8th SIMCER
International Symposium on Ceramics
Special Meeting on Biomaterials

Rimini
November 10–12, 1992

edited by
I. Stamenković
J. Krawczynski
8th SIMCER International Symposium on Ceramics

Biomaterials

Special Meeting of the Project EUREKA 294

Rimini
November 10–12, 1992

edited by
Ivan Stamenković · Johanna Krawczynski

German Cooperation in Scientific Research and Technological Development with the Faculty of Technology and Metallurgy (Institute of Inorganic Chemical Technology), University "Kiril i Metodij", Skopje
Biomaterials: German cooperation in scientific research and technological development with the Faculty of Technology and Metallurgy (Institute of Inorganic Chemical Technology), University "Kiril i Metodi", Skopje / Special Meeting of the Project EUREKA 284, 8th SIMCER International Symposium on Ceramics, Rimini, November 10 - 12, 1992.

Forschungszentrum Jülich GmbH; Centro Ceramico, Bologna - Italy.

Ed. by Ivan Stamenkovic; Johanna Krawczynski. - Jülich: Forschungszentrum Jülich, Zentralbibliothek, 1994

(Bilateral seminars of the International Bureau / Forschungszentrum Jülich GmbH; Vol. 17)

NE: Stamenkovic, Ivan [Hrsg]; Special Meeting on Biomaterials < 1992, Rimini >;
SIMCER International Symposium on Ceramics < 8, 1992, Rimini >;
Forschungszentrum < Jülich > / Internationales Büro: Bilateral seminars on...
Acknowledgements

We most cordially thank

- the International Bureau of Research Centre Jülich GmbH for its support of the bilateral project on "Oxide Ceramics and Composites" between RWTH Technological University of Aachen, Institut für Gesteinshüttenkunde / Glas, Bio- und Verbundwerkstoffe and the University of Skopje, Technological-Metallurgical Faculty

- Centro Ceramico Bologna for having organized the Special EU 294 Biomaterials Meeting on the occasion of the 8th SIMCER Conference in Rimini and having put at disposal the efficient conference facilities in the premises of the Rimini Exhibition Centre

- Mrs. Stefania BORTOLOTTI and Mr. Luciano MARESCALCHI of Centro Ceramico Bologna for the graphical work and the preparation of the manuscript for publication.
FOREWORD

Within the 8th International Symposium on Ceramics held in Rimini from 10th to 12th November 1992, the "Special Meeting" was exclusively dedicated to the EUREKA Project No. 294 - BIOMATERIALS.

The scientists and experts involved - coming from industries, universities and research centers - had an excellent occasion to present their own activities realized according to the accepted Working Programme which has established a systematic distribution of the work load among the participating institutions. Their technological and scientific papers were valuable contributions at the level of the internationally oriented 8th SIMCER Symposium on Ceramics, on the occasion of which many researchers from all over the world exchanged their newest achievements.

The highly promising results obtained and the efforts undertaken in the framework of the EUREKA 294 project confirmed that the working programme will be successfully fulfilled despite some regrettable incongruencies of national authorities in the field of project financing still persisting, thus jeopardizing full efficiency of the corresponding research teams.

We therefore hope that the proof of scientific quality and experimental engagement given in Rimini and documented by the publication of the present Proceedings will not in the last instance serve (over and above the purpose of communication and continuous information among our partner institutes and towards the wider international scientific community) that of stressing the value of the work also in its function as a (preparatory) step in the procedure of national funding - so vitally necessary for us - by the competent national authorities.

Jülich / Bologna
December 1993 / January 1994

The Editors
Partner Institutions in the EU 294 - Biomaterials Project

Prof. Dr. G. ONDRACEK
Institut für Gesteinshüttenkunde
Glas, Bio- und Verbundwerkstoffe
Mauerstraße 5
D - 52064 A A C H E N / FEDERAL REPUBLIC OF GERMANY

Prof. Dr. Panajotis NIKOLOPOULOS
Institute of Chemical Engineering and High-Temperature Chemical Processes
University of Patras
GR-26110 PATRAS / GREECE

Prof. Dr. Carlo PALMONARI
Prof. Dr. Ivan STAMENKOVIC
Centro Ceramico Bologna
Via Martelli 26
I - 40138 BOLOGNA/ITALY

Dr. C.J. STOURNARAS
CERECO - Ceramics and Refractories
Technological Development Company
P.O. Box 146
GR-34100 CHALKIDA / GREECE

Priv.Doz. Dr.med.
Klaus Michael STÜRMER
Abteilung für Unfallchirurgie
Universität-GHS Essen
Hufelandstraße 55
D - 45147 ESSEN / FEDERAL REPUBLIC OF GERMANY

Dr. Wielfried GLIEN
KERAMED-Medizintechnik
Keramische Werke Hermsdorf GmbH
Friedrich-Engels-Straße 79
D - 07629 HERMSDORF
FEDERAL REPUBLIC OF GERMANY
"Institutional participation" according to the 1987 Rules of Madrid
- as from 24.08.1989 on (frozen as from 31st May 1992)
Department of Materials Sciences
The Boris Kidric Institute of Nuclear Sciences
P.O. Box 522
YU-11000 BEOGRAD

as from 6.2.1992 on
Prof. Dr. M. MILOSEVSKI
Faculty of Technology and Metallurgy
University of SKOPJE
Rudjer Boskovic
91000 SKOPJE
New participating institutions

- as from 8.2.1993 on :

Dr.-Ing. Klaus LIEFEITH
Thüringer Arbeitsgemeinschaft Biomaterial e.V.,
Geschäftsstelle Rosenhof
D - 37308 HEILIGENSTADT
FEDERAL REPUBLIC OF GERMANY

- as from 30.11.1993 on :
  (instead of TEMAV-SAMATEC)

Ing. M.L. BOCCALARI
F.N. BOSCO MARENGO S.p.A.
S.S. 35 bis dei Giovi, km 15
I-15062 BOSCO MARENGO (AL) / ITALY

International Secretariat

International Bureau of
KFA - Research Centre Jülich GmbH

Dr. Johanna KRAWCZYNSKI

Ass. Gerd CARL
KFA - Jülich
RPA/Rechts- und Patentabteilung

D - 52425 JÜLICH
FEDERAL REPUBLIC OF GERMANY
## Contents

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. Krawczyński, G. Ondracek, I. Stamenkovic</td>
<td>Special Meeting EUREKA 294 - Biomaterials</td>
<td>1</td>
</tr>
<tr>
<td>J. Krawczyński, G. Ondracek</td>
<td>Biomaterials - a research concept</td>
<td>7</td>
</tr>
<tr>
<td>S. Agathopoulos, A. Tsoha, P. Nikolopoulos</td>
<td>Interfacial phenomena between oxides and various liquids</td>
<td>17</td>
</tr>
<tr>
<td>A. Galani, Th. Zambetakis, C.J. Stournaras</td>
<td>The influence of titania additions on mullite based ceramics</td>
<td>29</td>
</tr>
<tr>
<td>L. Esposito, A. Salomoni, I. Stamenkovic, A. Tucci</td>
<td>Processing of ZrO₂-Al₂O₃ powders: consolidation and characterization of final products</td>
<td>37</td>
</tr>
<tr>
<td>E. Dragoni, A.O. Andrisano</td>
<td>Stresses in ceramic prosthetic heads under axisymmetric loading: effect of taper friction, support conditions and spigot elasticity</td>
<td>47</td>
</tr>
<tr>
<td>A. Toni, A. Sudanese, S. Stea, A. Pizzoferrato, M.D. Marraro, F. Calista, A. Giunti</td>
<td>The biological interaction between bone tissue and ceramic implants</td>
<td>61</td>
</tr>
<tr>
<td>P.L. Ballarini, M. Grimaldi</td>
<td>Design and construction of a wear simulator for HIP prosthesis</td>
<td>67</td>
</tr>
<tr>
<td>G. Bovalini, P. Fassina, N. Zaghini</td>
<td>Preparazione di polveri per ceramici avanzati formatura e sinterizzazione</td>
<td>73</td>
</tr>
<tr>
<td>M. Milosevski, R. Milosevska, G. Ondracek, D. Spaseska</td>
<td>Preparation and Properties of Al₂O₃-SiO₂-TiO₂ Ternary Bioceramics</td>
<td>79</td>
</tr>
</tbody>
</table>
Special Meeting EUREKA 294 - Biomaterials

J. Krawczyński¹, G. Ondracek², I. Stamenkovic³

1. Int. Secretariate of EU 294, Research Centre Jülich GmbH
Jülich (Germany)

2. RWTH, Institut für Gesteinshüttenkunde - Glas, Bio- und Verbundwerkstoffe
Aachen (Germany)

3. Italian Ceramic Center
Bologna (Italy)

EUREKA

Is an inter-state open framework for frontier-crossing cooperation of European enterprises and research centres in the field of research and technology for civilian purposes

Characteristics

• **Bottom-up approach:** impetus for cooperation comes from below.
• **Project diversity:** free determination of topics.
• **Decentralised organisation:** the aim is not harmonisation of R&D policies, but utilisation of available potentials for jointly reachable goals.
• **Pragmatic contributions towards the European unification process:** mutual access to markets for cooperation partners early development of uniform rules and standards project-related elimination of specific trade hindrances.

Membership: 20 states and EC

- Austria
- Belgium
- Denmark
- Finland
- France
- Germany
- Great Britain
- Greece
- Hungary
- Iceland
- Ireland
- Italy
- Luxembourg
- Norway
- Portugal
- Spain
- Sweden
- Switzerland
- The Netherlands
- Turkey

Organisation

National Project Coordinators

EUREKA Secretariate Brussels
**High Level Group**

Represents the Ministers' Conference, prepares its decisions and supervises their realization; decides on EUREKA status of projects.

**Ministers' Conference**

Highest political decision making body consists of the ministers for R & D from member countries of EUREKA and one representative of EC decides on contents, structures and aims follows the development of EUREKA, evaluates results officially announces the new projects generally takes place once a year.

Since 1985, 10 Ministers' Conferences have taken place.

**Project Statistics**

- Number of EUREKA Projects (May 1992): 539
- Financial volume: more than 10 billions of ECU
- Project participants: more than 3 thousand of which: SME 521, research establishments 975

**EUROPEAN DIMENSIONS OF EU 294**

or: why are we cooperating?

Decisive criterion and hence scientific focus:
"Biocompatibility of implant materials"

- as a complex problem of compatibility between implants and the biosystem, i.e. the human body
- is influenced by distinct living conditions, standards and natural environment in various regions in Europe
- requires a statistical collective basis to enable valid conclusions
- european cross-sectional evaluation of the statistical data by participation of D, GR, I and institutions from the former Yugoslavia in EU 294
- joint research and development programme with sharing of work load and systematic division of labour

**PARTNER INSTITUTIONS**

3 institutions from the Federal Republic of Germany
- Rheinisch-Westfälische Technische Hochschule Aachen
- Universität / Gesamthochschule Essen
- Keramed Medizintechnik, Hermsdorf

application for inclusion into EU 294 received from Working Community Biomaterials of Thuringia, Heiligenstadt

3 institutions from Greece
- Institute of Chemical Engineering and High-Temperature Chemical Processes, Patras
Institutional participation: institutions from Italy:
- Centro Ceramico Bologna
- Officine Ortopediche Rizzoli SpA
- TEMA-V-SAMATEC, Medicina
- Istituto Ortopedico Rizzoli
- Università Modena

Institutional participation of partners from former Yugoslavia according to the 1987 Rules of Madrid for Third Country Participation:
- Materials Sciences Dept. of the Boris Kidric Institute of Nuclear Sciences, Vinca
- Technological-Metallurgical Faculty of the University of Skopje

International Secretariat:
International Bureau of Research Centre Jülich (D)

SCIENTIFIC PROGRAMME OF EU 294


Keyfocus, guideline of research: Improved biocompatibility

1) Ceramics, since all metals more or less corrode high-purity ceramics, since implants are being developed multi-component material to adapt properties of implant materials to various parts of the body. Grain morphology and porosity parameters (up to open porosity) must be controllable. Aim is manufacturing of implant material of tailor-made composition, with tailor-made properties and tailor-made microstructures.

- topics of research: synthesis of high-purity ceramic powders, study of binary and ternary systems of Aluminium, Silicon, Titanium and Zirconia. Powder compressing and shaping in the presence of carbon-sacrificed fibres by pressure slip casting graded microstructures via the composite concept.

