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Hydrodynamics: the key to space age materials?

Robert Gallagher reports on the development of new materials that can withstand extreme heat and radiation. The method dates back to Leonardo da Vinci!

In order to advance basic industrial processes and enter the age of plasma technologies, to colonize the Moon and Mars, we must develop new materials that can withstand higher energy flux densities than existing metals and ceramics. The next era in metals-refining technologies, may require materials that can withstand the flow of ionized metal ores and their constituent elements, over their surfaces at process temperatures up to 5,000°C. Existing industrial processes operate at maximum temperatures of about 1,600°C, such as in Basic Oxygen Process steel refining.

To make space travel a routine affair, we need lightweight structural materials that are as strong as aluminum or steel and yet can withstand the high energy flux densities of reentry from space into atmospheres at hypersonic speeds; we need "radiation proof" materials for shielding nuclear propulsion systems or protecting spacecraft from ultraviolet and gamma radiation, and insulators for spacecraft to investigate stars and "hot" planets.

To date, the drive for new materials has come from the National Aeronautics and Space Administration (NASA) and the military services. Development of the NASA Space Shuttle, which requires modern ceramics for reentry into the atmosphere, has pushed through the engineering of advanced materials. Without the programs sponsored by NASA and the Department of Defense (DoD), we would be unable to introduce the plasma technologies desperately needed to accelerate metals production and infrastructure development, into the world economy. Already the Shuttle ceramics program has yielded materials for the next-generation supersonic transport and for flexible rocket nozzles for the Strategic Defense Initiative program.

This article will review three ceramic materials developed by NASA and the DoD, from the standpoint of the fundamentally *hydrodynamic* nature of the properties of the crystals that lie at the basis of their success. When materials fail, it is because they cannot hold up under the specific conditions of the "turbulent" flow of gas, liquid, or solid over the material surface.

The problem of Space Shuttle reentry illustrates the general requirements for new materials. Reentry poses a problem for a spacecraft for two reasons:

1) The craft must fly from a region of space where there is no significant gaseous medium surrounding it, into the atmosphere, and make the transition from mere ballistic flight in orbit, to aerodynamic flight;

2) The craft must make this transition at high speeds. Shuttle reentry occurs at 27 times the speed of sound.

Were the spacecraft somehow able to reenter the atmosphere at 25 miles per hour, reentry would not expose the spaceship to hazards; in this hypothetical case, the vehicle would ease its way into the atmosphere, and its exterior could simply be composed of aluminum; unfortunately, this technique would require tremendous expenditure of fuel to slow the descent of the craft, fuel that would have to be carried aloft in launch from Earth, tremendously increasing the size of the launch vehicle and boosters, minimizing the payload, with the result that the method is impractical.

It is the necessary hypersonic speeds of reentry that make the transition from space flight to atmospheric flight so difficult, because the surface of the vehicle makes a rather sudden transition from a force-free orbit to immersion in supersonically streaming gas. By analogy, we might imagine the conditions that would confront a seaplane, were it to attempt an ocean landing at the speed of sound.

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Vought Corp.'s Reinforced Carbon-Carbon, a gray material, protects the Space Shuttle's nosecap and leading edges of its wings.

Vought Corp.

Thus, the ability to withstand such abrupt changes in surface boundary conditions, is a requirement for space-age materials. Because the Shuttle reenters at supersonic speeds, shock fronts form along all of its leading surface edges, such as the forward edges of the wings and the nosecap. Because its speed is hypersonic (many times the speed of sound), the Shuttle ionizes the gases it passes through, and a sheath of ionized gas or plasma forms around the surfaces exposed to the highest energy flux densities. These surface areas are subjected to temperatures up to 1,540°C, and must withstand an energy flux of about 600,000 watts per square meter for several minutes.

