	–	70	–
Strain to failure (%)	1.0	1.0	0.8	1.3	0.7
Coefficient of thermal expansion (K^{-1})	3.5×10^{-6}	3.5×10^{-6}	4.0×10^{-6}	4.0×10^{-6}	4.0×10^{-6}
Specific weight (g·cm^{-3})	<5.0	1.85	3.1	2.7	3.1
Diameter (μm)	10–150	12–14	10	14	10
Thermal conductivity (W·m^{-1} K^{-1})	–	>3	46	5	64
State of matter	–	Amorphous	Crystalline	Partial crystalline	Crystalline
Creep parameter*	>0.4	0.8	0.4	0.1	0.7
Strength (% RT value) after exposure to air					
At 1300°C for 100 hours	–	–	–	23	55
At 1500°C for 50 hours	–	80	–	0	–
Subcritical crack growth	–	No	Yes	No	Yes
Resistance to molten Si	–	Yes	No	No	No

*Bend-stress-relaxation measurements at 1400°C inert atmosphere.

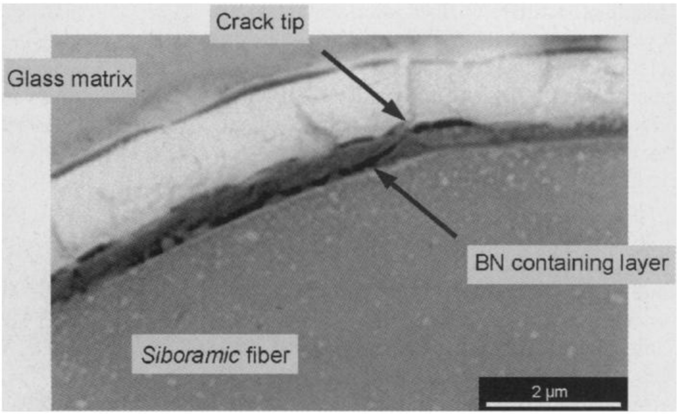

Fig. 6. SiBN$_3$C fiber embedded in a borosilicate glass matrix, showing crack deflection by the SiO$_2$/BN double-layer (SEM).

Quite generally, the properties of SiBN$_3$C are very satisfactory and already fulfill the requirements set by industry for the so-called third-generation high-temperature materials. Regarding tensile strength and mechanical strength as measured by Young's modulus, all ceramic fibers exhibit comparable values at ambient temperature. However, the oxidation resistance and creep behavior of the amorphous SiBN$_3$C fibers lead to excellent thermomechanical properties in air and at the envisioned working temperature. Finally, in regard to applications, SiBN$_3$C fibers have the added advantage of a low density, ~60% that of other ceramic fibers and ~30% that of a typical superalloy.

Summary

The superior performance of SiBN$_3$C compared with crystalline SiC-fibers and intermetallic compounds lies in (i) the spatial homogeneity of the polymeric intermediate down to the atomic level, which is a crucial prerequisite for the formation of an amorphous and relatively flaw-free, dense ceramic fiber, and (ii) the protective double-layer that forms during processing (continuous oxidation curing) to become an integrated part of the fiber. The properties of SiBN$_3$C ceramics can be summarized as follows: excellent resistance to oxidation, suitable for application in air up to 1500°C, resistance to molten Si at 1600°C, suitable for application up to 1800°C in an inert atmosphere, no microstructural changes up to 1800°C, low density (~1.8 g/cm^3), small coefficient of thermal expansion (3×10^{-6}/K), and a thermal conductivity of ~3 W/mK at 1200°C.

In the case of nonoxide fibers, the recently developed SiC fibers from Nippon Carbon, Ube SA, and Dow Corning have temperature capabilities up to 150°C higher than those reported for the standard Nicalon SiC fibers. However, because of high-temperature creep resistance as demanded by the aerospace industry, a general temperature limit in the range of 1300°C, at best, seems to exist for high-strength SiC fibers, whereas those SiC fibers having a sufficient creep resistance exhibit tensile strengths too low for reinforcement applications (*6*). Furthermore, because of their crystalline nature, stoichiometric SiC fibers are intrinsically prone to subcritical crack growth, which significantly limits their lifetime under load at high temperatures.

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REVIEW

Thermoelectric Cooling and Power Generation

Francis J. DiSalvo

In a typical thermoelectric device, a junction is formed from two different conducting materials, one containing positive charge carriers (holes) and the other negative charge carriers (electrons). When an electric current is passed in the appropriate direction through the junction, both types of charge carriers move away from the junction and convey heat away, thus cooling the junction. Similarly, a heat source at the junction causes carriers to flow away from the junction, making an electrical generator. Such devices have the advantage of containing no moving parts, but low efficiencies have limited their use to specialty applications, such as cooling laser diodes. The principles of thermoelectric devices are reviewed and strategies for increasing the efficiency of novel materials are explored. Improved materials would not only help to cool advanced electronics but could also provide energy benefits in refrigeration and when using waste heat to generate electrical power.

