Refractron

What is Izory ®?

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Historical Perspective

Ronald Garvie and his team of researchers in Australia developed partially (P) stabilized (S) magnesium (Mg) zirconia (ZrO2), Mg-PSZ, in the 1970's and named it "ceramic steel". Materials science researchers worldwide followed quickly with numerous technical publications involving zirconia-based ceramics. Studies stretched well into the 1990's. Among the best is "Science and Technology of Zirconia", volumes I-V. Since then, scientific fervor has slowly diminished seemingly because Mg-PSZ is perceived to be an "old technology". Arguably, that might be so but significant engineering challenges remained and do so to date. Structural applications were slow to develop for many reasons. Designers were unaware of Mg-PSZ, did not understand its advantages or were reluctant to use it because ceramics, unlike most metals, fracture easily, i.e. they "break". The term, "ceramic steel", in fact, precisely combats this perception. Also, highly demanding industrial technologies that might benefit from use of Mg-PSZ were not yet mature and, in turn, commercial sources for the ceramic remained limited. Finally, if a ceramic was actually required, designers always turned to the well established and readily available alumina, Al2O3.

Metallurgists had long established and harnessed the concept of "transformation toughening" and "transformation-assisted strength" for steels wherein the mechanism is a transition from a higher density, smaller volume crystalline phase to one of lower density and larger volume. This transition, termed "martensitic", can occur under an applied load or stress. A propagating crack is blunted by volume expansion with absorption of energy to impart resistance to fracture or "fracture toughness" (Kic). Garvie et al., realizing that the same mechanism was applicable to Mg-PSZ, developed unique ceramic processing to develop it. The key to their process was to establish and maintain in the microstructure a substantial volume fraction of the higher density crystalline phase of zirconia having tetragonal symmetry (T) during cooling of densified ceramic from elevated temperature. The T-phase crystallites were required to be of nanometer size and to be constrained in the ceramic matrix. Normal transform to the lower density monoclinic (M) variant on cooling would be avoided but could occur at and near room temperature by applied loads. By increasing overall toughness, fissuring from internal stresses due to unavoidable ceramic processing flaws such as pores and minor impurity phases also would be minimized.

Another branch of zirconia science emerging by the 1980's appreciated that a martensitic transition is possible by incorporating yttrium oxide (Y2O3) in place of MgO into the crystal structure of zirconia. This method required a special powder, however, rather than one prepared from the oxides by conventional ceramic processing. For scientific reasons beyond this scope, the powder had to consist of crystallites well below submicron in size and of high surface area so that when densified to ceramic at elevated temperatures the higher density T-phase would not transform appreciably to the larger volume M-variant on cooling and destroy parts. One way to produce this raw material is by a low temperature chemical method using precursor compounds of zirconium and yttrium. Another method is to melt volume quantities of the oxides, > 2500C, using an arc-furnace and then to treat the chemically homogeneous crystalline product for use by subsequent proprietary methods. Although many chemical routes are possible, all yield only small quantities that are ideal for laboratory studies but not for the volume production needed to make the ceramic commercially viable. Here, Tosoh in Japan (and later others) filled the void with their process by the 1980's and YTZP (yttrium tetragonal zirconia phase) became a ceramic reality.

Today, several companies in the USA market structural ceramic products. Refractron Technologies, Inc. (RTC) produces YTZP but specializes in Mg-PSZ of two types: standard grade Izory and Izory-X that is designed for applications requiring low internal and external surface concentrations of defects such as pores.

Mg-PSZ, Features and Benefits

Microstructure and Processing:

The microstructure of both Izory types seems abnormal and not especially aesthetic when compared to a customary fine-grained, high strength ceramic. It consists of large domains, 50-80 microns in size, of the cubic (C) variant of zirconia. Intergrown are nano-size lamellae of T-phase normally resolved by TEM or high resolution SEM. Some M-phase develops mostly at domain boundaries. Izory has a density of 5.75 g/cc while Izory-X ≥ 5.80. The former is quoted as a typical spec by almost all manufacturers. Since Mg-PSZ powder requires an organic binder to retain strength after pressing to shape and often to green machine, it generates open porosity during burnout on firing that contributes to defects when final density is attained at elevated temperatures. Although mechanisms are beyond this scope, the result is lower density and strength (MOR). Binder used for Izory-X allows for higher density and MOR but the penalty is somewhat higher cost. Obviously, powder without binder can be used but oven drying of tons of powder is needed followed by dry milling. Subsequent handling and green machining of large pressed parts are impossible.

Engineering Challenges:

Apart from the binder issue noted above, the selection of raw materials, ZrO2 and MgO (or its precursors), from several sources is important. Purity, availability and cost are among driving factors. The pressed powder requires a firing temperature >> 1650C to attain high density. Normally, when ceramic parts are small, this is not a problem. Most applications to date, however, require much larger parts, many containing several kilograms of powder (for example, see photograph below). In turn, large kilns are needed to produce product in volume.

Given large loads of product stacked at multiple levels and, hence, high thermal loading of kilns, development of the heating and cooling cycle is crucial as all fired parts must attain the same unique microstructure and resulting properties.