A fundamental concept for understanding the action of a fluid upon a material surface, is that of "surface of discontinuity," developed by Leonardo da Vinci (1452-1519), and elaborated by German hydrodynamicist Ludwig Prandtl early in the 20th century (see box). For materials considerations, the "surface of discontinuity" is a boundary of stationary fluid around a body, whose integrity affects whether or not the flows that a surface is subjected to, can damage it. Prandtl, the man who developed the principles of aerodynamics that made supersonic flight possible, explained:

> Right at the body . . . the fluid does not move relative to it. . . . Surrounding the surface of the solid body there is a thin layer where the velocity gradient generally becomes very large, *so that even with very small values of the velocity the shear stresses assume values that cannot be neglected.* (*Applied Hydro- and Aeromechanics*—emphasis added)

If the velocity of the streaming gas is hypersonic relative to the surface, as in the case of the Shuttle, "the shear stresses," i.e., the energy flux delivered to the surface at the apex of the shock front, becomes enormous. The surface of discontinuity itself begins to rotate, until finally, the flow over it rips the fluid boundary layer off the surface, in some cases, carrying part of the solid surface with it. In subsonic flow, such "turbulence" appears in the back of a vehicle; in supersonic flow, it appears along its leading edge. Thus surface materials for hypersonic flight must be designed with hydrodynamic properties to remove this energy from these areas.

In this report, we focus on materials with properties that enable them to withstand three types of intense hydrodynamic action (i.e., energy flux density): thermal shock, intense flashlamp radiation, and hypersonic atmospheric reentry.

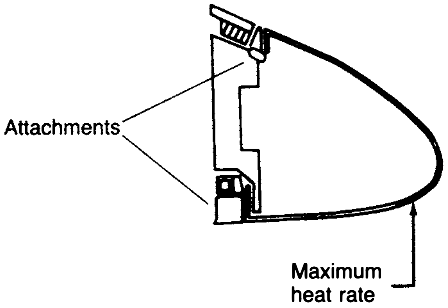
Coherent organic ceramics

The material on the surfaces of the Space Shuttle that withstands the highest energy flux, is a carbon-graphite composite ceramic, called "Reinforced Carbon-Carbon," developed in the late 1950s by the Vought Corporation for the U.S. Air Force and which, on the Shuttle, is at most a half-inch thick.

The material has the property that it distributes energy from the hottest portions of its surface to the cooler portions, through coherent hydrodynamic action in the form of vibrations of its crystal lattice. Its heat conductivity is asymmetrical: The material transmits energy preferentially in the direction parallel to its surface, rather than inward toward the aluminum structure of the orbiter's wing, and thus acts as a waveguide, dissipating energy building up on the leading edge of the surface of the wings. The thermal conductivity

FIGURE 1

Shuttle wing's edge designed to dissipate heat



The coherent transfer of heat over the exterior surface of a carbon-carbon composite panel on the Space Shuttle, dissipates energy from those areas subjected to the most intense heat of reentry, and at the same time enables temperatures to be low enough where metal attachments join the panel to the Shuttle, so that they do not melt.

Source: D. M. Curry, J.W. Latchen, G. B. Whisenhunt, "Space Shuttle Orbiter Leading Edge Structural Subsystem Development," presented at AIAA 21st Aerospace Sciences Mtg., Reno, Nevada, Jan. 10-13, 1983, AIAA Paper No. 83-0483

along the surface of the panels is 57% greater than its conductivity perpendicular to or through them.

As a result of this property, it is possible to attach the panels to the orbiter with metal fasteners that will not melt, because they can be located far enough away from the hottest regions of the panels, so that the places they must attach to are cool enough (**Figure 1**). The temperature of the inside surface of the panels is always lower than that of the directly opposite outside surface.

Reinforced Carbon-Carbon (RCC) has the additional property characteristic of graphite that it actually becomes stronger at higher temperatures; conditions adverse to most room-temperature materials strengthen and raise the "energy of the system" of these panels on the Shuttle, so that it is actually stronger during reentry than when the Shuttle is on the ground. This organic material covers 410 square feet on the orbiter's exterior. Vought is now using RCC to fabricate prototype turbines for a supersonic turbojet transport. In *Modern Ceramic Engineering* (Dekker, New York, 1982), D. Richerson proposed the use of materials similar to RCC for lining industrial furnaces. In fact, many existing designs for plasma furnace, propose graphite as a refractory material.

