Reliable Bioceramics – the Relevance of Materials and Processing Technologies

Ceramics is used in artificial joints, additionallly interesting applications for ceramics are established in the dental field. Yttria stabilised zirconia is used in prosthetic applications, i.e. crowns and bridges. Another interesting application is dental implants. At this time the breakthrough is still limited, because mainly one-piece implants are used, but many companies work in ceramic solutions for a modular system based on implant, abutment and crown.

Fig. 1
Ball-heads for ceramic hip joints (source: OxiMaTec)

Introduction

Ceramics on the basis of alumina, silica and magnesia are well known since centuries. Due to the fact that normally these ceramics are based on natural sources, they also contain other oxides like ironoxide, calciumoxide and alkaline oxides. In the early thirties of the last century alumina ceramics were sintered for the first time. This material has been qualified as an isolating component for spark plugs. In the fifties of the last century many new applications have been found, i.e. in the paper industry as de-watering elements, in the textile industry as thread guides, in pumps, etc. Its excellent wear resistance results from the high hardness and stiffness. Ceramics are chemically inert and therefore they have been qualified as corrosion resistant parts in the chemical and pharmaceutical industry.

New applications in ceramics normally need new materials with special properties. So, in the sixties of the last century a high purity alumina ceramics with a very uniform microstructure and a relatively high strength of about 400 MPa has been developed. But due to its high costs this material was limited to niche applications. When in 1968 the first hip joint surgery with ceramics was made in France, this high purity and high strength material has been qualified afterwards for biomedical applications. While in the first implants the ceramic ball-head and the stem were cemented, the big breakthrough has been achieved by the conical principle: the idea was to combine taper and ball-head without bone cement.

This conical principle sets the ceramics under tensile stresses. It is well known that ceramics don't like tensile stresses due to their brittleness. However with the above named high purity alumina with its reliable mechanical properties all doubts

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were overcome. During product development it has been shown that the wear of ceramics mated against polyethylene is only about one fourth compared to the pairing of metal/polyethylene in a hip-joint prosthesis system.

Although ceramics used in artificial joints, mainly in the hip, are the most famous. Additional quite interesting applications for ceramics are in the dental field. Yttria stabilised zirconia is already well established in prosthetic applications, i.e. crowns and bridges. Another interesting application is dental implants. The market for dental implants develops slightly. At this time the breakthrough is still limited, because mainly one-piece implants are used, but many companies work in ceramic solutions for a modular system based on implant, abutment and crown.

Fig. 2
Production of dental implants by ceramic injection moulding (CIM) (source: OxiMaTec)

High purity alumina and material improvements

Before bio-ceramics could be introduced into the market, a high purity alumina ceramic material had to be developed and qualified for bio-ceramic applications. The first approach has been the purification of corundum by washing with hydrofluoric and hydrochloric acid. Significant material improvement has been achieved, when new raw materials, i. e. alumina powders, with high purity and small grain-size came to the market. By qualification of these raw materials and optimisation of the body preparation processes, the grain-size of the ceramic was reduced and finally the mechanical strength could be improved up to about 480 MPa.

Introduction of the hot isostatic pressing (HIP) in 1994 brought an additional improvement. By this approach the material is sintered under oxidising atmosphere until a closed porosity is achieved. Then these parts are treated at high temperatures and pressures up to 200 MPa in order to achieve a very high density and to eliminate micro-defects within the microstructure. This treatment leads to a mechanical strength up to 650 MPa.

Yttria stabilised zirconia and zirconia matrix composites

This new class of ceramic materials became very popular in eighties of the 20th century. Due to its fine grained and metastable tetragonal microstructure its mechanical strength is about 1000 MPa. In addition, this material has an improved fracture toughness of 5,5–6 MPa $\sqrt{m}$ compared to alumina (3,8 MPa $\sqrt{m}$). The major disadvantage of this material is “hydrothermal instability”. This means that it can damage in humid atmosphere. However, if the material is made under proper conditions and grain-size and manufacturing technology is controlled well, it stays stable as ball-head. Clinical experience dated from 1986 have proved it.

Opposite to alumina, which stays stable in its modification after calcination, zirconia undergoes a reversible phase transformation at 1174 °C. This phase transformation from the monoclinic phase with a density of 5,85 g/cm^3 transforms to tetragonal (6,1 g/cm^3), which is combined with a volume reduction of about 4 %. Without any stabilising agent, i. e. yttria, there is a re-transformation and the volume increases again. The most common method to distribute the stabilising yttria homogeneously, it is already included in the powder processing by co-precipitation followed by calcination.