2) Proper contact between tissue or bone and allotropic materials, hence study of surface energies and their changes. Interaction between body liquids and implant materials compatibility of materials implants and hard tissue.

3) Modelling, design, qualification, characterization and laboratory realization and verification of prosthesis prototype development and manufacturing, in-vitro and in vivo clinical tests.

4) Feedback with materials parameters, industrial production

\(x\) frozen since 31st May 1992
ORGANISATION OF RESEARCH WORK IN EU 294 AND FRAMEWORK CONDITIONS OF RESEARCH

The organisation of research work is different in our various partner institutions and foremost depends on the financial support of research work.

Framework conditions:

- Precondition for EUREKA projects is a secured financing scheme
- The financing of the own project share is the responsibility of the project participants

and occurs in the national framework, i.e. in each partner state separately. In each country different rules apply.

* Federal Republic of Germany:

The EUREKA status does not by itself compellingly entail financial allocations. Funds can be applied for according to the special rules of the different research promotion programmes of the Federal Government, of the single states and of EC.

In Germany the support is therefore indirect:

- justification of projects as contributing to EU research problems
- umbrella agency is the responsible body of the State of Northrhine-Westfalia, the Working Community Biomaterials

which, together with DFG (German Research Society) finances a post-graduate programme (GRADUIERTENKOLLEG) characterized by

- exclusive development of total field of biomaterials
- connection of university research and teaching
- participation of ten professorial chairs of three different universities

Scientific topics of the Graduiertenkolleg in accordance with systematic sharing of work in the international EU-context:

- Interface relationships in the biosystem (tissue, body fluids)
- Production of laboratory samples of conventional and new materials
- Implant technology and biosuitable design of conventional and new biomaterials (bones and oral cavity)

RWTH Aachen together with the Medical Department of the Aachen Technological University and the University of Essen furthermore works on:

- how do ceramics or biomaterials fit to the biosystem in case of hard tissue?

A type of new ceramics is being developed in form of ceramics with interconnected porosity.

In order to allow the tissue to grow into the implant material, a type of connection is necessary between them, which guarantees a good fixation.

The Aachen Institute works here together in a certain contact with industry in view of transfer of these investigations from a model system into a real one.

* Italy

The Italian Government is going to support the Italian contribution to EU 294 by 8.4 Mio ECU, the bulk of which is for the implementation phase, i.e. R&D and initial exploitation of results.
The Italian partners concentrate on the development and behaviour of materials, with special emphasis on the relationship between materials with additional compounds and hard tissue, i.e.

- comparative studies of bioceramic components
- R&D of advanced bioceramic materials (prospective biomaterials candidates, powder preparation procedures, consolidation techniques)
- design and qualification and characterization of ceramic biocomponents (designing, laboratory realization and verification of prosthesis prototype development and manufacturing)
- investigation of coating processes and techniques suitable for biocomponents upgrading (coating materials, coating techniques, investigation of processing variables on properties of coatings)
- in vitro-in vivo biocompatibility tests
- products clinical testing (behaviour of implants)
- mechanical - tribological studies

**Greece**

Effective direct support of EU-294 activities by the Greek Government in the first phase by nearly half a million of ECU.

Main research topic of the GR partners in the systematic sharing of work between the international partners:

Interaction between body liquids and implant materials

- wetting and bonding experiments in order to determine the surface and interfacial energies in ceramic-metal biocomposites
- interface investigations between ceramic phases and cell cultures in order to correlate interfacial energy and biocompatibility
- study of the ternary system Aluminium-Silicon-Titanate
- property characteristics of ceramics produced by conventional and sol-gel powders
- biocompatibility and haemocompatibility testing of bioceramic materials

**Institutional contribution from Skopje University**

Developing new bioceramics by:

- sol-gel synthesis of ternary oxide systems (Alumina - Titania - Silica),

their consolidation and characterization with regard to thermophysical and mechanical properties
- porose structure creation applying carbon fibres.

**Institutional contribution from Vinca/Belgrade Institute**

The contribution of the Boris Kidric Institute Vinca was directed toward injection moulding of bioceramic materials.
Number of projects by fields of technology

Gesamtzahl aller EUREKA-Projekte: 539
davon mit deutscher Beteiligung: 174

Gesamtzahl
mit
deutscher
Beteiligung

Umweltforschung und -technologie
Pertigungstechnik
Materialforschung
Transport- und Verkehrstechnologie
Laser-technik

Biotechnologie, Medizinforshung
Informations-technik
Kommunikations-technik
Energieforschung und -technologie

Financial volume of projects by technology fields

Von dem Finanzvolumen (ca. 21,4 Mrd. DM) derzeit 539 Projekte entfallen auf

Umweltforschung und -technologie
Pertigungstechnik
Materialforschung
Transport- und Verkehrstechnologie
Laser-technik

Biotechnologie, Medizinforshung
Informations-technik
Kommunikations-technik
Energieforschung und -technologie

- 6 -
In order to base materials for medicine on an interdisciplinary scientific concept biomaterials have to be conceived as those, which are biocompatible and adaptable with respect to their properties towards the biosystem ("biocompatibility and biofunctionality"). Biocompatibility describes the interaction between a living system and an allotrophic material introduced into this system. This interaction first becomes apparent at the interface.

In materials science a differentiation is made between:

- interfaces in nonequilibrium
- interfaces in equilibrium

Interfaces are thermochemically in nonequilibrium ("unstable") if their constituents interact with each other, i.e. react with each other chemically or are dissolved into each other. The termination of such a process is a materially different, "stable" system. In contrast, interfaces in equilibrium are formed by constituents which neither react chemically with each other nor are they dissolved into each other. If these considerations are transferred to allotrophic materials in the biosystem then at their interface to the living tissue bioinert materials are "in equilibrium", the interface is stable. As shown in Fig. 1, their bioactivity is 0.

The expression "bioinert" is used in this context to mean "thermochemically defined" since the Consensus Conference of European Biomaterials has recommended that this term should otherwise not be used.

In comparison to the interface between bioinert materials and the biosystem, the interface between bioactive materials and the living system is subjected to interactions and is therefore unstable. Events at unstable interfaces are generally complex and not restricted to the interface.

These events gradually involve the area surrounding the interface and ultimately perhaps the whole system. Frequently it cannot be predicted when stability will be achieved and which status of the system this corresponds to. The upper limiting curve of the positive bioactive (= biocompatible) region or the lower limiting curve of the negative bioactive (= bioincompatible) region in Fig. II.1 corresponds to this situation. In contrast, with - for example - resorbent materials, the stable final status is as a rule more easily reached. For biocompatible materials, the lower limiting curve in the positive bioactive region of Fig. 1 corresponds to this situation.

Negative bioactive, i.e. bioincompatible, materials will not be discussed further in this consideration, but for positive bioactive, biocompatible materials long-term kinetics must be taken into consideration requiring many years or even decades of observation - not
only of the interface. If intermediate layers - such as connective tissue or protein deposits - are formed (cf. Fig. 2), i.e. the situation is biotolerant or - expressed in terms of materials science metastable, then the interaction between the biosystem and biomaterial is temporarily blocked or at least retarded.

The most scientifically appropriate and most readily understandable case is therefore that of the stable interface between the biosystem and bioinert material (cf. Fig. 2). It restricts the implant to itself and its sole permanent contact position to the biosystem is the always controllable - interface. This is therefore one prior subject of this concept. The problem to be investigated is the adhesive strength which can be achieved between known metallic, polymer and ceramic bioinert materials and "hard tissue" (bone or cartilage), and the way in which interface behaviour towards soft tissue and body fluids can be characterized.

The fundamental scientific law for the formation of an interface in equilibrium is given by equation (1)

\[
G_{\alpha\beta}^{\text{ex}} - G_{\alpha}^{\text{sf}} - G_{\beta}^{\text{sf}} = \Delta G_{\alpha\beta}^{\text{ad}}
\]  

(1)

\(G_{\alpha\beta}^{\text{ex}}\), \(G_{\alpha}^{\text{sf}}\), \(G_{\beta}^{\text{sf}}\) = surface enthalpies of the \(\alpha\), \(\beta\) phases (e.g. tissue and implant material)

\(G_{\alpha\beta}^{\text{sf}}\) = interface enthalpy of the interfaces between the \(\alpha\)-phase and the \(\beta\)-phase

\(\Delta G_{\alpha\beta}^{\text{ad}}\) = adhesion enthalpy for the interface between the \(\alpha\)-phase and the \(\beta\)-phase.

Accordingly, an interface is formed if - and only if - the total of the surface enthalpies of the two constituents forming the interface is greater than the interface enthalpy, i.e. the value of the adhesion enthalpy according to equation (1) must be negative - and proportional to the adhesion. This should also be valid for interfaces between the biosystem and allotropic bioinert materials.

The adhesion described by equation (1) can only be effective if the atoms in the interface may approach each other at spacings in the order of magnitude of \(10^{-10}\) m, because according to Fig. 3 this is the distance below which interatomic forces become effective. Whether they can take on the equilibrium spacings according to Fig. 4 ensuring maximum bonding (adhesion) in this order of magnitude depends on the interface structure.

In adherent interfaces (Fig. 5), the atomic spacings are closest to the equilibrium spacing. Whilst partially adherent and inadherent interfaces denote different approaches towards equilibrium spacing. The term "adherent" corresponds to phase boundaries and substitutes "coherent", which can correctly be used only for grain boundaries.

The interface structure which is formed depends on the X-ray structure (Fig. 3) of the components forming it or their aggregate status. Interfaces between liquid and solid phases should be able to correspond most closely to the energetic conditions and therefore clearly reflect the influence of surface and interface energies in wetting studies. The wetting of biomaterials by body fluids or their simulates is therefore a major focus of the herewith presented concept.
As equation (1) shows, a correlation between the surface enthalpy of an implant material alone and the adhesion to the biosystem is not justifiable. Wherever such correlations have been published they either occurred by chance or should be regarded as special cases, not to be generalized. Nevertheless, the surface enthalpies of allotropic materials have a decisive effect on interface formation towards the biosystem and it must be regarded as a disadvantage of most conventional implant materials including ceramic materials such as aluminium oxide, that they are single-phase, i.e. not variable in their composition, since by varying the material composition the surface enthalpy can be varied and thus adapted to the requirements of the biosystem. For this reason, ternary bioceramics are being developed and compared to conventional biomaterials with respect to their interface formation and surface enthalpies within the framework of the present concept. Since the in-vivo formation of interfaces with bone and cartilage in the biosystem is complicated and time-consuming, it should, if possible, be replaced by a simulation, particularly in order to reduce animal experiments. The search for such a simulation is a further objective of work based on this concept.

Cell culture tests have long been a preliminary stage for animal experiments. As a rule, they provide initial qualitative information on biocompatibility or bioincompatibility. Whether they are also able to provide preliminary information for adhesion and interface formation for bioinert materials by correlation to their surface enthalpies is a further research topic being dealt with here, where further discussion refers to the simulation of bone and cartilage:

In its structure and properties hydroxylapatite is most similar to bone. In the sense of a first approximation, hydroxylapatite is therefore to be brought into contact with conventional and new biomaterials as a bone sim ulate. The interfaces between hydroxylapatite and bioinert biomaterials are then to be analysed in comparison to the interfaces between bone and bioinert biomaterials in order to find out, whether hydroxylapatite in combination with implant materials may serve as a bone-simulating material. The load on an interface is the greater, the greater the difference in properties is between the phases it joins (coefficient of expansion, modulus of elasticity). Failure to adhere in the interface is the more probable, the "more unfavourable" the geometry of the interface is with respect to the effective stress: smooth interfaces fail more readily than rough, pin implants fail more easily than screw implants. If the idea of roughness is continued to the extreme via surface profiling (screw) then one arrives at an implant material with open porosity into which the bone can grow (Fig. 6) composite concept).

