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Research in Fine Ceramics

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ABSTRACT

In the modern world, it is difficult to imagine how we could live comfortably without man-made products or equipment fabricated from advanced materials. In every day life, we use mobile phones, computers, etc. Even in our bodies we have false teeth, artificial lenses (in our eyes) artificial hip joints, synthetic heart valves, etc. In outer space, we have man-made satellites orbiting the earth and spacecrafts traveling into the universe.

Today, four types of materials are playing an important role in materials processing, those being metal, ceramics and polymers where a combination of at least 2 of these types forms what are called composites. Each type has its own prominent properties which are appropriate to its range of applications. Today’s ceramics are fine ceramics. In short, they are “solid inorganic nonmetal materials made by firing”. We can produce them by putting the atomic compositions of various elements together through scientific formulation and the sintering process. One may ask “what is the difference between classical ceramics? (bricks, porcelain and pottery) and fine ceramics”. There is a vast difference. The secret of fine ceramics is that their properties lie in their unique microstructure. They have fine tiny grains packed together, with each piece fitting in unison with another. Their grains and grain boundaries are all scientifically controlled. Each microstructure type generates specific physical reactions with electricity, magnetism or environmental changes. Classical ceramics on the other hand, are more porous and irregular.

Fine ceramics can be divided into 2 main groups namely “Functional Ceramics and Structural Ceramics” as is shown in Figure 1.

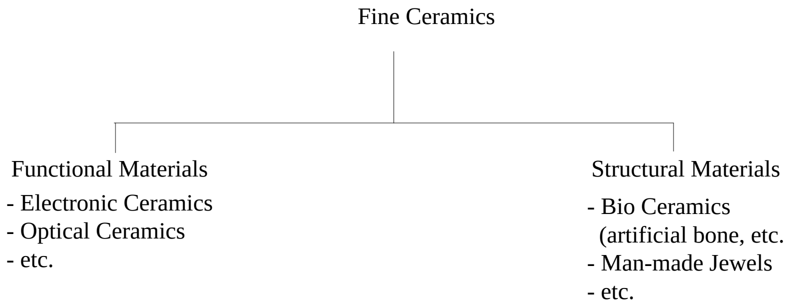


Figure 1 Classification of Functional and Structural Ceramics.

In this article, we shall confine our discussion only some of the 2 types of ceramics which are Electronic Ceramics and Bio Ceramics.

Electronic Ceramics

Electronic ceramics are classified by their electromagnetic properties as follow:

- Dielectrics
- Temperature Sensors
- Piezoelectric
- etc.

Dielectric Ceramics

If we look into a TV set, we will find hundreds of ceramics components fabricated in electronic circuits. Many of them are ceramic capacitors and filters. The technologies for manufacturing these components are well-established. Dielectric ceramics have long been very important electronic components since they have the capacity to store electricity in a short time scale using polarization. They are excellent materials for capacitors. Capacitors can perform many functions in electronic circuits, for example as by pass circuits or tuning circuits used in sustaining high voltages. (Moulson and Herbert, 2003 a)

An excellent material employed in many capacitors is barium titanate ($BaTiO_3$) based ceramics. These ceramics possess a very high dielectric constant (~20,000) with an exceptionally low electric loss (< 0.04) depending on their processing characteristics. Comparison of the dielectric constant of $BaTiO_3$ with other more conventional materials is shown in Figure 2.

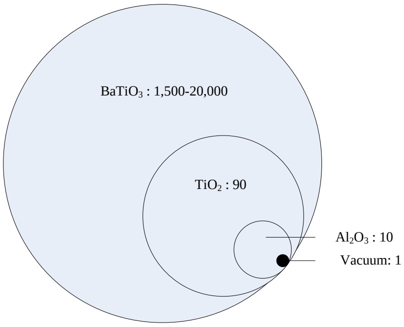


Figure 2 Comparison of the dielectric constant of various materials (Developedfrom Moulson and Herbert, 2003 b)

To date, many researchers are still working to develop giant dielectric constant materials (Intatha *et. al.,* 2008, Makchareon *et. al.,* 2011). However, the dielectric losses found in these samples are still quite high and are not good enough to be used in electronic circuits.