In order to enhance the hydrothermal stability another approach has been made by coating pure zirconia particles with the stabilising yttria. By this approach a gradient of yttria within the zirconia grains can be achieved, which i) leads to a finer microstructure, ii) leads to a higher hydrothermal stability and iii) leads to a higher fracture toughness. When this material has been developed, small amounts of alumina were added to the system.

Meanwhile new materials based on zirconia as raw material have been developed: “in situ” platelet reinforced zirconia matrix materials. Within these materials the stabilisation takes place by using yttria and ceria as stabilising components. Furthermore, alumina and lanthanum oxide are added. During sintering then the formation of a tetragonal solid solution of the zirconia takes place as well as the formation of hexagonal platelets with the chemical composition $LaAl_{11}O_{18}$. As it has been shown, by this approach materials with tailored properties are achieved. The most important result of these new materials is that they do not undergo any hydrothermal decomposition reaction. Furthermore the high mechanical strength properties are improved: mechanical strength is kept at a high level and the fracture toughness has been increased up to 12 MPa $\sqrt{m}$.

Due to the high strength and fracture toughness of these new material investigations have been started to qualify these materials for screws in modular dental implants. Another interesting medical application is in surgical instruments.

Zirconia toughened and platelet reinforced alumina

Zirconia toughened alumina is well known since 1977. By homogeneous distribution

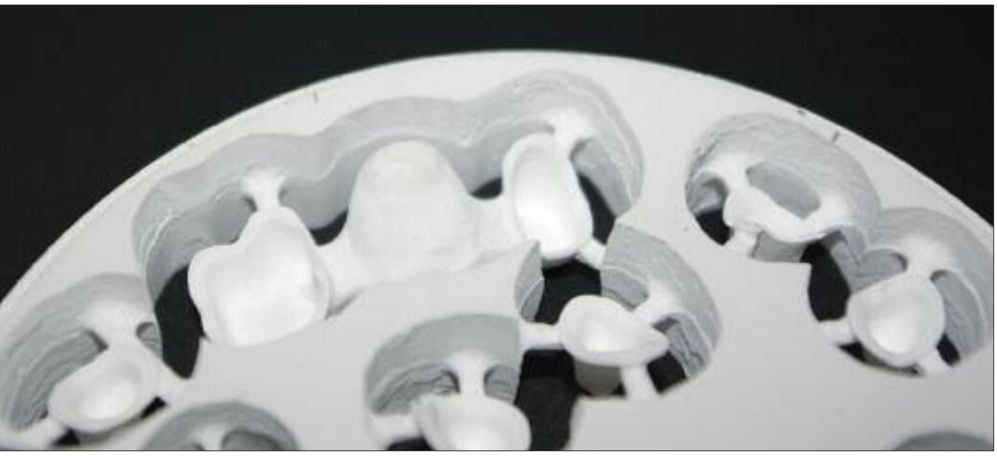

Fig. 3
Crowns and bridges based on Y-TZP (source: OxiMaTec)

of zirconia particles in a size up to 0,5 µm these can be kept in its tetragonal modification as metastable particles. In principle, up to a zirconia concentration of about 10 vol.-% it is possible to retain the metastable tetragonal phase without any additional stabilizing oxide, like yttria or ceria. At higher zirconia concentrations it becomes quite difficult to retain the metastable modification without stabilizing agent. Dispersion of zirconia within the alumina matrix leads to an increase in mechanical strength and fracture toughness with a slightly reduced hardness. Its typical mechanical strength properties are between 600–800 MPa. Although zirconia toughened alumina had higher mechanical strength, there was never a breakthrough for biomedical applications.

Beginning of the nineties of the 20th century an additional component has been introduced into the zirconia toughened alumina: "in situ" platelet reinforcement. The theoretical background for this approach has to be related to intensive studies of crystal structures. Calcium- and strontium aluminate crystallites have an extended hexagonal shape. This means that grains have a diameter to thickness ratio of about 5 : 1 to 10 : 0,5. The inclusion of such platelets into a matrix of alumina with dispersed zirconia leads to a very high strength of more than 1200 MPa. By addition of small amounts of chromia it has been possible to retain the high hardness and to keep the material relatively tough with a fracture toughness of about 6 MPa $\sqrt{m}$.

Finally the combination of these excellent mechanical properties convinced engineers within the bioceramic field to exploit this material for ball-heads and inserts. Even femoral knee joints became available with this material. Its clinical experience now is about 15 years and it sounds that at this moment it is the most successful bioceramic material worldwide. Even its pink colour became something like a trademark. The patent for this material was filed in 1991 and first surgeries took place in 1998. Taking into account the hydrothermal decomposition reaction of yttria stabilised zirconia, this reaction is even possible in an alumina matrix composite material. Therefore additional development work has been spent in order to overcome this effect. Now qualification for biomedical applications has been started. This material will have a big future, because there is no corrosion under hydrothermal conditions. As consequence of this, there is no phase transformation from tetragonal to monoclinic zirconia. No volume increase related to phase transformation will occur. With other words: the elimination of any hydrothermal decomposition reaction makes bioceramics even more save than they are now. Furthermore, the higher fracture toughness is an additional factor in order to enhance the reliability further.