A bone-biomaterial composite thus arises with maximum mechanical anchorage which distributes the interface adhesion almost homogeneously through the composite material and mechanically supports it. But also other arguments support the composite concept as, for example, concerning the acetabular (hip joint cup). Substituting a natural hip joint the tribological system is changed from one with lubricant (synovia) to an artificial one without synovia. Could the disadvantages with respect to friction and abrasion be reduced if a natural bone forms partly the surface of the acetabular via a composite cup? Does synovia reappear in that case and could wettability take place? In any case the composite material concept provides the theoretical basis for precalculating the porosity structures capable of ensuring an optimum adaptation of properties always proceeding from the bone into the implant. The production of biomaterials with "tailor-made" open porosity and a study of their healing kinetics is similarly a priority of research team work as described here.
In the case of interfaces between solid phases, the kinetics of their origin will be of significance, i.e. the question of which aggregate states of the phases occurred during interface formation; if a phase from the gaseous aggregate state, from melts or solutions is deposited on the surface of the other solid phase then the adaptability of the atoms in the newly formed interface is great ("epitaxy").

In contrast, if solid phases are joined by sintering then the adaptability is less. Reactive layers on the solid surface can temporarily increase atomic mobility and thus optimize the interface structure on the basis of the principle of reaction sintering.

If bone and cartilage grow rapidly and without impedance on the bioinert material surface then the interface structure is largely adapted. However, if deposited protein layers or soft tissue occur then the interface adhesion is disturbed. Growth-stimulating resorbent coatings of allotropic implant material may therefore encourage optimum interface structure. This must be studied by a comparison,

• firstly for interfaces of hydroxylapatite in contact to bioinert materials coated with materials with which hydroxylapatite interacts, i.e. which it dissolves or with which it reacts (simulation of coated implants),

• secondly for interfaces between bone and bioinert implant materials coated with resorbent materials,

which is a further goal of this research team work.

Porous materials are weakened by their mechanical properties - precisely by their porosity. After being introduced into the biosystem it takes a certain time until the pores are filled with bone (healing period). On the other hand, load has a positive effect on the formation of bone and cartilage so that this healing period should not be exclusively a period of rest. In order to reduce the risk of a material fracture in spite of porosity, the implants should only display open porosity in their jacket zone. In the core zone, on the other hand, the porosity should be replaced by a secondary phase which displays adhesion to the implant ceramic and thus modifies its properties in such a way that the desired load during the healing phase and later does not represent an unjustifiable risk (Fig. 7) The equations to calculate such "graded microstructures" are provided by the composite material concept as - for example - Young's modulus for porous materials (Fig. 8).

Up to here the organization has been based on a lab-scale. The final aim, however, concerns industrial implant production.

The transfer of laboratory specimen fabrication of multicomponent, multiphase, porous, bioinert biomaterials with graded microstructure and defined surface enthalpies to industrial implant fabrication is - quite literally - a separate field and should be treated as such. But contact to industry is indispensable here. This step completes the presented programme summarized in Fig. 9 as a jigsaw puzzle, which is going to be performed by special organization:

After simulation experiments, cell culture test and animal experiments, an examination of material behaviour in the human biosystem is unavoidable since biomaterials are to be introduced into this biosystem as "biological spare parts" in the form of bioworkpieces ("implants").
It is quite obvious that the dental sector serves as the "introductory region" in the human system since body reactions in the dental sector can be directly observed and operations undertaken immediately. Nevertheless, the number of patients with relevant syndromes remains limited ("sample populations" in the sense of material sciences). In order to obtain reproducible results, however, certain "statistical collectives" are necessary. Furthermore, for a reliable extrapolation of reproducible results it is also necessary that they should reproduce all possible state conditions which may influence the results: nutrition and climate, habits and specific dispositions in various regions of the world. These requirements are accommodated by the organization of the research programme adapted to the research goals: not only various faculties of different German universities are involved (Arbeitsgemeinschaft und Graduiertenkolleg Biowerkstoffe des Landes Nordrhein-Westfalen, Thüringer Arbeitsgemeinschaft Biomaterialien) but also bilateral cooperation with various republics of the former Yugoslavia, Israel and Egypt, as well as cooperation within the framework of the Eureka Project 294 ensures that different ways of life in east and west, north and south are included in the results under real ecological conditions and that their reliability is ensured "statistically".

The Biomaterials Project is organized therefore on an interdisciplinary, interfaculty, interregional and international basis.
Fig. 1 - Bioactivity and biocompatibility

Fig. 2 - Bioactivity and interaction
Fig. 3 - Structural division and order of magnitude

Fig. 4 - Atomistic equilibrium spacing and binding energies
Fig. 5 - Adherent (a), partially adherent (b) and inadherent (c) phase boundary

Fig. 6 - Composite material concept and interface integration

Fig. 7 - Graded implant structure
Fig. 8 - Comparison between Young's modulus of elasticity for porous alumina and bone

Fig. 9 - Research program of the postgraduate group
Interfacial phenomena between oxides and various liquids

S. AGATHOPOULOS\textsuperscript{1}, A. TSOGA\textsuperscript{1}, P. NIKOLOPOULOS\textsuperscript{2}

1. Institute of Chemical Engineering & High Temperature Chemical Processes
   Patras (Greece)

2. Chemical Engineering Dept., Univ. of Patras
   Patras (Greece)

INTRODUCTION

Ceramic oxides are classified as inert biomaterials suitable for hard tissue replacements i.e. total hip joints, or teeth. Properties that recommend the ceramic oxides for biomedical applications are the good chemical stability and inertness as well as the good mechanical behaviour which is closest (than other materials i.e. metals or polymers) to those of hard tissues. The weak point of ceramics is the brittleness.

The widely used pure oxide is the aluminium oxide. On the other hand, glasses are used in many applications whenever an inorganic material is in contact with living tissues. Moreover, the glass surfaces can be modified in such way that can provide bioactive properties. Except of these, there are also two very interesting ceramics used in many advanced applications, the zirconium and the titanium oxide. Therefore the production and characterization of new mixed ceramic biomaterials is very interesting. The ceramics tested in this work contain the oxides Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, TiO\textsubscript{2} and ZrO\textsubscript{2} in various compositions.

The study and the understanding of the interfacial phenomena can be used in order to estimate the adhesion between two phases in contact. In case where a liquid phase is in contact with a solid one, wetting experiments can be carried out. An established method to determine the interfacial phenomena between solid and liquid phases is that of the sessile drop technique where a liquid drop lies on a solid substrate (Fig. 1). The general equation (1) holds at the interface in solid-liquid-vapour systems under thermodynamic equilibrium and correlates the wetting and the bonding behaviour:

\[ W_a = Y_{SV} + Y_{LV} - Y_{SL} \quad (1) \]

where \( Y_{SV} \) and \( Y_{LV} \) are the surface energies of solid and liquid respectively, \( Y_{SL} \) is the interfacial energy and \( W_a \) is the work of adhesion. For the sessile drop technique the following equation holds:

\[ Y_{SV} = Y_{SL} + Y_{LV} \cdot \cos \theta \quad (2) \]

where \( \theta \) is the contact angle.

Introducing eq. (2) into (1) we obtain:

\[ W_a = Y_{LV} \cdot (1 + \cos \theta) \quad (3) \]
In this paper the sessile drop technique is used to determine:

a. The compatibility between mixed oxides and human liquids. This part of the paper is an "in vitro" evaluation of the biocompatibility [1].

b. The adhesion between ceramic and metallic phases. These experiments are of importance in the development of joining techniques as well as the production of ceramic-metal composite materials (cermets), in order to confront the disadvantage of brittleness.

EXPERIMENTAL RESULTS

The surface of the solid substrates used in all experiments, were polished (≤ 5 µm), and were cleaned in ultrasonic apparatus and finally the surface was observed by metallographic microscope.

a. Wetting experiments by body liquids

The tested ceramic materials are listed below:

1. SiO₂-TiO₂ (eutectic, amorphous, “Sample 3”)
2. SiO₂-TiO₂ (eutectic, crystalline & amorphous, “Sample 4”)
3. SiO₂-TiO₂ (eutectic, crystalline & amorphous, “Sample 4’’)
4. SiO₂-TiO₂ (eutectic, crystalline, “Sample 5”)
5. Al₂O₃-SiO₂ (3/2 mol)
6. Al₂O₃-TiO₂ (eutectic)
7. Al₂O₃ (slip-casting)
8. Al₂O₃-ZrO₂ (80-20 wt%, slip-casting)
9. Al₂O₃-ZrO₂ (40-60 wt%, slip-casting)
10. Al₂O₃-ZrO₂ (20-80 wt%, slip-casting)
11. ZrO₂ (stab. Y₂O₃ 3 mol%, slip-casting)
12. Al₂O₃-ZrO₂ (60-40 (+3 mol% Y₂O₃), slip-casting)
13. ZrO₂ (stab. 8 mol% Y₂O₃, slip-casting)

In order to compare the wetting behaviour of these ceramics with other more common used materials, we used as reference materials the following ones:


In order to estimate "in vitro" the biocompatibility of all the above listed materials we used the following liquids (it is also presented their surface energies, \( Y_{LV} \) at \( ≈ 30^\circC \) which was measured by the ring method):

1. Distilled water \( Y_{LV} = 72 \text{ dyn} \cdot \text{cm}^{-1} \)
2. Normal Saline (Ringer solution) \( Y_{LV} = 72 \text{ dyn} \cdot \text{cm}^{-1} \)
3. Total blood (human, + EDTA) \( Y_{LV} = 63 \text{ dyn} \cdot \text{cm}^{-1} \)
4. Plasma (from human blood) \( Y_{LV} = 59 \text{ dyn} \cdot \text{cm}^{-1} \)
5. Bovine serum \( Y_{LV} = 61 \text{ dyn} \cdot \text{cm}^{-1} \)
6. Synovial Fluid (artificial) \( Y_{LV} = 63 \text{ dyn} \cdot \text{cm}^{-1} \)
The ringer solution had the composition (wt%): 0.80% NaCl, 0.02% KCl, 0.02% CaCl₂ and 0.01% NaHCO₃, and pH ≈ 7.9. The artificial synovial fluid was prepared by mixing 70% (vol%) ringer solution and 30% bovine serum. The total blood contained small additives of anticoagulant EDTA to inhibit the formation of clot. Figure 2 demonstrates the contact angles determined for all the examined systems at -30 °C. The general conclusions arisen from Fig. 2 are summarized as follows:

• In all examined systems the contact angles are less than 90° (good wetting).
• In most systems the water behaves in the same manner with human liquids as well as the artificial synovial. Therefore the water can be used in a gross evaluation of contact angles.
• The wettability gets generally better in case of high SiO₂ concentrations.
• Very good wettability is also observed in case of α-SiC (covalent bonds).
• The other systems show poor wettability by all the liquids examined. The values of contact angles in these systems are compared with those of hydrophobic polymers.
• The contact angle is independent on the production process of the ceramic substrate.

The work of adhesion can be calculated using the eq. (3) and the values of YLV presented before. The values of Wₐ are plotted in Fig. 3. From this figure we come to the following conclusions:

• The values of Wₐ in a particular substrate with various liquids present small dispersion.
• The contact angle is independent on the liquid and depends only on the substrate.
• The values of the work of adhesion have an upper limit of about 0.150 J/m². The low values of Wₐ is an evidence that Van der Waals forces act at the solid-liquid interface. Considering that the ionic character of Al₂O₃ is 63%, ZrO₂ 73%, SiO₂ 51% and SiC 12%, it is concluded that when the ionic character of the substrate increases, the contact angle increases and the work of adhesion decreases (Fig. 4).

b. Wetting experiments with liquid metallic phases

The metals and the alloys used were of high purity. The experiments were carried out in an induction furnace under inert atmosphere of argon 1 atm. The accuracy of the temperature measurements were ±10 °C. The influence of metal vapour existed in the furnace atmosphere on the surface energy of ceramic substrates was assumed to be negligible.

Figures 5, 6 and 7 present the temperature effect on contact angle for the ceramics Al₂O₃, ZrO₂, and (SiO₂, MgAl₂O₄, MgO and TiO₂), respectively, in contact with various molten metals and alloys. Figure 8 presents the effect of the ceramic substrate on the contact angle for the metals Sn (Fig. 8a), Cu (Fig. 8b), and Ni (Fig. 8c). In this figure the experimental values of the contact angle for the mixed oxide ceramics are also plotted.