Ceramic engineers are beginning to recognize in their empirical work, that hydrodynamic concepts, such as wave propagation, are useful for describing the physical principles underlying advanced materials. For example, thermal conductivity, the rate of increase in energy flux density through a material per degree of temperature, is a hydrodynamic property dependent on the vibrational characteristics of a material, and is critical to the functioning of Reinforced Carbon-Carbon on the Space Shuttle. Richerson uses hydrodynamic concepts in his discussion of it:

> The [energy] carriers [in heat conduction] are electrons or phonons, where phonons can be thought of simply as quantized lattice vibrations. The amount of dissipation is a function of [wave] scattering effects and can be thought of in terms of attenuation distance for the lattice waves. . . . In ceramics the primary carriers of energy are phonons and radiation. . . . For crystalline ceramics . . . lattice vibrations are the primary mode of heat conduction.

Indeed, Leonardo recognized vibration as a fundamental hydrodynamic property, and used simple water waves as a straightforward example (see box).

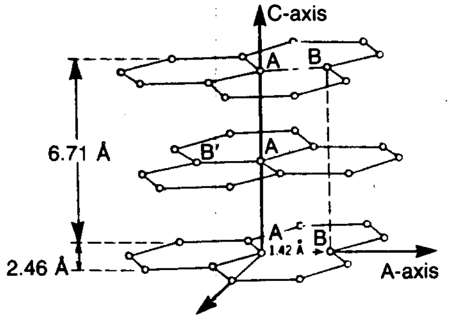
The property of asymmetric thermal conductivity, is a fundamental characteristic of graphite. Its crystal structure, shown in **Figure 2,** gives some picture of the basis of this asymmetry. Richerson writes:

> Because of its layer structure, graphite is anisotropic [it exhibits preferred directions for thermal conductivity—ed.]. Within the layers the bonding is strong and periodic and does not result in severe scattering of thermally induced lattice vibrations, resulting in high thermal conductivity in this direction (8.4 W/cm°K). Only weak van der Waals bonding occurs between layers, and lattice vibrations are quickly attenuated, resulting in much lower thermal conductivity in this direction (2.5 W/cm°K).

Some pyrolytic graphites have a thermal conductivity in the A-crystal direction 100 times that in the C-direction (**Figure 2**).

FIGURE 2

The asymmetry of graphite



This drawing of a graphite crystal lattice illustrates its asymmetry, the reason that energy is more rapidly transmitted in the plane parallel to the carbon rings (the "A-axis"), than perpendicular to them (the "C-axis").

Source: J. E. Hove and W.C. Riley (eds.), *Ceramics for Advanced Technologies,* Wiley, New York, 1965

In other respects, graphite approximates an ideal material. It becomes stronger with increasing temperature, and is lighter compared to other refractory materials. It possesses a high strength to weight ratio.

The extremity of hydrodynamic conditions or magnetohydrodynamic conditions—e.g., plasma conditions in the case of the Shuttle—that a material must withstand, are the appropriate definition of the temperature it tolerates. In all high-temperature environments, materials must withstand streamings across a solid-gas, solid-liquid, or solid-solid boundary layer.

Materials as waveguides

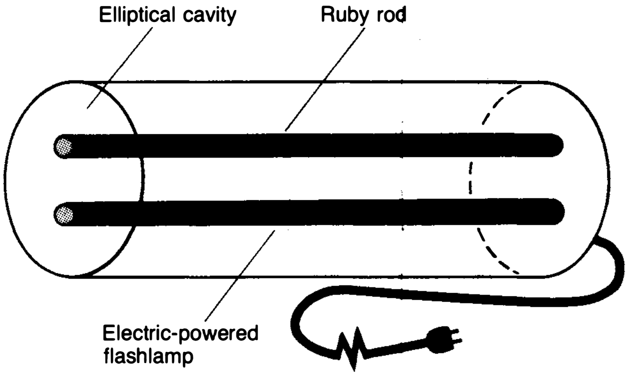
Materials *themselves* must also have appropriate hydrodynamic characteristics, as illustrated by the case of the Shuttle carbon-carbon composites. If the science of hydrodynamics applies to gases and liquids, then it must also certainly apply to solids, and be able to inform us in our search for new materials. Although a solid may perhaps be an extreme force-free configuration of matter, the classic example of a singer whose voice shatters glass, shows that solids are by no means free from hydrodynamic effects. Solids are only slow-moving liquids, or as Leonardo wrote, they are the "residuum" of fluids. The existence of mountain ranges ("wave crests"), testify that the movements of the continents is hydrodynamic as well. The vibrational waves of heat and sound flow through solids as they do through liquid and gas, and in fact, simple waves in solids display the same characteristics as simple water waves, in so far as they do not transport matter. These hydrodynamic characteristics of solids are fundamental to the production of coherent light by solid-state lasers. Leonardo recognized that light, heat, sound, and water waves were all cases of the same fundamental "hydrodynamic" phenomenon.