Forming technologies for geometrically complex bioceramic parts

Manufacturing of ceramic ball-heads and inserts are made by the typical methods of powder technology: manufacturing of a ready-to-press powder, pressing, machining, sintering and then grinding in order to achieve the required geometrical shape. This approach to forming has to be related to the relatively simple geometric design of these products. It becomes more difficult for machining a femoral component for the knee joint. This needs a high consumption of ready-to-press material as well as long machining time.

Dental implants made out from ceramic materials become more and more important. These are much smaller and geometrically more complex. A one-piece designed part normally still is achieved by mechanical machining methods. However the manufacturing of a two-piece implant is difficult to machine. Certain innovative geometrical designs cannot be machined, even taking into account extremely high machining costs. In order to achieve the required design, these parts are manufactured by ceramic injection moulding.

Ceramic injection moulding requires a mould, which at first it quite expensive. Furthermore, significant deviations of the geometrical design can occur due to the high shrinkage. It is therefore mandatory to adapt the feedstock with the mould in order to achieve finally the required design. In order to achieve the required design, it is mandatory to know the feedstock for injection moulding and its behaviour during injection moulding, de-binding and sintering.

Several companies offer feedstock for ceramic injection moulding. So, the manufacturer of ceramic parts can focus on the injection moulding, de-binding and sintering. For standard applications this approach seems to be o.k. For medical applications the manufacturer should know more about the feedstock itself, especially the organic ingredients. However, this is normally the secret of the compounding companies and it is not disclosed. So, in order to make reliable products one has to know the feedstock composition and behaviour during injection moulding, de-binding and sintering.

Many publications describe that ceramic injection moulding only can be applied for small and thin ceramic parts, because of the difficult de-binding process. Again, if there is no knowledge about the organic ingredients, de-binding becomes difficult.

However if the ingredients are known, big and thick-walled parts can be de-binded up to a thickness of about 8 mm. This means that, if the organic system of the feedstock is understood quite well, nowadays it is possible to manufacture ceramic femoral knee-joint by this process.

An interesting alternative process for knee joint manufacturing may be the direct coagulation casting process. This process is especially for bigger parts quite interesting. A slurry is casted into a mould and by a chemical reaction this slurry finally coagulates and a solid part comes up. Within this processing technology, de-moulding is the most critical processing step, because the wet strength of casted parts is quite low. On the other hand, geometrically complex parts with a certain size can be made near-net-shape. The costs for the moulds are much lower than for ceramic injection moulding. However its precision is not as good, as it is for ceramic injection moulding.

Both processes described above are quite good alternatives for conventional pressing and green-machining. Additional attempts with printing technologies are under investigations as well. However up-to-date this is still research, because of the limited mechanical strength.

Future perspectives

Since the first surgery of a ceramic hip-joint ball-head in 1968 many changes have occurred. Significant design, material and process improvements took place. Safety and reliability of the products have been improved significantly. Regulatory affairs became more and more difficult and the qualification of new products takes much longer than it has been the case for the past 45 years. However this guarantees a further improved safety of the products.

Ceramic ball-heads mating against ceramic inserts is an excellent pairing for young and active patients. The new materials based on an alumina matrix and having an improved fracture toughness will be the future materials for this. Ceramics mating against ultra high molecular weight polyethylene (UHMWPE) will substitute more and more the pairing metal/PE. Due to its very high fracture toughness and mechanical strength alumina and platelet reinforced zirconia will play an important role in the future mated against UHMWPE.

In dental applications the aesthetic aspect plays a very important role. Its major focus at this time is the translucency of the materials. Unfortunately, the platelet reinforced materials are opaque and therefore are not in the focus of the dental industry.

Fig. 4
Modular ceramic dental implant (source: OxiMaTec)

Its only qualification at this time is for screws in modular dental implants. Another interesting application of the high fracture toughness ceramic materials is seen in spinal implants. Other applications will show up in the near future.

Acknowledgement

This paper is dedicated to *Dr Erhard Dörre* (1927 – 2008). Because of his material innovations and his longterm investigation, including discussion with surgeons in the early 70th, finally high purity alumina could be qualified for biomedical applications. Without all his background information the author of this paper would not have recognized the potential for zirconia and platelet reinforced alumina in medical applications.