The general conclusions are summarized as follows:

• The metals and alloys examined do not wet the pure or mixed oxides, (bad wetting) in the investigated temperature range.
• In all examined systems the contact angles decrease when the temperature of the system increases.
• The high melting point metals show a better wettabiity than those with low melting point.
The interfacial energy, $Y_{SL}$, for the systems examined are calculated by eq. (2) and using the values of contact angles and the literature values [2,3] of the surface energies of solid oxides ($\text{Al}_2\text{O}_3$, $\text{ZrO}_2$) and of the liquid metals and alloys that listed in Table 1. Figure 9 shows the linear temperature dependence of the interfacial energy in $\text{Al}_2\text{O}_3$/liquid metal systems (Fig. 9a) and $\text{ZrO}_2$/liquid metal systems (Fig. 9b). The surface energy, $Y_{SV}$, of the oxides are also plotted (dashed line). The point where the lines of $Y_{SL}$ is crossing with the $Y_{SV}$, ($Y_{SL} = Y_{SV}$), indicates the transition temperature from bad-wetting to good-wetting condition.

Using the semiempirical equation [2]:

$$Y_{SL} = \left(K \cdot \frac{V_{\text{Metal}}}{V_{\text{Oxide}}} + 1\right)^{\frac{1}{2}} (Y_{SV} \cdot Y_{LV})^{\frac{1}{2}}$$

where $K$ is constant, depends on the oxide substrate, $V_{\text{Metal}}$ and $V_{\text{Oxide}}$ are the molar volumes of the metal and the oxide, respectively, the interfacial energy at the melting point of the metals for various oxide/liquid metal systems can be calculated ($Y_{SV}$, $Y_{LV}$ from Table 1). Fig. 10 and 11 show a good agreement between the values taken from eq. (2) and those from eq. (4) for the systems $\text{Al}_2\text{O}_3$/liquid metals and alloys ($K = 4.2$) and $\text{ZrO}_2$/liquid metals and alloys ($K = 3.28$), respectively.

Acknowledgements The present work was performed in the framework of the EUREKA (EU-294) Project and is financially supported by the Greek Ministry for the Industry, Energy and Technology.

REFERENCES

Table I - Linear temperature functions of the surface energy for solid oxides and liquid metals and alloys [2,3]

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Surface energy [J·m⁻²]</th>
<th>Mean Lin. Exp. Coeff. α [K⁻¹]</th>
<th>Molar Volume V₂₉₃ [cm³]</th>
<th>( R_{Oxygen/\text{Metal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( 2.559 - 0.784 \cdot 10^{-3}T )</td>
<td>( 8.1 \cdot 10^{-6} )</td>
<td>25.618</td>
<td>2.80</td>
</tr>
<tr>
<td>( \text{ZrO}_2 )</td>
<td>( 1.428 - 0.431 \cdot 10^{-3}T )</td>
<td>( 9.4 \cdot 10^{-6} )</td>
<td>20.219</td>
<td>1.715</td>
</tr>
<tr>
<td>(CaO stab.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liq. Metals &amp; Alloys</th>
<th>( T_m ) [K]</th>
<th>Surface energy for ( T-T_m ) [J·m⁻²]</th>
<th>Molar Volume at ( T_m ) [cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>429</td>
<td>( 0.560 - 0.09 \cdot 10^{-3}(T-T_m) )</td>
<td>16.33</td>
</tr>
<tr>
<td>Sn</td>
<td>505</td>
<td>( 0.544 - 0.07 \cdot 10^{-3}(T-T_m) )</td>
<td>16.96</td>
</tr>
<tr>
<td>Bi</td>
<td>544</td>
<td>( 0.372 - 0.09 \cdot 10^{-3}(T-T_m) )</td>
<td>20.75</td>
</tr>
<tr>
<td>Pb</td>
<td>600</td>
<td>( 0.468 - 0.13 \cdot 10^{-3}(T-T_m) )</td>
<td>19.40</td>
</tr>
<tr>
<td>Ag</td>
<td>1234</td>
<td>( 0.912 - 0.15 \cdot 10^{-3}(T-T_m) )</td>
<td>11.58</td>
</tr>
<tr>
<td>Cu</td>
<td>1356</td>
<td>( 1.311 - 0.29 \cdot 10^{-3}(T-T_m) )</td>
<td>7.95</td>
</tr>
<tr>
<td>Ni</td>
<td>1726</td>
<td>( 1.754 - 0.28 \cdot 10^{-3}(T-T_m) )</td>
<td>7.58</td>
</tr>
<tr>
<td>Co</td>
<td>1768</td>
<td>( 1.831 - 0.29 \cdot 10^{-3}(T-T_m) )</td>
<td>7.68</td>
</tr>
<tr>
<td>Fe</td>
<td>1809</td>
<td>( 1.825 - 0.27 \cdot 10^{-3}(T-T_m) )</td>
<td>7.97</td>
</tr>
<tr>
<td>Bi-Pb</td>
<td>397</td>
<td>( 0.415 - 0.09 \cdot 10^{-3}(T-T_m) )</td>
<td>19.73</td>
</tr>
<tr>
<td>Bi-Sn</td>
<td>412</td>
<td>( 0.430 - 0.05 \cdot 10^{-3}(T-T_m) )</td>
<td>18.40</td>
</tr>
<tr>
<td>Sn-Pb</td>
<td>458</td>
<td>( 0.525 - 0.09 \cdot 10^{-3}(T-T_m) )</td>
<td>17.45</td>
</tr>
</tbody>
</table>

Fig. 1 - The sessile drop technique in a) bad (θ > 90°) and b) good (θ < 90°) wetting conditions
Fig. 2 - Values of contact angles formed between various solid substrates and various body liquids at \( \equiv 30^\circ C \)

<table>
<thead>
<tr>
<th>Contact Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
</tr>
<tr>
<td>Stainless Steel</td>
</tr>
<tr>
<td>( Al_2O_3 ) (HLD)</td>
</tr>
<tr>
<td>( SO_3 )</td>
</tr>
<tr>
<td>( SO_2\cdot TiO_2 ) (nu, amorph, S-4)</td>
</tr>
<tr>
<td>( SO_2\cdot TiO_2 ) (nu, amorph, S-4)</td>
</tr>
<tr>
<td>( Al_2O_3\cdot TiO_2 ) (HLD)</td>
</tr>
<tr>
<td>( Al_2O_3\cdot TiO_2 ) (HLD)</td>
</tr>
</tbody>
</table>

Fig. 3 - Values of work of adhesion for systems of solid substrates in contact with various body liquids at \( \equiv 30^\circ C \)

<table>
<thead>
<tr>
<th>Work of Adhesion (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
</tr>
<tr>
<td>Stainless Steel</td>
</tr>
<tr>
<td>( Al_2O_3 ) (HLD)</td>
</tr>
<tr>
<td>( SO_3 )</td>
</tr>
<tr>
<td>( SO_2\cdot TiO_2 ) (nu, amorph, S-4)</td>
</tr>
<tr>
<td>( SO_2\cdot TiO_2 ) (nu, amorph, S-4)</td>
</tr>
<tr>
<td>( Al_2O_3\cdot TiO_2 ) (HLD)</td>
</tr>
<tr>
<td>( Al_2O_3\cdot TiO_2 ) (HLD)</td>
</tr>
</tbody>
</table>
Fig. 4 - Influence of ionic character of ceramics on contact angle and work of adhesion in ceramic/body liquid systems

Fig. 5 - Temperature effect on contact angle formed by liquid metals (a) and alloys (b) on Al2O3

Fig. 6 - Temperature effect on contact angle formed by liquid metals (a) and alloys (b) in ZrO2
Fig. 7 - Temperature effect on contact angle formed by liquid metals and alloys on SiO₂ (a), MgAl₂O₄ (b) MgO and TiO₂ (c)
Sn on Ceramics

Cu on Ceramics

Ni on Ceramics

Fig. 8 - The influence of ceramic substrate on the contact angle. Sn (a), Cu (b), Ni (c)
Fig. 9 - Temperature dependence of the interfacial energies in Al₂O₃/liquid metal (a) and ZrO₂/liquid (b) systems. Dashed lines the surface energies of Al₂O₃ (a) and ZrO₂ (b)
Fig. 10 - Correlation between calculated and experimentally estimated values of the interfacial energies, $Y_{SL}$, in $\text{Al}_2\text{O}_3$/liquid-metal and -alloy systems at the melting point of the liquid phases.

Fig. 11 - Correlation between calculated and experimentally estimated values of the interfacial energies, $Y_{SL}$, in $\text{ZrO}_2$/liquid-metal and -alloy systems at the melting point of the liquid phases.
The influence of titania additions on mullite based ceramics

A. GALANI, Th. ZAMBETAKIS, C.J. STOURNARAS

Cereco S.A.
Chalkida (Greece)

ABSTRACT
The difficulties to produce pure mullite ceramics via pressureless sintering are well known. Neither conventional nor sol-gel powders can result to pore-free ceramics when subjected to pressureless sintering.
In this work, the influence of TiO₂ additions on the sinterability and the properties of mullite based ceramics is investigated as an attempt to produce pure, pore free ceramics in the Al₂O₃-SiO₂-TiO₂ system suitable as biomaterials for medical prosthesis.
The results presented concern ceramics made from conventional powders as part of a further study already in progress where conventional ceramics in the system Al₂O₃-SiO₂-TiO₂ will be compared with ceramics made by sol-gel powders.

INTRODUCTION
The experimental production and investigation of ceramics in the ternary system alumina-silica-titania is the objective of this study. A potential application of these ceramics may be in the field of biomaterials because silica, alumina and titania are typical biocompatible ceramic materials.
The main obstacle for the utilization of mullite ceramics is the remaining porosity when both the conventional and the sol-gel method of production are employed (1-6). In a previous study to develop mullite ceramics the authors have concluded that very dense specimens cannot be produced by pressureless sintering (7).
In the present work, the influence of TiO₂ additions on the sinterability and the properties of mullite ceramics is investigated in order to define the compositions with the best characteristics. These materials can be proposed for use in the field of medicine.
This is the first part of a study which includes a similar investigation on ceramics produced from sol-gel powders.

EXPERIMENTAL PROCEDURE
The conventional route for the production of ceramics was followed by mixing of high purity materials, wet milling, shaping and sintering at various temperatures.
The raw materials used were pure α-alumina (Mandoval AKP 30), silica (ALFA products) and titania (ALFA products). The powders were characterized by X-ray diffraction analysis while the particle size distribution was measured using a laser particle size analyser. Mixtures of these powders were prepared. The mole ratio of the Al₂O₃ and SiO₂ powders was kept constant and equal to that of mullite while the TiO₂ percentage was varied between 0 and 50 mole% (Table 1).
Extensive grinding is required in order to reduce the inhomogeneity of the raw materials mixture so that the specimens can be more easily sintered to high density. The grinding process comprised a 4 days wet ball milling using zirconia balls as grinding media followed by vibratory wet milling for 4 hours. The powders were cold isostatically pressed (300 MPa) to form green bars (compacts) with relative densities of the order of 72%. The bars were then cut to pellets which were fired for 3 hours at four different temperatures: 1300, 1400, 1500 and 1600 °C.

Laser particle size analysis was used for the examination of the effectiveness of the grinding process, while the sintering behaviour of the powders was studied employing a Netzsch dilatometer. The influence of the firing temperature on the characteristics of the ceramic body was studied. Porosity and density were measured using mercury porosimetry (Quantachrome A-33 Mercury Porosimeter) and the Archimedes method. X-ray diffraction analysis was performed on the sintered samples (Siemens D 500 Diffractometer) for phase characterization. Their microstructure was studied by the optical microscope. Hardness measurements (Vickers scale) were also performed (Carl-Frank hardness tester).

RESULTS AND DISCUSSION

a) Raw materials

X-ray diffraction analysis showed the presence of pure α-alumina in the alumina powder and of pure quartz in the silica powder. The titania powder consists of rutile with small amounts of anatase.

Initial Al₂O₃ and TiO₂ powders are quite fine (the 90% of their particles are under 1.3 μm and 5 μm respectively), while silica powder has a much larger grain size (only 50% is under 17 μm) (Table 2).

Grinding was followed by particle size distribution and specific surface area measurements of all mixtures (Table 3). In all six compositions, particles are smaller than 6 μm indicating a satisfactory breakdown of SiO₂ particles during grinding.

b) Dilatation measurements

In order to find the appropriate sintering conditions, dilatation measurements on the six compositions (Table 1) were performed.

The thermal shrinkage of the mullite sample (MTO) begins at 1200 °C and it continues at a steady rate up to 1450 °C where the thermal shrinkage is about 6%. At this temperature, sintering has not yet been completed.