The development of solid-state lasing dealt with serious materials problems that required hydrodynamic solutions. A solid-state laser consists of a rod of ceramic material about 6 mm in diameter, with a small amount of the so-called dopant atoms, such as chromium, which emit coherent light when excited by a flashlamp (**Figure 3** shows a schematic diagram of solid-state laser). It was necessary to engineer materials whose crystals would guide the flashlamp light output onto the dopant atoms, yet withstand an intensity of flashlamp radiation on the order of the energy flux density of a blast furnace in order to produce laser light at significant power levels. Materials without these characteristics fracture under the intense flashlamp radiation required. Solid-state laser materials also have to be transparent to the wavelength of light emitted by the dopant, so that the laser power would not thereby be diminished.

The first significant breakthrough in this area, was the development of synthetic ruby, a form of the aluminum-oxide mineral corundum which occurs in nature, doped with chromium. Ruby absorbs blue-green light very well and strongly couples to a xenon flashlamp, and is transparent to the wavelength at which chromium lases as a ruby dopant. But it also has a high thermal conductivity with which to dissipate energy, and is transparent to a wide spectrum of the infrared—properties which increase its fracture-resistance.

FIGURE 3

Elliptical focusing in solid-state lasers



In modern solid-state lasers, an elliptical cavity concentrates the output of an electric-powered flashlamp, located at one focus of the ellipse, upon the ceramic laser rod located at the other focus. The ends of the laser rod are finely machined so that one acts as a mirror, and the other as a semi-transparent mirror, through which the light beam generated passes.

All solid-state lasers developed since ruby are made out of crystalline ceramics. They are rated in mum continuous power in watts that they can absorb per centimeter of length without fracturing. It is precisely this property that determines the maximum power output of a solid-state laser, and that determines that the power output of a continuously operating solid-state laser, is considerably lower than that of a pulsed one. When the energy flux density of the pumping exceeds this carrying capacity of the waveguide, the waveguide breaks down, and fractures.

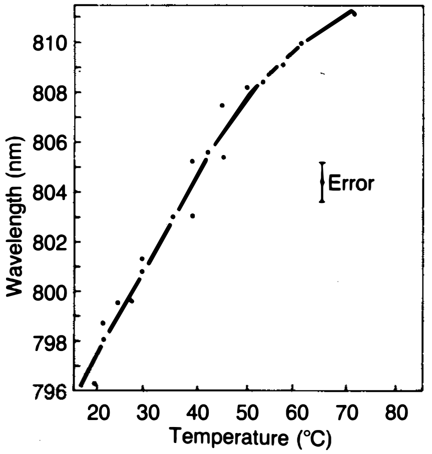
Tunable waveguides

Solid-state lasers like ruby are useful for producing a specific wavelength of laser light, and have found many applications. However, many industrial and aerospace applications require laser sources that are tunable, lasers in which it is possible to continuously modify the emission wavelength by using some property of the lasing medium.

Laser chemistry requires tunable sources of coherent light, since the excitation of distinct chemical reactions requires distinct wavelengths of light. A tunable laser provides an excellent tool for studying the spectroscopy of matter, that is, the wavelengths that a substance absorbs and emits when excited by a light source. This application is the basis of designs for laser radars for the Strategic Defense Initiative program. A tunable laser system can determine, from the backscatter of different wavelengths of light off a target, just what the molecular composition of the atmosphere is along

FIGURE 4

Emission wavelength of alexandrite varies with temperature



Alexandrite lasers show that heat is a form of electromagnetic action. The wavelength of light output by alexandrite solid-state lasers, can be varied by changing the alexandrite crystal temperature and hence its vibration, demonstrating that hydrodynamic effects are fundamental to the operation of the device.