Temperature Sensor Ceramics (Thermistors)

There are 2 types of temperature sensor materials. The first type called positive coefficients (PTC) are ceramic semiconductors whose resistance experiences an abruptly increase when the temperature exceeds a certain level. This is achieved by properly designing the microstructure of these ceramics, i.e. arranging an obstacle in the grain and grain boundary. When the temperature reaches a certain level (the so called Curie temperature, T_C) the obstacle increases the resistance thereby stopping the current from flowing to neighboring grains. Practically, their resistance increases form 10^2-10^8 Ω.

The PTC effect can occur with specially doped and processed $BaTiO_3$. This effect has only been in ceramics (it does not exist in single crystal form). Attention here has been focused on the lanthanum-doped $BaTiO_3$ (BLT). Other donor dopants would be possible, e.g. yttrium (A-site) or niobium, tantalum or antimony (B-site).

Figure 3 shows a typical characteristic of the PTC thermistor (BLT). (Moulson and Herbert, 2003 c)

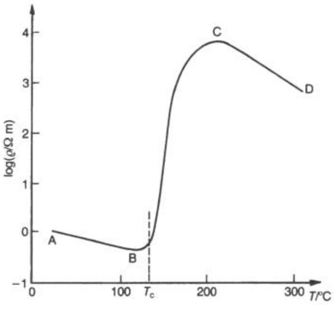


Figure 3 Typical characteristic of PTC thermistor material (Moulson and Herbert, 2003 c)

With proper dopants, the Curie temperature can be shifted up and down depending on the working temperature. (Moulson and Herbert, 2003 d) The PTC effects cannot be explained by standard Band Theory. Many observations have been made to explain the conduction mechanism of these PTC materials resulting in establishment of several theories (Heywang, 1961; Jonker, 1964), while other models are still being developed. (Cao and Kuboyama, 2009)

Another type of thermistors is the negative temperature coefficient (NTC). This effect can be explained using simple semiconductor theory to show that the resistivity of the materials decreases with rising temperature. The NTC effect has been widely used in medical applications such as clinical thermometer hypodermic needle probes. The materials employed are mainly oxides of nickel, manganese etc. with proper dopants. The characteristic of the resistance V.S. temperature relationship is shown in Figure 4.

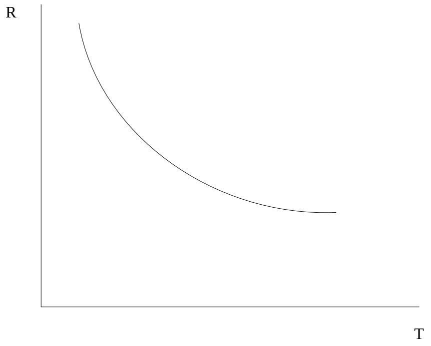


Figure 4 Typical characteristic of NTC thermistor material

Both PTC and NTC thermistors are already manufactured widely. For instance PTC are used as safe heating elements in modern passenger train heaters, curling irons electronic mosquito-repellent devices, while NTCs are used in temperature sensors, infrared ray sensors, etc.

Piezoelectric Ceramics

Some ceramics can expand or contract depending on the voltage applied to them. This effect is called the “direct effect” and is due to the structure of the materials. When a pressure is applied to them positive charges appear on one side and negative ones on another, inversely, when exposed to a tension, an opposite polarity occurs (indirect effect). Thus this kind of ceramic can convert electrical energy into mechanical energy and vice versa. These types of ceramic are called “Piezoelectric Ceramics”. Figure 5 shows these effects, both the direct and indirect effects.