The addition of TiO₂ in the initial mullite compositions improves sinterability. As the amount of TiO₂ increases, the dilatation curves move towards lower temperatures (Fig. 1) (the onset temperature of shrinkage is between 1000 and 1100 °C) while the maximum shrinkage increases (10-13% at 1400 °C depending on the TiO₂ percentage). The samples shrink steadily up to 1400 °C and above this temperature the shrinkage strongly decelerates. A different behaviour is observed for the sample with 50 mole% TiO₂ (MT5). Its shrinkage is arrested between 1300 and 1400 °C and it commences again above 1400 °C. The final shrinkage at 1450 °C is 8%.
c) **Densities-Porosities**

Density measurements (mercury porosimetry or Archimedes method) prove that the TiO₂ additions to the mullite samples facilitate their sintering. It can be noticed (Fig. 2) that the maximum density for the mullite sample (MT1) is obtained after 3 h at 1600 °C (8% remaining open porosity). The maximum density for samples containing TiO₂ additions is achieved at lower temperatures (1500 °C for the sample containing 10 mole% TiO₂ - MT1 - , 1400 °C for all the other samples -MT2, MT3, MT4-). The remaining open porosity of these samples is zero (Fig. 3)

When firing temperature exceeds the above mentioned values, density is decreased and porosity is slightly opened. This is probably due to the partial transformation of the crystal phases to glass, which is accompanied by a sample volume expansion, creating porosity.

The addition of 50 mole% TiO₂ results in fired specimens richer in glassy phase with zero porosity at 1500 °C but with relatively lower density.

d) **X-Ray diffraction analysis**

X-ray diffraction analysis (XRD) of the pure mullite composition (sample MTO) showed that the mullitization has been completed after sintering at 1600 °C for 3 h (Fig. 4). When sintering was performed at lower temperatures (1400 or 1500 °C) the main phases were corundum and silicon oxide.

The samples that contained TiO₂ additions (10-30% : MT1-MT3) showed the formation of mullite and mixed oxide Al₂O₃.TiO₂ (Aluminium Titanium Oxide) above 1400 °C. At 1600 °C the reaction of the formation of Aluminium Titanium Oxide is completed and this phase along with mullite are the main phases present in the sample. At this temperature a glassy phase is also formed which does not appear at lower temperatures. Higher amounts of TiO₂ seem to inhibit the mullite formation and to enhance the Al₂O₃.TiO₂ and the glassy phase formation. The sample, consisting of 40 mole% TiO₂ (MT4), after sintering at 1600 °C for 3 h, showed the presence of a small amount of mullite while the main phase was Aluminium Titanium Oxide (Fig. 5) The sample with 50 mole% TiO₂ melted at this temperature.

e) **Optical microscopy observations**

Observation of the samples under optical microscope leads to the same results as those obtained by XRD. The presence of a glassy phase in the samples that contain TiO₂ additions after sintering at 1600 °C is obvious (Fig. 6a).

No mullite grains appear in the samples with high amounts of TiO₂ (40% or 50%) prepared after sintering at 1600 °C (Fig. 6b).

f) **Hardness measurement**

Vickers hardness versus firing temperature for all samples is shown in Fig. 7. As it can be observed increases improvement is achieved, pure mullite sample (MTO) exhibits increase in hardness as the sintering temperature increases from 1400 °C to 1500 °C, while very little improvement is achieved when the sintering temperature is 1600 °C.
This result can be attributed to the high density that is achieved at 1500 °C. The formation of a glassy phase that takes place at 1600 °C inhibits further improvement of the hardness.

The samples containing TiO₂ additions initially exhibit an increase in hardness as firing temperature increases followed by a decrease in hardness for further temperature raising due to formation of significant amounts of a glassy phase. The sintering temperature in which maximum hardness is achieved is 1500 °C for the sample containing 10% TiO₂, while for the other samples (20-40% TiO₂) the temperature is 1400 °C. The maximum hardness value for all these samples (0-40% TiO₂) is almost the same: 1050 HV.

A totally different behaviour is presented by the sample containing 50% TiO₂. The hardness is too low compared to the other samples and it continuously increases with increasing of sintering temperature. This result verifies once again that such an excessive TiO₂ addition to the mullite promotes significant glass formation which in turn results in very low hardness values. The highest hardness value obtained at this temperature is 600 HV.

CONCLUSIONS

On the basis of the present results the following can be concluded:

1) Sintered pure mullite samples were produced with firing at 1600 °C for 3h. Their porosity reaches the value of 6%, their morphology is quite uniform and their Vickers hardness is about 1060.

2) TiO₂ additions improve sintering behaviour. From all the mullite-titania compositions that were tested, the one which contains 20% TiO₂ when fired at 1400 °C for 3 h, (consisting of Al₂O₃·TiO₂ oxide and mullite) gives the best combination of properties (highest hardness, zero porosity).

3) A further study is in progress, where the present findings will be compared with results from TiO₂-Al₂O₃-SiO₂ ceramics produced via sol-gel powders.

REFERENCES

Table 1 - wt% nominal compositions of the samples

<table>
<thead>
<tr>
<th></th>
<th>MTO</th>
<th>MT1</th>
<th>MT2</th>
<th>MT3</th>
<th>MT4</th>
<th>MT5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>28,2653</td>
<td>25,5440</td>
<td>22,849</td>
<td>20,1200</td>
<td>17,3559</td>
<td>37,0523</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>71,7947</td>
<td>65,0205</td>
<td>58,1610</td>
<td>51,2141</td>
<td>44,1785</td>
<td>14,5563</td>
</tr>
<tr>
<td>TiO₂</td>
<td>---</td>
<td>9,4355</td>
<td>18,99</td>
<td>28,6659</td>
<td>38,4656</td>
<td>48,3914</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2 - Particle size analysis results of the raw materials used

<table>
<thead>
<tr>
<th></th>
<th>90%</th>
<th>50%</th>
<th>spec.surf.area m²/gr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfa silica</td>
<td>&lt;57 μm</td>
<td>17 μm</td>
<td>0,8</td>
</tr>
<tr>
<td>AKP 30</td>
<td>&lt;1,3 μm</td>
<td></td>
<td>8,8</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt;5 μm</td>
<td>&lt;3 μm</td>
<td>2,8</td>
</tr>
</tbody>
</table>

Table 3 - Particle size analysis results of the powders after grinding

<table>
<thead>
<tr>
<th></th>
<th>90%</th>
<th>50%</th>
<th>spec.surf.area m²/gr</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTO</td>
<td>&lt;5 μm</td>
<td>&lt;3 μm</td>
<td>3,2</td>
</tr>
<tr>
<td>MT1</td>
<td>&lt;4,8</td>
<td>&lt;2,7</td>
<td>3,8</td>
</tr>
<tr>
<td>MT2</td>
<td>&lt;4,1</td>
<td>&lt;1,9 μm</td>
<td>4,4</td>
</tr>
<tr>
<td>MT3</td>
<td>&lt;3,9</td>
<td>&lt;1,5 μm</td>
<td>5,4</td>
</tr>
<tr>
<td>MT4</td>
<td>&lt;2,6</td>
<td>&lt;1 μm</td>
<td>6,9</td>
</tr>
<tr>
<td>MT5</td>
<td>&lt;6,5 μm</td>
<td>&lt;1,8</td>
<td>4,6</td>
</tr>
</tbody>
</table>
Fig. 1 - Dilatation measurements on mullite-titania samples of different compositions

Fig. 2 - Density of the titania-mullite samples versus sintering temperature

Fig. 3 - Porosity of the titania-mullite samples versus sintering temperature
Fig. 4 - X-ray diffraction analysis of the pure mullite samples.  
a) after sintering at 1400 °C; b) after sintering at 1500 °C; c) after sintering at 1600 °C

Fig. 5 - X-ray diffraction analysis of the sample containing 40 mol% TiO₂.  
a) after sintering at 1400 °C; b) after sintering at 1500 °C; c) after sintering at 1600 °C
Fig. 6 - a) Optical microscope picture of the pure mullite sample sintered at 1600 °C for 3 h; b) Optical microscope picture of the sample containing 40 mol% TiO₂ sintered at 1600 °C for 3 h

Fig. 7 - Hardness versus sintering temperature of the mullite-titania samples
1. INTRODUCTION

The scientific and application efforts of materials scientists and surgeons in the field of alumina hip joint head showed a brilliant successes demonstrating its own broad medical and social acceptance. This prosthesis shows a high wear resistance if coupled with UHMWPE acetabular cup making of alumina the most diffused ceramic head in surgery (1). However, the risk of failure through fracture is considered as a fairly high and one could notice, for example in USA, the trends toward the development of new generation of ceramic heads (2).

As the strongest candidate of new generation of materials emerged the zirconia ceramics attracting last decade significant interests; its excellent mechanical properties, particularly the flexural strength and the fracture toughness, are highly appreciated. Still remain, however, some open questions with zirconia and particularly the tribological behaviour, the chemical compatibility and the long term stability.

The work of Tsukuma et al. (3) has shown the increase of flexural strength of zirconia containing different percentages of alumina; for instance, three point bending strength of pressureless sintered 2 mol% yttria stabilized zirconia increased from 1170 MPa up to 1360 MPa if 20 wt% of alumina were added.

Within EUREKA PROJECT 294 the studies of microstructural, mechanical and tribological characteristics of zirconia-alumina and alumina as a reference material have been programmed. The main objectives covered the investigations concerning the ceramic processing and synthesis of ceramic samples and components, hopefully of improved behaviour. A series of attempts to increase the wear resistance of zirconia, but not jeopardizing substantially the strength and toughness, were done by investigating the influence of shaping techniques, sintering cycles and alumina content added to partially stabilized zirconia. The following overall program was therefore accepted:

- **powders**: Yttria partially stabilized zirconia, high purity alumina and their mixtures;
- **shaping techniques**: Slip casting, pressure slip casting and cold uniaxial pressing;
- **characterization of the fired samples**.

In this paper will be described only the experimental part concerning:

- PS Zirconia (3 mol% of Yttria; powders Z and, with binder, ZB) and
- PS Zirconia containing 20 wt% Alumina (powders 8Z2A and, with binder, 8Z2AB).

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1 Starting powders

The main characteristics of the starting powders are given in Table 1 toghether with the other powders planned to be studied in the frame of the Project BU 294.
Tab. 1 - Characteristics of starting powders

<table>
<thead>
<tr>
<th>POWDER</th>
<th>Composition</th>
<th>Mean crystallite size /Å</th>
<th>Surface area, m²/g</th>
<th>Mean unit particle /µm</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>3mol% Yttria stabilized ZrO₂</td>
<td>359</td>
<td>6</td>
<td>0.3</td>
<td>• low viscosity slips</td>
</tr>
<tr>
<td></td>
<td>with binder</td>
<td></td>
<td></td>
<td></td>
<td>• acceptable casting rates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• excellent sinterability</td>
</tr>
<tr>
<td>ZB</td>
<td>3mol% Yttria stabilized ZrO₂ with binder</td>
<td>250</td>
<td>—</td>
<td>0.3</td>
<td>• greens of limited density</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• excellent sinterability</td>
</tr>
<tr>
<td>8Z2A</td>
<td>3mol% Yttria stabilized ZrO₂ with 20 wt% Al₂O₃</td>
<td>259</td>
<td>16</td>
<td>ZrO₂: 0.1</td>
<td>• low viscosity slips</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al₂O₃: 0.3</td>
<td>• low casting rates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• high sinterability</td>
</tr>
<tr>
<td>8Z2AB</td>
<td>3% Yttria stabilized ZrO₂ with 20 wt% Al₂O₃ with</td>
<td>251</td>
<td>—</td>
<td>ZrO₂: 0.1</td>
<td>• acceptable compressibility</td>
</tr>
<tr>
<td></td>
<td>binder</td>
<td></td>
<td></td>
<td>Al₂O₃: 0.3</td>
<td>• high sinterability</td>
</tr>
<tr>
<td>6Z4A</td>
<td>3% Yttria stabilized ZrO₂ with 40 wt% Al₂O₃</td>
<td>220</td>
<td>13-15</td>
<td>in progress</td>
<td>experiments in progress</td>
</tr>
<tr>
<td>4Z6A</td>
<td>3% Yttria stabilized ZrO₂ with 60 wt% Al₂O₃</td>
<td>240</td>
<td>11-12</td>
<td>in progress</td>
<td>experiments in progress</td>
</tr>
<tr>
<td>2Z8A</td>
<td>3% Yttria stabilized ZrO₂ with 80 wt% Al₂O₃</td>
<td>270</td>
<td>9-10</td>
<td>ZrO₂: 0.1</td>
<td>• low viscosity slips</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al₂O₃: 0.4</td>
<td>• acceptable casting rates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• high sinterability</td>
</tr>
<tr>
<td>A**</td>
<td>100% α-Al₂O₃</td>
<td>n. d.</td>
<td>9-11</td>
<td>0.16</td>
<td>• low viscosity slips</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• acceptable casting rates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• excellent sinterability</td>
</tr>
</tbody>
</table>

*Powders produced by TOSOH (Japan); **Powder produced by Baikowski (France).