Source: J. Walling, "Alexandrite Lasers," *Laser Focus*, Feb. 1982

the path to the target, providing important data for laser defense targeting systems.

Solid-state laser ceramics do have a property which yields tunable solid-state lasers from some materials, although not in ruby. In acting as a waveguide for flashlamp radiation in solid-state lasers, the ceramic crystal determines, in a way specific to each, the precise laser emission wavelength within a range determined by the dopant. This is because the energy transitions that produce coherent light involve not only the so-called electronic transitions of the dopant, but also involve, to some degree, the hydrodynamic, or vibrational characteristics of the crystal lattice. This is indicated by the fact that the same energy transition in chromium will produce different wavelengths of light, depending on the characteristics of the crystal in which it is imbedded. In ruby, the ^{2}E energy transition of chromium produces laser light at 694 nanometers; in alexandrite, a compound of ruby and beryllium oxide, the same transition produces light at 680 nm. (One nm is one billionth of a meter.)

To produce tunable solid-state lasers, what was required was a closer coupling between these vibrations of the crystal and the emission of the dopant. In a class of solid-state lasers known as *vibronic,* tunable vibrations of the ceramic crystal lattice, permit continuous tuning of the laser emission wavelength over a broad range. A group of laser physicists at Allied Corp. wrote: "The stimulated emission of photons is intimately coupled to the emission of vibrational quanta (phonons) in a crystal lattice. In these 'vibronic' lasers, the total energy of the lasing transition is fixed, but can be partitioned between photons and phonons in a continuous fashion." In the case of Allied's alexandrite laser, this property enabled development of a solid-state laser, continuously tunable over the range of 700-818 nm.

Confirming the close relationship between heat and coherent light, alexandrite's emission wavelength is tunable by varying the temperature of the crystal (**Figure 4**). The close coupling between light (photons) and heat or vibrational energy (phonons) in alexandrite, clearly demonstrates that light, heat, and sound are each forms of electromagnetic action.

In addition to displaying the vibrational hydrodynamic

Leonardo da Vinci and the hydrodynamics of surfaces

The concept of "surface of discontinuity," conceived by Leonardo da Vinci and elaborated hundreds of years later by German hydrodynamicist Ludwig Prandtl (1875-1953), provides a valuable framework for investigating the action of flowing gases, fluids, or solids, over a material surface. The "surface of discontinuity" is a boundary of stationary fluid around a body, whose integrity affects whether or not the flows that a surface is subjected to, can damage it.

Leonardo and Prandtl both established that the formation, development, and characteristics of the "surface of discontinuity" between fluids, gases, and solids, are fundamental to determining the subsequent evolution of hydrodynamic action. Dino de Paoli provides a detailed account of their work in "Leonardo da Vinci and the True Method of Magnetohydrodynamics," in the January-February 1986 issue of *Fusion*.

Using water surface as an example, Leonardo discussed how the surface of discontinuity is distinct from both substances it separates:

> The surface of a thing is not part of it. . . . It must needs be therefore that a mere surface is the common boundary of two things that are in contact: Thus the surface of water does not form part of the water, nor does it consequently form part of the atmosphere. . . . What then divides water from air? There should be a common boundary which is neither air nor water. . . . Therefore they are joined together and you cannot raise up or move air without the water. . . . Therefore a surface is the common boundary of two bodies which is noncontinuous and does not form part of either. (Arundel Collection, 159v)

properties of simple water waves that do not transport matter, waves akin to shock waves that *do* transport matter occur in solids in crack propagation or fracture. Although cracking appears to occur "instantaneously," it actually propagates through a material at a measurable rate. Since such waves are catastrophic for a machine part—for example, fracture of a ruby rod under high intensity flashlamp radiation—it is a priority to find a solution to such destructive shocks. The solutions discovered to date are hydrodynamic in nature.

One type of such destructive waves occurs when materials are subjected to "thermal shock," that is, cooling from high temperatures, resulting in the material passing through one or more crystalline phase transformations which can each produce cracking. Strengthening materials against thermal shock, or against other uncontrolled effects of phase transformations, is the focus of much research, and is referred to as "transformation-toughening."