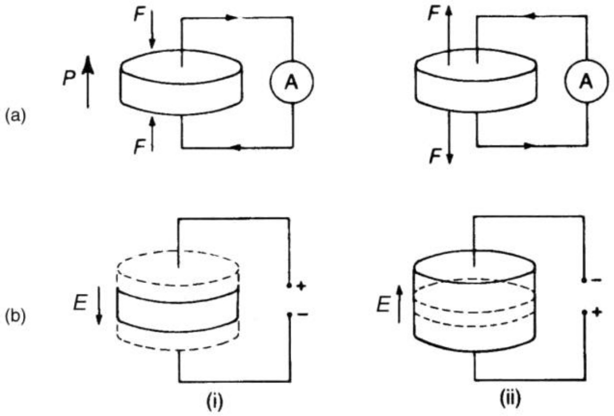


Figure 5 (a) The direct and (b) the indirect effects. The broken lines indicate the original dimensions. (Moulson and Herbert, 2003 e)

One of the most favored classes of piezoelectric ceramics are the lead zirconate titanate ($Pb(TiZr)O_3$, PZT) and other lead based materials, for instance, lead titanate (PT), lead zirconate (PZ), lead magnesium niobate (PMN) etc. These lead based materials exhibit an excellent ability to transform electrical energy to mechanical energy or vice versa and so are called "high coupling constant" materials which also have a high Curie Temperature, enabling them to used at high temperatures. These superior characteristics enable them to be used as ultrasonic cleaners, igniters, sonars etc. Hence they are widely manufactured in industry and sold in the world market. However, lead based materials are not environmental friendly due to toxicity of the lead vapor (during processing). Many researchers are now intensively working to develop lead free materials, for instance, barium zirconium titanate (BZT) (Jarupoom *et al.,* 2010) and barium titanium stannate. (Tawichai and Rujijanagul 2009) Nevertheless, the properties of these materials, i.e. piezoelectric properties, etc. are too low compared to that of lead based ceramics. The search for lead free materials with improved properties is still in progress.

Bio Ceramics

This section will focus on a general overview of bio ceramics including hydroxyapatite and other related compounds. During the past four decades, a revolution has occurred in the use of ceramics to improve the quality of life. This type of ceramic is especially designed for the repair, reconstruction and replacement of diseased or damaged parts of the body. These so called "bio ceramics" can be composed of alumina, hydroxyapatite, bioglass bioactive glass-ceramic or bio composite (polyethylene-hydroxyapatite). Ceramics are also widely use in dentistry as restorative materials, where they are referred to as dental ceramics (Preston, 1998). Other bio ceramics are normally used as implants to repair parts of the body, usually hard tissues of the musculo-skeletal system, such as bones, joints teeth. Though many ceramics compositions have been tested for use in the body (Hench and Ethridge, 1982), few have achieved advantageous enough properties to warrant human clinical application.

Generally medical materials (biological materials or bio materials are defined by Clemson Advisory Board as follow:

“A bio material is a systemically pharmacologically inert substance designed for implantation with or incorporation with living system”.

A bio ceramic requires the formation of a stable interface with the living host tissue. However, no material implanted in living tissue is inert. The living tissues always respond to the implanted materials. According to Hench (Hench, and Ethridge,1961) four types of responses can occur. (Table I)

Table I. Types of Implant-Tissue Responses (Hench, 1961)

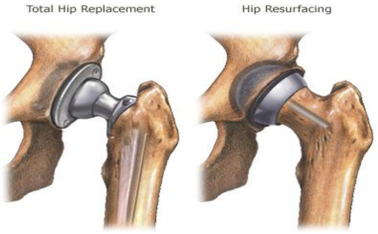
Toxic materials	Surrounding tissue dies
Non-toxic and biological inert	Fibrous tissue forms
Non-toxic and bioactive	Interfacially active forms
Non-toxic and dissolves	Surrounding tissues replace it

Therefore bio materials must have appropriate properties such as compatibility, non-toxic, inert and tough, optimized mechanical strength, optimal mass and density and and can be produced in large quantity at low cost (Wang and D. branzino, 2006; Narayan, 2009).