In every case zirconia is a mixture of tetragonal and monoclinic crystal phases and alumina is α phase. All the powders are characterized by high chemical purity and fine unit particles.

During this part of the research two powder types were investigated: 3 mol% yttria stabilized zirconia without or with 20 wt% of α alumina. These powders were shaped by slip casting (powders Z and 8Z2A) or by cold uniaxial pressing (powders ZB and 8Z2AB).

SEM (Mod. T 330, Jeol, Japan) examination reveals that the powders were characterized by the presence of spherical and fairly compact agglomerates ranging within 10 and 100 µm.

The unit particles are also spherical; they are submicronic and show a narrow size distribution. The two powders 8Z2A and 8Z2AB demonstrate a bimodal particle size distribution due to the presence of zirconia and alumina; it must be remarked that the zirconia particles are smaller than those of the powder Z and this fact substantially contributes to its high surface area.
2.2 Shaping

2.2.1 Slip casting and pressure slip casting
The slips were prepared by homogenization in a centrifugal mill with zirconia jar and balls of the "as received" powders with deionized water and deflocculant; the milling time was 30 minutes. The characteristics of the investigated slips are given in Table 2.

<table>
<thead>
<tr>
<th>POWDER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
</tr>
<tr>
<td>8Z2A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid content, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slip casting</td>
</tr>
</tbody>
</table>

| Pressure slip casting | 33 | 21 |

<table>
<thead>
<tr>
<th>Deflocculant* content, wt% of solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range investigated</td>
</tr>
</tbody>
</table>

| Optimized                           | 0.5 | 1.8 |

*DOLAPIX CE 64 "Zschimmer & Schwarz"(Germany)

The viscosity measurements of the prepared slips were performed by a viscometer (Mod. 39 Fann Instr.Corp., USA); the viscosity curves of the slips containing optimized deflocculant contents are shown in Fig. 1.

![Viscosity curves of slips prepared with Z and 8Z2A powders.](image)

Fig. 1 - Viscosity curves of slips prepared with Z and 8Z2A powders.
Slip casting was done in gypsum moulds having the total porosity of about 50%; discs of 28mm in diameter and thickness up to 8mm were cast. Pressure slip casting experiments were done using a self designed device assembled with an hydraulic press. The cast samples were produced at pressure of 10MPa in form of discs of 60 mm in diameter while thicknesses ranged between 12 and 45 mm. From the casting rate curves for both of the used techniques, shown in Figg. 2 and 3, it can be noticed:

- to obtain the same thickness, pressure slip casting requires from 1 to 2 orders of magnitude shorter time if compared to slip casting;
- by pressure slip casting it is quite feasible to obtain very high thickness, up to 47 mm compared to 12 mm obtained by casting in plaster moulds;
- the slip prepared with powder 8Z2A has lower casting rates than the slip with powder Z; this can be related to the higher packing efficiency of finer zirconia particles in 8Z2A, 0.1 μm, in comparison with those in powder Z, 0.3 μm.

![Fig. 2 - Casting rates of slips with optimized deflocculant content.](image1)

![Fig. 3 - Pressure slip casting rates (at 10 MPa) of slips with optimized deflocculant content.](image2)
The SEM examination of cast greens revealed:
• the greens of powder Z are characterized by an homogeneous microstructure; a
  restricted number of agglomerates or their own fragments were observed;
• the greens of powder 8Z2A are characterized by an high homogeneity. Some areas of
  lower compactness were observed, that could be ascribed to the finesse of zirconia
  particles.
The microstructures of green samples obtained by slip casting in plaster moulds and
pressure slip casting were, from qualitative point of view, basically the same.

2.2.2 Cold pressing (reference samples)
The cold uniaxial pressing of powders ZB and 8Z2AB was carried out by an hydraulic
single effect press (Off. Mecc. Bertoni e Cotti, Italy) using different steel dies enabling us

to produce discs of 25 mm in diameter or bars of 4x4x45 mm.
The influence of pressing pressure on green samples density is shown in Fig. 4.

![Graph showing the interdependence between density of greens and pressing pressure](image)

Fig. 4 - Interdependence between density of greens and pressing pressure
(theoretical densities: ZB: 6.05 g/cm³ and 8Z2AB: 5.50 g/cm³).

It is clear that the density values of all pressed bodies are ranging within relatively low
levels and hardly superate 46% TD. This is in accordance with the fact that the powders
used in the present study contain very fine particles and, consequently, are characterized
by relatively low compressibility.
The increase of pressing pressure up to 120 MPa was not sufficient to create closer
packing of particles and/or agglomerate fragments and therefore one must expect high
shrinkage levels after sintering.
The pressed samples were produced at a pressure of 70MPa: so obtained samples of both
powders have the relative density of 43% TD.
The SEM examination of pressed bodies revealed fairly homogeneous microstructures.
3. SINTERING

All the green samples, slip cast, pressure slip cast and cold pressed, were sintered in air using the same thermal cycle: heating up to 800 °C at 10°C/min soak at 800 °C for 1 hour; heating up to 1500 °C at 3°C/min, soak at 1500 °C for 2 hours and cooling down to room temperature at 1 °C/min.

4. CHARACTERIZATION OF CONSOLIDATED SAMPLES

4.1 Physical properties and microstructure

Using the laboratory measurement techniques the appropriate characterization of consolidated samples was done; typical values obtained within this part of experimental work are given in Table 3.

<table>
<thead>
<tr>
<th>Tab.3 - Characteristics of consolidated samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE</td>
</tr>
<tr>
<td>Shaped by</td>
</tr>
<tr>
<td>Green density, g/cm³</td>
</tr>
<tr>
<td>Slip casting</td>
</tr>
<tr>
<td>Cold pressing</td>
</tr>
<tr>
<td>Density of sintered samples, g/cm³</td>
</tr>
<tr>
<td>Slip casting</td>
</tr>
<tr>
<td>Cold pressing</td>
</tr>
<tr>
<td>Linear shrinkage after sintering, %</td>
</tr>
<tr>
<td>Slip casting</td>
</tr>
<tr>
<td>Cold pressing</td>
</tr>
<tr>
<td>Mean grain size*, μm</td>
</tr>
<tr>
<td>Slip casting</td>
</tr>
<tr>
<td>Cold pressing</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

*by SEM

The SEM observations of both slip cast and pressure slip cast Z samples revealed as they are highly homogeneous and contain predominantly submicronic and narrow sized grains. The presence of rounded areas, with clusters of micropores, could be noticed in
some cases; this could be attributed to the agglomerates still existing in the slips. Further efforts toward better deagglomeration were therefore accepted as unavoidable powders pretreatments. The sintered 8Z2A samples previously cast or pressure cast show highly homogeneous microstructures. The zirconia grains remained submicronic while the alumina ones slightly superated one micrometer. However, some abnormally grown alumina grains could be noticed underlining the necessity of further optimization of sintering thermal cycle.

4.2 Mechanical properties

The flexural strength was determined using a testing machine (mod. M30K, J&J, England). The sintered specimens 2x2.5x25 mm edge cut and with tolerances of +/-0.02mm were machined from discs. All the surfaces were ground and the longitudinal edges were chamfered at a distance of 0.012 +/- 0.003 mm as measured along the faces of the test piece; only the surface under tensile stress was polished to a mirror finish. All the specimens were heated at 1000 °C for 1 hour to compensate the residual stresses due to the previous machining. A batch of 37 specimens for every material was chosen and four-point bending test was performed with a crosshead speed of 0.5 mm/min. The outer and inner loading spans were 20 and 10 mm respectively. The experimental data were evaluated with the estimator (i - 0.5)/N and the least squares method. The hardness was determined by Vickers indentation technique on a mirror polished surfaces, using a semi-automatic hardness tester (mod. 3212, Zwick, Germany); the loads ranged between 49.05 to 294.3 N in air and at room temperature. The lengths of the cracks arising from the corners of Vickers indentations were measured to evaluate $K_{Ic}$ [4].

Hardness, $K_{Ic}$, flexural strength and Weibull modulus $m$ of the investigated samples are given in Table 4.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$H_v$ GPa</th>
<th>$K_{Ic}$ MPa$^{0.5}$</th>
<th>$\sigma$ MPa</th>
<th>Weibull modulus, $m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z slip cast</td>
<td>13.3</td>
<td>6.0</td>
<td>766</td>
<td>11.7</td>
</tr>
<tr>
<td>ZB</td>
<td>13.3</td>
<td>5.7</td>
<td>703</td>
<td>17.0</td>
</tr>
<tr>
<td>8Z2A slip cast</td>
<td>14.3</td>
<td>6.1</td>
<td>in progress</td>
<td>in progress</td>
</tr>
<tr>
<td>8Z2AB</td>
<td>14.3</td>
<td>5.8</td>
<td>858</td>
<td>18.6</td>
</tr>
</tbody>
</table>
It could be noticed that the addition of 20 wt% of alumina to the partially stabilized zirconia, i.e. 8Z2A and 8Z2AB, produced the samples of higher hardness in comparison with ZA and ZB without reducing of fracture toughness. Moreover, the 8Z2AB samples were characterized by higher values of $\sigma$ if compared with the ZA and ZB samples; this could be probably correlated with higher microstructural homogeneity of mixed powders sample characterized also by high Weibull modulus.

4.3 Tribological characterization

The tribological characteristics of the materials were studied at room temperature, in air and in unlubricated conditions, using a "pin-on-disk" apparatus. The discs were tested against $\alpha$-alumina (AL 23, Degussa, Germany) pins at different sliding rate conditions (5). All of the examined couples, within the experimental conditions used, have given low mean values of the friction coefficient, less than 0.2; the couple 8Z2AB/Alumina presented the lowest values of $\mu$, always less than 0.1. In Table 5 the wear rate values for the different disc materials are shown.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Sliding distance m</th>
<th>Sliding rate m/s</th>
<th>Friction coefficient $\mu$</th>
<th>Wear rate of disc $\mathrm{mm}^3/mN$</th>
<th>Wear rate of pin $\mathrm{mm}^3/mN$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z Slip cast</td>
<td>3000</td>
<td>0.3</td>
<td>0.15</td>
<td>192.00 $\times 10^{-5}$</td>
<td>0.13 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7</td>
<td>0.19</td>
<td>252.00 $\times 10^{-5}$</td>
<td>1.19 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.15</td>
<td>14.00 $\times 10^{-5}$</td>
<td>1.44 $\times 10^{-5}$</td>
</tr>
<tr>
<td>ZB</td>
<td>3000</td>
<td>0.3</td>
<td>0.15</td>
<td>158.80 $\times 10^{-5}$</td>
<td>0.26 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7</td>
<td>0.13</td>
<td>149.20 $\times 10^{-5}$</td>
<td>1.24 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.14</td>
<td>27.50 $\times 10^{-5}$</td>
<td>0.45 $\times 10^{-5}$</td>
</tr>
<tr>
<td>8Z2B</td>
<td>3000</td>
<td>0.3</td>
<td>0.08</td>
<td>11.50 $\times 10^{-5}$</td>
<td>10.0 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7</td>
<td>0.03</td>
<td>9.14 $\times 10^{-5}$</td>
<td>6.04 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.06</td>
<td>6.80 $\times 10^{-5}$</td>
<td>0.13 $\times 10^{-5}$</td>
</tr>
</tbody>
</table>

Zirconia, independently from the forming method, presented fairly high wear rate, particularly at low sliding rate. By adding 20% of alumina, the composition corresponding that of the powder 8Z2AB, allowed to improve substantially the tribological behaviour in respect to samples of zirconia: in fact, the wear rate of samples prepared with 8Z2AB decreased notably.
4. CONCLUSIONS

- The powders of partially stabilized zirconia and zirconia containing 20 wt% alumina were characterized and densified by slip casting or cold pressing followed by sintering.
- Slip casting, traditional and under pressure, gave the ceramic bodies of more homogeneous microstructures than those obtained by cold pressing.
- The modulus of rupture and the toughness of both Z and 8Z2A bodies were higher than the values of commercial alumina ceramics.
- According to the wear and friction tests performed the wear resistance of 8Z2AB approached those of alumina ceramics.
- Further experiments concerning the powders mentioned are under way.