Applications and Properties:

Alumina, metal alloys and tungsten carbide in the form of large tubes, rings, rods and spheres traditionally found use as structural products for oil and gas drilling, wire drawing and high speed can production industries worldwide. Pertinent applications require resistance to friction/wear to enhance service life, low mass and, of course, low lifetime cost. Oil and gas drilling, including fracking of sands and shales, uses mud pumps that circulate the abrasive fluid of rigs. Here, the structural material serves as a tubular sleeve that fits inside of a steel shell where it is subjected to contact with the fluids and an elastomeric or metal piston. In wire drawing, the material is used as capstans to pull the wire through dies at speeds that can exceed 6,000 feet per minute. Aluminum beverage can manufacturers use the material as tapered dies that sequentially “neck” the metal. Lines produce over 3,000 cans per minute. The latter two applications also use proprietary lubricants.

Initially, alumina replaced the metals and carbide in all industries because of its combination of lower mass, wear rate and cost. Eventually, YTZP, despite much higher cost (see below), replaced alumina for can production because of greater durability due to its very high strength and modestly better resistance to fracture. More recently, Mg-PSZ has made significant inroads in all three markets, dominating oil and gas drilling and wire drawing. Its increasing use is due to its property advantages that result in lower producer and user in-service costs. The table below compares the most important properties of structural Mg-PSZ, YTZP and alumina ceramics.

Izory and Izory-X have the best resistance to impact by far. This is because resistance to fracture, Kic, is about twice that of YTZP and almost three times better than alumina; hence, the term “ceramic steel”. Alumina chips and fractures easily during machining and during handling by producer and user precisely because of low Kic. The modulus of rupture, MOR, although less than YTZP, is far better than alumina. To attain higher MOR, however, YTZP is “hipped” at elevated pressure and temperature after conventional firing and this, apart from another factor, adds to substantially higher cost. Smaller YTZP parts for can tools can be hipped but larger mud sleeves and tubes for wire drawing in volume are not possible for technical and economic reasons. Mg-PSZ can be hipped when parts are small, but expensive, special equipment is needed.

Izory and Izory-X have the lowest hardness (Hv) but this is deceiving. Lower Hv combined with high Kic allows for faster, more aggressive machining to demanding tolerances that save labor costs. But, in addition, lower Hv provides for improved ceramic surface finish by machining/polishing operations. In turn, finer surface finish means less friction between the ceramic and moving components and longer service life. Less friction also is a consequence of another, often neglected but difficult to measure, application specific, feature of Mg-PSZ. It has been reported that its un-lubricated coefficient of friction, μ, when sliding with hard steel is the lowest among all oxide-based ceramics.

The lower abrasion resistance of Mg-PSZ shown is to be expected as the highest hardness, 30 micron alumina, is used on a traveling belt. Since wear via scratching dominates, it is obvious that alumina followed by YTZP shows better performance. However, this condition is not of practical importance for the applications discussed. In fact, wear resistance scales better inversely with the ease of machining noted earlier, i.e. Mg-PSZ the easiest; alumina the most difficult.

Cost to the producer and user also is buried in the densities. Given a fixed volume for a large structural part, more ceramic powder is needed for YTZP and Mg-PSZ. Raw material for alumina is the least expensive. Mg-PSZ raw materials are modestly higher and some cost is added due to the unique processing required. This differential, however, is offset by extended service-life for the user and by faster machining with high yield and lower labor costs for the producer. On the other hand, YTZP raw material is the most expensive by at least a factor of six, primarily due to costs associated with yttrium-based chemicals and to the unique processing routes required to produce the powder. The need to hip, where possible, adds substantially more cost.

In-Field Use

RTC Izory components have proven their cost-effective use versus alumina and metals for well over ten years in oil and gas drilling and for more than six years in wire drawing. Izory-X has been tested and used with success for more than four years as can tool dies.

Izory and Izory X, Future Outlook

Mg-PSZ is the ideal alternative structural ceramic for other markets where a lower cost, strong, tough product of low wear must be used. Many other industries also use large pumps, valves, dies and other components subjected to wear. Some require contact with flowing aqueous-based, sometimes particle-laden fluids. Others, as in chemical industries, involve warm to hot, potentially corrosive liquids and gases. Izory, for example, has tested well as valve material and in pumps for the aluminum-making Bayer process. Because corrosion resistance depends on numerous factors, it is impossible to predict performance of the ceramic. Thus, each application must be considered on a case by case basis, taking into account the likely need for a testing protocol before acceptance ■

Table I	*Izory®*	*Izory®X*	YTZP	Al_2O_3
MOR (MPa) ASTM 4-point	575	> 600	> 1400	350-400
Fracture Toughness, (Kic, $MPa\cdot m^{1/2}$) ASTM C-1421 Chevron Beam	10 to 12	10 to 12	5 to 6	3.5 to 4
Hardness Hv (Vickers) ASTM C-1327-08	1150	1250	1600	1800
Abrasion Resistance ASTM G174**	Good	Good	Better	Best
Density (g/cm^3)	5.75	5.80	6.08	3.90

** 30 micron alumina used without additives to lubricate