Ceramic refractory brick in iron and steel furnaces provides a good example of *poor* thermal shock resistance. The purpose of refractory brick is to reflect as much heat as possible back into the furnace, and at the same time to present a low enough temperature to the steel shell enclosing the brick walls, that the furnace is not destroyed. Obviously, the brick must be stable at high temperatures.

Prandtl applied this principle to the study of the flow of fluids over surfaces. He wrote:

> Surrounding the surface of the solid body there is a thin layer where the velocity gradient generally becomes very large, so that even with very small values of the velocity the shear stresses assume values that cannot be neglected. (*Applied Hydro- and Aeromechanics*, Dover, New York, 1934)

These "shear stresses" are expressed in vortex formation:

> any small internal friction changes the discontinuity in velocity into a gradual transition in a layer with rotation. In the domain in which this continuous change takes place we have a layer of vorticity formed out of vortex filaments. . . a surface of discontinuity may therefore be considered as a surface distribution of vortices, i.e., a vortex surface. (*Fundamentals of Hydro- and Aeromechanics*, Dover, New York, 1934)

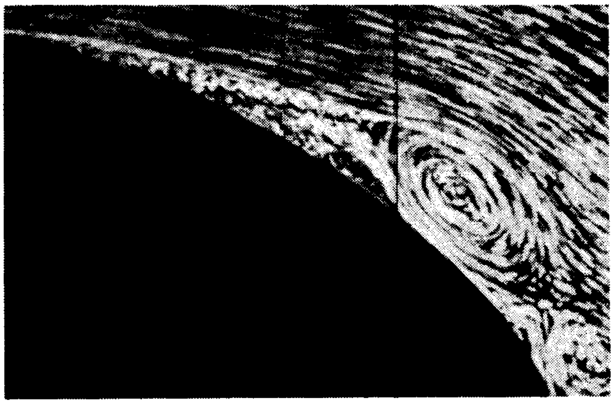
The effect is that the surface of discontinuity itself begins to rotate, until finally, the flow over it literally *rips* the fluid boundary layer off the surface, in some cases, carrying part of the solid surface along with it. The figure shows a "vortex surface" in the movement of water around a cylinder, just before the boundary layer is torn off. The high frequency vortices that flow over surfaces subjected to high energy flux, illustrate why a wavelength can always be associated with a given energy flux density.

Leonardo also recognized that the principal means of hydrodynamic energy transfer is vibration, i.e., wave action that does not transport matter:

> if you cast two little stones . . . in water, you will see two separate quantities of circles . . . which growing, come to encounter each other, one circle intersecting the other, always maintaining for centers the places struck by the stones. The reason is that although there is some evidence of movement, the water does not leave its location, because the opening made in it by the stones closes up again at once and this motion made by the sudden opening and closing produces a certain shaking, which can be called trembling rather than motion. . . . take heed of those straws which by their lightness stand on the water; notwithstanding the wave made under them by the coming of the circles, they do not leave their first locations. (Institut de France Ms. A 61r)

As the accompanying text documents, these are the hydrodynamic principles which underlie advanced industrial and aerospace materials.

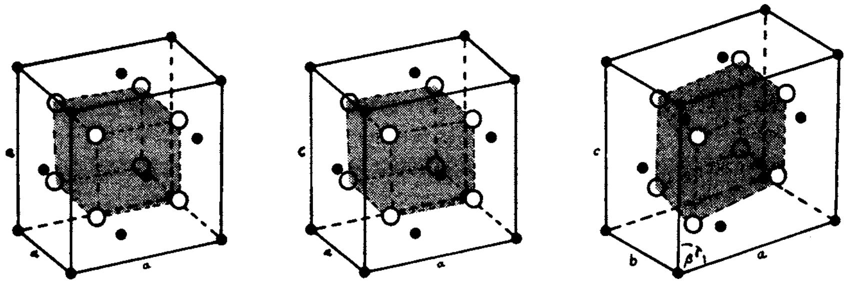
Rotation of boundary layer about a cylinder



This photograph shows a moment in the evolution of the surface of discontinuity on a cylinder into a "vortex surface," as water follows around the cylinder, just before the boundary layer is torn off.