ACKNOWLEDGEMENTS

The authors kindly acknowledge S. Degli Esposti and D. Naldi for their help in the experimental work.

REFERENCES

Stresses in ceramic prosthetic heads under axisymmetric loading: effect of taper friction, support conditions and spigot elasticity

E. DRAGONI¹, A.O. ANDRISANO²

1. Department of Mechanics, University of Bologna, Bologna (Italy)
2. Faculty of Engineering, University of Modena, Modena (Italy)

ABSTRACT

The outcome of a nonlinear finite element stress analysis of ceramic heads for artificial hip joints is presented. The analysis mainly covers the influence of taper friction, support conditions and stem elasticity on the hoop stress distribution at the head bore surface. The paper quantifies how much the maximum tensile stress lowers with increasing frictional coefficient, with stiffening of the support and with stiffening of the spigot material. An appreciable rise of the maximum tensile stress upon unloading of the head is also pointed out for the cases of cup support. The computational findings are found in close correspondence with photoelastic measurements of taper pressures and encourage the use, for preliminary design purposes, of an approximate theoretical model retrieved from the literature.

1. INTRODUCTION

This paper documents a parametric stress analysis of ceramic universal heads for total hip replacement which undergo the axisymmetric loading shown in Figure 1. Chief aim of the study is to find out the effects on the stress level played by three parameters, namely (a) the frictional coefficient at the taper press fit, (b) the outer support conditions of the head and (c) the elastic modulus of the stem spigot. The residual stress field that remains frozen within the head upon removal of the load is also evaluated. The analyses are performed by means of the finite element (FE) method. The numerical forecasts are confronted with photoelastic results for a particular combination of the above variables and to an elementary analytical model retrieved from the literature.

Due to the preeminent structural role of prosthetic hip balls, a wealth of technical literature exists which deals either with the stress analysis or with the fatigue strength assessment of this crucial component. For the part of stress analysis, experimental methods (photoelasticity, strain gauges) or numerical ones (finite elements) are generally favoured because the complex geometry of the joint prevents the attainment of reliable exact solutions. The most detailed photoelastic work to date in the investigation by Fessler and Fricker (1989) in which a comprehensive bibliographic survey pertaining to this subject is also to be found. Though to a lesser quantitative extent, photoelasticity has been used also by Soltész and Heimke (1982) to explore the effects of a cone angle mismatch between head and spigot. Thanks to its relative simplicity, the strain gauge technique has won wide popularity (Kleer et al., 1985; Kleer et al., 1987). However, the usefulness of this method is jeopardized by its obvious inability to measure the tensile taper hoop stresses which are of greatest concern in ceramic heads. As regards the numerical
methods, a refined, nonlinear FE analysis of hip joints has been recently published by Andrisano et al. (1990a). In that contribution, the frictional interaction between stem and head is modelled for the first time without resorting to the crude assumptions previously introduced by other authors (Kleer et al., 1985; Kleer et al., 1987; Seidelmann et al., 1982).

The present paper represents the outgrowth of Andrisano's et al. (1990a) work. The FE method is again adopted for its unparalleled flexibility in coping with model changes. Because of the need to control such subtle parameters as frictional coefficients and elastic moduli, this versatility proved invaluable in the present case. The axisymmetric configuration of Figure 1 is examined, in which true unilateral contact at both headspigot and head-cup interfaces is accounted for. The shape of the head corresponds to a medium neck design (Andrisano et al., 1990a; Dörre et al., 1991) and the outline of the cup, showing a draining centre hole, is consistent with a commercial version of the implant. Although in contrast with the in vivo circumstance of a 30 degree deviation of the load from the joint axis (Paul, 1967), the axisymmetric assumption is well representative of the relevant stress response of the head. As a matter of fact, the transverse component of the total hip load has a negligible effect on magnitude and distribution of taper hoop stresses (Fessler and Fricker, 1989) which embody the major structural hazard of this fragile part.

The reference assembly of Figure 1 postulates full conformity at the taper engagement between spigot and head and at the spherical coupling between head and cup. In order to simulate gross geometric inaccuracies of the spherical pair, loading of the head against a plane was also performed. Conversely, no allowance was made for cone errors at the press fit.

The results of the investigation can be summarized as follows. (a) The higher the taper friction, the lower the tensile hoop stresses in the head. This effect is so dramatic that, in comparison with the frictionless situation, frictional coefficients of 0.1, 0.2 and 0.5 produce a stress decrease of three, five and fifteen times, respectively. (b) The softer the supporting cup, the higher the hoop stresses. This effect is modest for realistic frictional coefficients (≤ 3) and increasingly significant for increasing friction. For instance, if a coefficient of friction of 0.1 is assumed, the maximum circumferential stress experiences a mere 35 per cent increase on switching from a rigid, closely conforming cup to a planar support (point contacts). Conversely, the stress is more than doubled if a frictional coefficient of 0.5 is considered. (c) The stiffer the spigot, the lower the hoop stresses. This influence is perceivable but not strong, the maximum stress induced by a rigid spigot (Eₜ → ∞) being 80 per cent of that generated by an aluminium spigot (Eₜ = 70 GPa). Apart from the case of planar support and excluding the idealized frictionless situation, it is also demonstrated that, though slightly, the hoop stresses generally increase upon removal of the load. The numerical results further indicate that the simple analytical model proposed by Fessler and Fricker (1989) provides useful estimates of maximum hoop stresses when the head is loaded against a plane. Likewise, application of the FE method to a configuration for which photoelastic data are available (Andrisano et al., 1990b) leads to excellent agreement between taper contact pressures.
1.1 Nomenclature

- \( D \) = outside diameter of head
- \( E_S, E_h, E_c \) = Elastic moduli of spigot, head and cup, respectively
- \( f \) = coefficient of friction
- \( I \) = axial length of taper contact
- \( p_c \) = contact pressure
- \( P \) = axial load
- \( x \) = axial position along contact
- \( \varepsilon_\theta \) = taper hoop strain
- \( \nu_S, \nu_h, \nu_c \) = Poisson's ratios of spigot, head and cup, respectively
- \( \sigma_n = 4P/(\pi D^2) \) = nominal stress
- \( \sigma_\theta \) = taper hoop stress
- \( \sigma_{\theta\text{max}} \) = maximum taper hoop stress
- \( \tau_c \) = shear contact stress
- \( \tau_S \) = slipping shear contact stress

2. METHOD

The FE calculations reported in this paper were performed with the general purpose package ABAQUS, version 4.8-4 (Hibbit et al., 1989), installed on the DEC Microvaac 3500 computer of the Laboratory for Computational Mechanics (LAMC) of the University of Bologna. A detailed description of the numerical model and of the solution procedure employed in the analyses is covered in the following subsections.

2.1 Mesh selection

The FE grid idealizing the complete joint is shown in Figure 2. All the elements were eight-noded, displacement-formulation, biquadratic-interpolation, axisymmetric quadrilaterals with full integration. The only exception to this choice occurred in the model intended for duplicating photoelasticity, where the incompressible behaviour of epoxy at oven temperature enforced the use of hybrid elements.

The mesh of Figure 2 comprises 192 elements and 653 nodes for the spigot, 256 elements and 849 nodes for the head and 140 elements and 469 nodes for the cup. The adequacy of the grid was established through a mesh convergence procedure carried out on the head alone. More precisely, three grids were compared. Starting with a crude prototype, a second mesh was derived by subdividing each element in four. From this, the final mesh of Figure 2 was obtained through a further element quadruplication. All models gave comparable results in terms of maximum taper stresses when loaded by a rigid stem and supported by a rigid cup. The richer mesh was retained for its superior performance in coping with the (compressive) stress concentrations at the contact edges (Section 3.1). After this step, the grids of spigot and cup were generated with the main concern of element regularity and contact node correspondence (Section 2.4).

2.2 Loading

The joint was loaded by a force \( P \) evenly distributed over the cross section of the stem (Figure 2). To avoid interaction between applied pressure and taper stresses, the loaded section was placed more than one diameter away from the cavity mouth.

Each analysis included two phases. A first loading step, in which the force was gradually increased up to a convenient load level, followed by a final unloading step, during which the force was progressively released down to zero. As explained later (Section 3.4), the loading path differed substantially from the unloading one in terms of stress response to a given load. Yet, both behaviours were remarkably linear. This allowed the taper stresses consequent to loading and those consequent to unloading to be normalized over the maximum load, independently of its particular value.
2.3 Boundary conditions
The complete model was restrained in the direction of loading by setting to zero the axial displacement of the nodes located on the lower surface of the cup (line a-a in Figure 2). Individual axial constraining of stem and head was ensured by the interfacial forces arising at the contacts. The reduced model simulating point contact against a plane (line b-b in Figure 2) was constrained axially entirely by means of interface elements. Though not strictly required by the axisymmetry of the problem, also the radial degree of freedom of the nodes lying on the symmetry axis was removed in both complete and reduced models.

2.4 Description of contact
Unilateral contact at spigot-head and head-cup (head-plane) engagements was taken into account by means of six-noded interface elements. Use of these elements called for the coincidence, in the undeformed model, of the nodes pertaining to each pair of mating surfaces. This requirement gives to the mesh of Figure 2 an appearance of material continuity at the transition region from one component to the other. In reality, stem, head and cup are disjointed.
A frictional coefficient varying from 0 to 1 (in steps of 0.1) was assumed at the taper fit between spigot and head. In line with the contact description supported by ABAQUS, the coefficient of friction, \( f \), corresponds to the simple Coulomb law \( \tau_c \leq \tau_s = \mu p_c \) which restricts the maximum magnitude, \( \tau_s \), of the shear contact stress, \( \tau_c \), to a fraction of the local contact pressure, \( p_c \). For the sake of simplicity, no friction was assumed at the head-cup interface. Since the relative tangential movements between these two parts were always found to be small, this simplification is not believed to have altered perceivably the taper stresses. Moreover, it is consistent with the low frictional coefficient actually measured in vivo (Fricker, 1991).

2.5 Materials
The materials of the three components were assumed elastic and, apart from the photoelastic simulation, they were assigned the properties typical of a stainless steel spigot (\( E_s = 210 \) GPa, \( v_s = 0.3 \)) engaging with an alumina head (\( E_h = 380 \) GPa, \( v_h = 0.22 \)) resting on an alumina cup (if any). In evaluating the effect of the stem elasticity, the Young's modulus of the spigot was varied in the range from 70 MPa (aluminium) to infinity. Similarly, for the assessment of the influence of the support, infinite stiffness of the cup was also assumed. In adherence with the experimental conditions of Andrisano et al. (1990b), a Young's modulus of 10 MPa and a Poisson's ratio of 0.5 were adopted for all parts in the run aimed at reproducing the photoelastic test.

2.6 Solution scheme
Despite the linearity of both macrogeometrical response and material formulation, the need to cope with the stick-slip frictional behaviour and with possible opening of contact interfaces makes the problem inherently nonlinear. A profitable way to handle boundary nonlinearities of this kind is to condense the contacting bodies into (separate) linear superelements for which only the interfacial degrees of freedom are kept active (Cook,
1974; Dragoni, 1992). Although this does not improve the accuracy of the output data, it dramatically reduces the time to convergence needed by the iterative solution scheme. Regrettably, such an opportunity could be only partly exploited in the present case. Due to an acknowledged inconsistency, ABAQUS version 4.8-4 does not support the superelement capability if coupled with a non-symmetric Jacobian matrix. As well documented in specialized literature (Hibbit, 1979), unsymmetry of the Jacobian is triggered by a variety of causes, among which substantial shear stresses as those arising at the spigot-head taper play a role.

Because of this deficiency, the superelement generation was invoked only at the lowest frictional coefficients (≤ 0.2), for which the unsymmetric allocation of the Jacobian could be skipped without prejudice of the convergence. The rest of the analyses, involving friction values up to 1, were carried out by iterating over all the degrees of freedom of the model.