Some metal, ceramic and polymers which have been used as the bio-materials are as follow:

Bio-materials

Metal : Fe, Au, Ag, Pt, Ni, Mg
Ceamics: Alumina, Cerocium, Calcium Aluminate, Pyrolytic Carbon, Barium Titanate
Polymers: Polymethyl-methacrylate, Polyethylene, Polyacrylonitrile, Teflon, Nylon Silicone



Metallic Biomaterials
(from http://www.fda.gov/ucm/groups/fdagov-public/documents/image/ucm242627.jpg)

Ceramic Biomaterials
(from http://www.rjldentalceramics.com/page/our_product_range)

Polymer Biomaterial
(from http://www.biotextiles.wordpress.com/vascular-prosthesis)

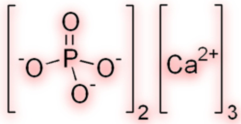
Figure 6 shows some bio-materials used as a replacement in the body

According to Davis (Davis, 2003), ceramics play an important role in replacing human organs. The desired properties of implantable bioceramics are summarized as follow:

Bio inert	alumina and zirconia
Reabsorbable	tricalcium phosphate
Bioactive	hydroxyapatite, bio-active glass and glass ceramics
Porous for tissue in growth	hydroxyapatite coat metal
etc.	

Among bioceramic materials, hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, has shown the most significant promise as a material which can improve the quality of human life. It is a ceramic with an excellent compatibility and bioactivity with the human body (Murugan and Ranakrishna, 2005; Kalita *et al.*, 2007; Banerjee *et al.*, 2007), which makes it a material of interest for medical applications. Moreover, porous HA ceramics can be used as a platform for controlling drug delivery systems. However, HA porous ceramics usually exhibit poor mechanical properties, such as fracture toughness, etc. Recently it was found that nanocrystalline HA offers an approach to overcome some limitations of conventional HA materials. Nanostructured HA materials can improve the sinter ability and densification due to their greater surface area which can subsequently improve their fracture toughness and other mechanical properties. Pure hydroxyapatite powders can be derived from natural bovine bone (Ruksujarit *et al.*, 2010). Employing the vibro-milling process nanoparticles of HA can be obtained, (Ruksujarit *et al.*, 2008) and the strength of the ceramics was found to increase due to a reinforcement of the nanorod HA, formed during sintering.

Calcium phosphate, $Ca(H_2PO_4)$ is also one of the most important materials. It can be used as artificial bone, as well as for solid or porous coatings on other implants. Calcium phosphate can be crystallized into hydroxyapatite and other compounds such as tricalcium phosphate, depending on its Ca:P ratio and the presence of water impurities and temperature. Calcium phosphate is an important raw material for the production of phosphoric acid and fertilizers. It is also a mineral salt found in rock and bones. Tricalcium phosphate is commonly used in porcelain and dental powders. It can also be employed as a tissue replacement for repairing bone defects. (Paderni *et al.,* 2009). There are two types of tricalcium phosphate i.e α and β having the formula of $Ca_3(PO_4)_2$. Ca/P molar ratio 3:2.



This ceramic can be used alone or in combination with a biodegradable, reabsorbable polymer such as polyglycolic acid (CaO and Kuboyama, 2009). Porous beta-tricalcium phosphate scaffolds can also be employed as a local drug delivery in bone (Kundu *et al.,* 2010). A combination of tricalcium phosphate and hydroxyapatite can form biphasic calcium phosphate (BCP), having Ca/P molar ratio ~1.67 which is close to that of human bone. Many researchers are still working on synthetics from this apatite family and their applications. Those who are in the field or interested can follow the work of Davis, JR., Wang J., Narayan. R., etc.

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