L. Prandtl and O. Tietjens

FIGURE 5
Phase transformations in zirconia crystals



a) cubic b) tetragonal c) monoclinic

Crystal phase name	Shape	Temperature range (°C)
Zirconia		
Cubic	Cube	2,370–2,680[1]
Tetragonal	Rectangular solid	1,150–2,370
Monoclinic	Rectangular solid	R.T.–1,150

[1] Melting point
R.T. = room temperature.

Source: A. H. Heuer, "Fracture-tough ceramics: the use of martensitic-toughening in ZrO_2-containing ceramics," in *Frontiers in Materials Technologies,* 1985

Solid zirconium oxide (zirconia) can exist in three crystal shapes: cubic (a rectangular solid where all sides are squares); tetragonal (a rectangular solid where two sides are squares); and monoclinic (a rectangular solid where no sides are squares). Energy can transform once crystal into another. Mixing (alloying) other metal oxides with zirconia, permit solids composed of the high-temperature cubic form to exist at room temperature.

These zirconia solids can be strengthened against fracture by making them a mixture of cubic and tetragonal crystals. In response to the propagation of a crack through the solid, the tetragonal crystals are transformed into monoclinic crystals. This transformation of the medium in which the crack propagates, halts it. In the diagrams, the small filled circles are Zr; the large open circles are oxygen.

Basic Oxygen Process (BOP) steel furnaces are lined with two layers of brick to protect the furnace. Both layers are made from magnesium oxide impregnated with tar or pitch. But once the lining is burnt into the BOP furnace in start-up, it is stable *only* at high temperatures. If a furnace is shut down, in cooling the ceramic brick passes through a thermal-shock-induced phase transformation, and crumbles into fragments. To restart the furnace, it must be relined. The example shows why a primary concern of materials engineers, is to develop light, "transformation toughened" materials. To date, most work on transformation toughening in ceramics has investigated the properties of various zirconium oxide (zirconia) alloys.

The heating of a zirconia part to high temperatures, results in the formation of a symmetric cubic crystal lattice. As the material cools, it passes through two phase transitions to less symmetric tetragonal and monoclinic crystal forms (**Figure 5**), and cracks into pieces, or crumbles to powder due to the effects of thermal shock, before reaching room temperature. Two techniques are used to stabilize the high temperature cubic form of the material for use in a wide range of temperatures, and strengthen it against fracture.

'Transformation toughening'

1) Addition of a small percentage of a number of metal oxide solvents (such as magnesia, calcia, yttria, and other rare earth oxides), stabilizes the cubic form, so that it may be used at room temperature. However, stabilized zirconia has poor fracture strength.

2) By decreasing the amount of metal oxide solvent added to zirconia, i.e., stabilizing it only partially, zirconia may be made into a metastable composition of predominantly cubic crystals and rectangular tetragonal crystals. The vibrational stress of a crack propagating in this ceramic alloy, induces a transformation wave of tetragonal crystals into monoclinic, that propagates with the crack, changing the character of the medium the crack is propagating in, and halting it. It is as if the transformation wave nullified the fracture wave. As a result, fracture does not occur, only microcracks. In this case of transformation toughening, a built-in phase transformation wave toughens the material against phase transformations that occur as a result of intense energy flux density. This alloy of cubic and tetragonal zirconia, has been called "partially stabilized zirconia" (PSZ). Ceramics engineers refer to the addition of the metal oxides solvents and/or the tetragonal zirconia crystals as "doping" the host cubic zirconia crystal.

Work at Cummins Engine Co. in Columbus, Indiana, has demonstrated the superior qualities of this transformation-toughened zirconia. Cummins is testing various materials, for use as insulators in the U.S. Army program to develop an adiabatic diesel engine. Cylinder liners made of fully stabilized zirconia developed multiple cracks during testing. Replacement liners made of PSZ survived extensive tests without cracking.

In another example of PSZ's superior qualities, metal dies for extrusion of brass rod usually require rework due to bore wear, after only 10 to 50 extrusions. Dies made from the partially stabilized zirconia have lasted, without rework, for over 6,000 extrusions of 1.9 cm-diameter bar, extruded from 30.5 cm-diameter billets at 900°C.