Imagine having generators that directly convert heat to electricity, or refrigeration devices that use electricity to pump heat from cold to hot, both without any moving parts or bulk fluids [liquids or gases like chloroflurocarbons (CFCs) or hydrochloroflurocarbons (HCFCs)]. Such thermoelectric (TE) devices already exist. They are lightweight, small, and inexpensive, and they completely eliminate the need for CFCs or HCFCs and heavy compressors in small-scale refrigeration. Most refrigeration failures are due to gas leaks or to the failure of moving parts in the compressor. The former, of course, may also pose environmental problems. TE devices are potentially much less prone to failure because no moving parts are involved. Currently, the world market for TE cooling devices is still small (about \$80 million to \$160 million per year). Major uses for these TE devices include cooling laser diodes and electronic coolers for picnic baskets. These same devices can also be used as electrical generators when a source of heat is present. Yet, if these TE devices are so useful, why are they not more widely used?

Presently, the use of TE devices is limited by their low efficiencies. The efficiency of a refrigerator is expressed by the coefficient of performance (COP), which is the amount of cooling divided by the electrical energy input needed to obtain that cooling. The laws of thermodynamics tell us that a maximum efficiency, called the Carnot efficiency, cannot be exceeded. The COP at Carnot efficiency is just $T_{\mathrm{cold}}/(T_{\mathrm{hot}} - T_{\mathrm{cold}})$, where T_{hot} and T_{cold} are the temperatures of the ambient environment and of the coldest part of the refrigerator, respectively. The real efficiency of any device is often given as a percentage of the Carnot efficiency. Present TE devices operate at about 10% of Carnot efficiency, whereas the efficiency of a compressor-based refrigerator increases with size: a kitchen refrigerator operates at about 30% of Carnot efficiency and the largest air conditioners for big buildings operate near 90%. Today's TE devices are particularly useful when rapid on-off cycling is required at low temperature differences. Moreover, TE devices are used, for example, when the efficiency is a less important issue than small size, low weight, or high reliability. However, there is no known limit to the potential efficiency of a TE device, except for the Carnot limit.

The efficiency of a TE device is determined by the materials used in making the device, and thus the current focus of research is on finding better materials. If the low efficiencies can be overcome and if new materials can be made at reasonable cost, it would revolutionize the cooling industry. Other industries, such as microelectronics, could also benefit from the development of active cooling technologies. The national semiconductor roadmap (*1*) indicates that higher operating frequencies, higher capacitances, and larger chip sizes will result in doubling of the heat dissipation requirements from 1997 to 2005. In addition, the potential to operate devices below room temperature holds the promise of improved reliability and speed of CMOS-based microprocessors. Likewise, when used as electrical generators, TE devices could tap the waste heat generated in engine combustion to make automobiles more efficient, for example. Thus, the economic benefits of finding higher efficiency TE materials would be large. A conservative estimate is that the world market for efficient TE materials alone (at current TE materials prices) is billions of dollars per year. If one includes the value added to systems including the TE devices, such as home refrigerators or computers and many new applications, the economic impact could be huge. Here I discuss the current status of research to improve the materials used to fabricate TE devices.

Improved Devices

A schematic of a TE cooler is shown in Fig. 1A. Currently available devices are made by joining two doped semiconducting materials together, one *n*-type and the other *p*-type. If a current flows from the *n*-type material to the *p*-type, the dominant carriers in both materials move away from the junction and carry away heat. The junction thus becomes cold because the electrical current pumps heat away from the junction. This effect was discovered in 1834 by Jean Peltier, a French scientist. The heat flow (dQ/dt, measured as energy per second) away from the junction is equal to the magnitude of the current (I) times the Peltier coefficient (Π), so that $dQ/dt = \Pi I$. If there are no heat inputs to the junction, the junction temperature must decrease. If the materials are chosen carefully, Π will be large enough to produce significant cooling (temperature drop of ~50°C). Such a device can also be used to generate electricity when the junction is intentionally heated. In this case, the heat is partly transported by the flow of the electrical carriers from the junction to the base, which generates a voltage between the two ends of the device (Fig. 1B).

In addition to the heat flow away from the junction in a TE cooler, there are heat generation effects to consider. Driving electrical current through the device causes the familiar

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