The tetragonal-to-monoclinic transformation is called "martensitic," after a similar stress-induced crystal transformation that occurs in the strongest carbon steels. A propagating crack pumps energy into the local crystal medium, which in turn undergoes this martensitic transformation, reordering the local medium so as to neutralize the crack. *Without the energy supplied by the propagating crack, the martensitic transformation wave of tetragonal to monoclinic zirconia, would not occur.* There is a "barrier" in the form of an amount of energy required to produce the transformation. A. H. Heuer of the American Ceramic Society has written:

> The mechanism responsible for [PSZ's] superior properties . . . is the stress-induced martensitic transformation of these tetragonal particles to monoclinic symmetry in the stress field of a propagating crack. . . . A well developed transformation zone ('wake') [is found] around arrested cracks. . . .

And elsewhere,

> If [the stress] exceeds a critical value, the nucleation [transformation to a monoclinic structure] is barrierless. . . . Once nucleation occurs, growth velocities of martensitic interfaces can approach the speed of sound.

This ability to hydrodynamically neutralize shocks, is probably not a unique property of zirconia. The generalization of this form of transformation toughening to other ceramics, was recently discussed by Heuer:

> Transformation toughening in ceramics . . . should not be confined to ZrO_2 containing ceramics—all that is required is an irreversible stress-induced transformation . . . ZrO_2 from its melting point at 2,680°C to approximately 2,360°C exists in a face centered cubic structure. . . . This structure type is quite common for a significant number of oxides, including HfO_2, ThO_2, many rare earth oxides, UO_2, etc.

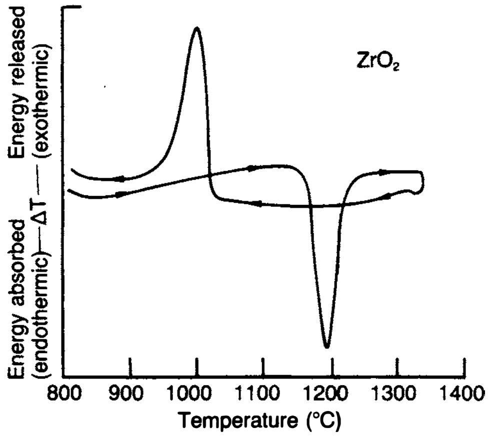
Energy transformations

Although energy is required to produce the martensitic transformation, or to move from any crystal phase to another, once movement from a higher to a lower energy states occurs, energy stored in achieving the higher energy state is released. (**Figure 6** shows the energy absorbed or released in one such phase change.)

As zirconia is cooled, it descends the ladder of energy levels, and it gives off energy in the form of heat and sound. D. R. Clarke measured the acoustic emission in cooling a solid pellet of pure, unstabilized zirconia from 1,400°C through the martensitic, tetragonal to monoclinic phase transformation.

FIGURE 6

Solids possess energy levels



The graph shows energy absorption and emission in the tetragonal-monoclinic phase transformations of zirconia. Transformation of one crystal configuration of a solid substance into another, requires either the absorption or emission of a large amount of energy. Thus distinct crystal states correspond to distinct energy levels.

Source: D. R. Clarke, "Acoustic emission characterization of the tetragonal-monoclinic phase transformation in zirconia," in *Science and Technology of Zirconia II, Advances in Ceramics*, Vol. 12, American Ceramic Society, Columbus, Ohio, 1984

> As the pellets were cooled from the sintering temperature, no acoustic emission was detectable until 1,160°C [compare this with the phase transformation graph of **Figure 6**], when "burst" type of emissions . . . were observed. . . . The temperature at which the abrupt increase in emission occurred corresponded with the temperature of the tetragonal to monoclinic transformation.

This energy loss expresses itself as a degradation in the dynamic strength of the material, as a decline in the "energy of the system."

The distinct crystal phases of zirconia and other materials correspond to distinct energy levels or wavelengths, that serve as distinct degrees of freedom in the fabrication of ceramic products, and in the self-reorganization of a material under stress. The fact that only certain crystal phases are allowed by nature, reminds us of the fact that in the solar system there are only a finite number of force-free planetary orbits.

We have seen that, deliberately or not, modern materials science is dependent on hydrodynamic phenomena for its success. Perhaps a more deliberate application of these principles discovered by Leonardo da Vinci and elaborated by others, would lead to useful results.