3. RESULTS AND DISCUSSION

The following presentation is mainly concerned with the tensile hoop stresses developing in the head at the taper surface. Significant tensile stresses were spotted at the inner point of the bore crown (Fessler and Fricker, 1989) only in the unrealistic case of point contact onto a plane. This agrees with the usual bursting character of head failures in vivo.

The stress values are normalized over the mean stress, σₙ = 4P/πD², referring to the outside head diameter, D. As anticipated in Section 2.2, this normalization is meaningful due to the linearity between load and stresses during both loading and unloading. With the sole exception of Section 3.4, which is devoted to the effect of unloading, the stress results discussed below refer to the loading path. The meaning of the notation seen in the illustrations is clarified in Section 1.1 and in Figure 1.

3.1 Effect of frictional coefficient

The distributions of circumferential stresses along the bore generator are collected in Figure 3 for several frictional coefficients in the range from 0 to 1. In this case, the head is loaded through a steel spigot (Eₛ = 210 GPa, vₛ = 0.3) and supported by a conforming alumina cup (Eₖ = 380 GPa, vₖ = 0.22). The plots of Figure 3 evidence that the hoop stresses are tensile and fairly uniform over most of the contact length, but tend to become compressive at both contact edges. This result confirms the photoelastic findings of Fessler and Fricker (1989) and the FE predictions of Andrisano et al. (1990a). The rationale behind this is the occurrence of theoretically infinite pressure spikes (i.e. pₛ → +∞) at the edges of the contact (Oda et al., 1972; Johnson, 1985). In the absence of significant axial stresses at these points, the Hooke’s law Eₕεₕ = (σₕ + νₛₕₕₕ) requests that the hoop stress become (infinitely) negative for the hoop strain to stay finite.

An effective rendition of the stress dependence on the frictional coefficient is offered in Figure 4, where the maximum hoop stress anywhere along the taper is plotted against the coefficient of friction. The curve corresponding to the same loading and support conditions as above is denoted by the star symbol. It is easily verified that, when compared with the frictionless engagement, taper frictional coefficients of 0.1, 0.2 and 0.5 produce a stress decrease of three, five and 15 times, respectively. Together with the considerable scatter of tensile strength values typical of ceramics, this strong sensitivity to
3.2 Effect of support conditions

Referring to a frictional coefficient of 0.1 and to a steel spigot ($E_s = 210$ GPa), Figure 5 details the taper hoop stress profiles for three support conditions of the head. The case of alumina cup (stars), already shown in Figure 3, is compared with the limit cases of rigid cup (squares) and of point contact against a plane (circles). According to intuition, the softer the support the higher the stress, the increase being of about 35 per cent on replacing the rigid cup with the planar support. Qualitatively, the trend of Figure 5 was observed for any other frictional coefficient. From a quantitative point of view, however, the incidence of the support increases with the coefficient of friction. This is clearly appreciated from Figure 4 where, similarly to the basic case of alumina cup (stars), the peak taper stress is plotted against the frictional coefficient also for the extremes of rigid cup (squares) or no cup at all (circles). Quite usefully, these two limit curves bound the range of variation of the maximum hoop stress taking place in the head, no matter what the actual support conditions will be.

3.3 Effect of spigot elasticity

Figure 6 highlights the change in taper hoop stress distribution caused by variation of the spigot elastic modulus. Support through an alumina cup and a taper coefficient of friction of 0.1 are now assumed. The diagram compares the stresses consequent to loading of the head through a steel spigot (stars) to those arising from the engagement with either an ideally undeformable ($E_s = \infty$, squares) or an aluminium ($E_s = 70$ MPa, circles) spigot. Though unplausible from a biomechanical standpoint (Ducheyne and Hastings, 1984), the case of aluminium exemplifies the softest metal stem that could be conceivably implemented.

The curves of Figure 6 show that the hoop stress profile lowers and flattens for increasingly stiffer spigot materials. The same behaviour was detected also for all other frictional coefficients in the range 0-1, with a fairly constant 20 per cent stress decrease on passing from the aluminium stem to its rigid counterpart. The detrimental effect of lowering the stem Young's modulus is primarily imputable to shortening of the spigot under compressive axial load. As the material softens, the spigot cross section by the hole entry ($x/l = 1$ in Figure 6) tends to come closer to the exit section ($x/l = 0$) so that, in consequence of the tapered geometry, a virtual widening of the cone angle is produced. This movement brings the entry sections of the spigot to dig into the mouth surface of the bore, thus leading to a local contact pressure increase which is responsible of the hoop stress rise displayed in Figure 6.

3.4 Effect of unloading

Besides turning the compressive stem load into tensile head stresses because of wedge action, a further weak point of the press fit concept is the permanent storage of those stresses owing to irreversibility of taper movements. The head is thus called to endure the stresses brought into existence by the highest load ever experienced by the joint. Slow growth of embedded defects up to critical size is the threatening aftermath. In the attempt
to get rid of this shortcoming, alternative attachments have been proposed by Zeibig and Sandrolini-Cortesi (1980), Wordsworth and Weightman (1986) and by Andrisano et al. (1990a). However, the taper design is so widely spread that a precise evaluation also of the residual stress field carries considerable interest.

The distribution of the taper hoop stresses locked within the head upon unloading (circles) is compared in Figure 7 with the stress profile at the end of the loading step (stars). The data refer again to the basic configuration of alumina cup support and steel spigot with a taper frictional coefficient of 0.1. The astonishing conclusion is that removal of the load causes an appreciable increase of the overall stress level. This result is due to loss of outer containment consequential upon ejection of the ball from the socket at vanishing loads. Consistent with this explanation, substantial invariance of the hoop stresses followed unloading of the head in contact with the plane. At the same time, an even greater stress rise than in Figure 7 originated in unloading the head supported by the rigid cup.

Contrary to the particular case of Figure 7, frictional coefficients higher than 0.1 generally affected also the peak hoop stress. For the head resting on the alumina cup, the highest stress increment upon load removal amounted to about 15 per cent of the maximum loading stress (Figure 4) and derived from a frictional coefficient of 0.6.

4. COMPARISON WITH PREVIOUS WORK

This section is devoted to comparing the above results with published data stemming from approaches other than the FE one. In particular, a direct comparison was possible with both analytical (Fessler and Fricker, 1989) and experimental (Andrisano et al., 1990b) methods. These are covered separately in the follow-up.

4.1 Analytical model

As already remarked, the complex geometry of the head and the involved unilateral boundary conditions make the discovery of exact stress solutions very unlikely. Nonetheless, if based on a set of simplifying assumptions, the development of elementary analytical models is still possible. Fessler and Fricker (1989) have proposed one such model. According to their approach, the overlapping portion of head and spigot is partitioned into an infinite number of infinitesimal, independent slices. Frictional interaction of head and spigot in each slice is ultimately described in terms of contact pressure. This, in turn, is linked to the relative movement of the spigot into the head by means of the thick pipe theory. Final requirement of axial equilibrium gives, sequentially, the spigot penetration, the contact pressure profile and the hoop stress distribution at the head taper surface.

Application of this model to the present head geometry (Figure 1) resulted in the axial distribution of hoop stresses displayed in Figure 5 (dashed line). The analytical curve is to be compared with the FE forecasts valid for the planar support (circles), because the cup is not included in the elementary model. Interestingly, although the two curves disagree in both shape and location of the maxima, the magnitudes of their peak values correspond favourably. As shown in Figure 4 (dashed line and circles), the agreement is excellent for the whole range (0.1-0.3) of plausible stem-head frictional coefficients (Fessler and Fricker, 1989a) and remains acceptable up to the highest values (0.5-0.6) reported in technical literature (Seidelmann et al., 1982; Sotelo et al., 1984; Kleer et al., 1985).
4.2 Photoelasticity

The raw outcome of a frozen-stress photoelastic analysis on a model hip joint identical in proportions with the assembly of Figure 1 has been published by Andrisano et al. (1990b). Partial elaboration of the same material has become available more recently (Bertuzzi, 1991; Strozzi, 1992) in the form of taper contact pressures. In order to compare the present results with those sources, the complete FE model of Figure 2 has been analyzed by adopting the actual material properties ($E_s = E_h = E_c = 10$ MPa, $\nu_s = \nu_h = \nu_c = 0.5$), taper friction coefficient ($f = 0.6$) and axial load ($P = 215$ N) that were measured experimentally.

In Figure 8 the photoelastic contact pressure distribution along the taper surface (stars) is compared with the FE predictions based on the above parameters (squares). The degree of correlation is very good over much of the contact length, the sharpest disagreement occurring by the outer end of the taper ($x/l = 1$) where the pressure gradient is strong. Interestingly, the FE pressure distribution correspondings to the reference combination of steel spigot, alumina head and alumina cup with a frictional coefficient of 0.6 (circles) is nearly indistinguishable from the profile supplied by the FE replica (stars) of the photoelastic model. This endorses the use of the photoelastic technique for hip joint stress analysis also if the relative stiffness and the Poisson's ratios of the actual materials cannot be exactly matched, which is a recognized limitation of the method (Stansfield, 1976). As far as three-dimensional configurations are concerned, for which the cost of FE model generation and analysis is still high, photoelasticity can then be regarded as a competitor of computational approaches.

5. CONCLUSIONS

An axisymmetric, nonlinear finite element analysis of the stress state within prosthetic ceramic heads has been performed for various taper coefficients of friction, support conditions and spigot elastic moduli. It has been proved that the peak tensile hoop stress at the head taper wanes, in descending order of importance, the higher the frictional coefficient, the stiffer the supporting cup and the stiffer the spigot. The stress pattern locked into the head upon removal of the load has also been evaluated, showing that the maximum residual tensile stress is usually greater than its live counterpart at end of loading. Finally, corroborated by a favourable comparison with a photoelastic benchmark, the numerical results have been used to validate a literature theoretical model.

REFERENCES


- 54 -
Fig. 1 - Hip joint assembly with main dimensions

Fig. 2 - FE idealization of the joint showing loading and constraints
Fig. 3 - Distributions of tensile hoop stresses along bore generator for various coefficients of friction

Fig. 4 - Dependence of maximum taper hoop stress on frictional coefficient and support conditions
Fig. 5 - Distributions of tensile hoop stresses along bore generator for three support conditions

Fig. 6 - Distributions of tensile hoop stresses along bore generator for three elastic moduli of the stem
Fig. 7 - Effect of unloading on the hoop stress distribution along the bore generator

Fig. 8 - Comparison between photoelastic and FE predictions of contact pressure distribution along taper
The biological interaction between bone tissue and ceramic implants

A. TONI¹, A. SUDANESI¹, S. STEA², A. PIZZOFERRATO², M.D. MARRARO³, F. CALISTA¹, A. GIUNTI¹


ABSTRACT

In total hip arthroplasty ceramic coating may cause significant biological reaction, depending upon the coating composition. Seven cases of revision surgery of alumina (Al₂O₃) coated cobalt-chrome alloyed hip prosthetic stem gave the chance to study the alumina coating-bone interface, showing a demineralized layer in the bone lining the ceramic, with a depth averaging 100 μm. The demineralization was due to diffusion of aluminium ions into the matured bone ingrown around the hip prosthetic stem. X-ray diffractometry showed in the coating high levels of gamma-alumina.

INTRODUCTION

Among various ceramic coatings, the plasma-spray application of aluminum oxide (Al₂O₃ or alumina) has been used widely (10, 20) in clinical application. Such a ceramic coating has been described as being inert and entirely compatible with bone both in vitro by means of cell culture techniques (12,14) and in vivo with experimental implants (1, 7, 8, 9, 21); the ionic diffusion from Al₂O₃ was considered negligible and consequently the material was regarded as extremely safe (3, 6, 17) from a biological perspective. Recently we identified several patients with pain following total hip arthroplasty performed with a cementless alumina-coated stem. As no radiographic signs of loosening or evidence of sepsis could be detected, evaluation of the clinical picture in these patients was difficult. The discrepancy between the clinical presentations and the diagnostic work-ups required caution regarding surgical indications, nevertheless eight patients with functionally-limiting hip pain underwent surgical stem revision, enabling further investigation of the bone-prosthesis interface.

MATERIALS AND METHODS

Between November, 1985 and December, 1989 we implanted 238 cementless anatomic ceramic arthroplasties (AN.CA.™, Cremascoli S.p.a., Italy) in 216 patients (20). The femoral implant is anatomically designed and fabricated of cobalt-chrome alloy (ASTM F75), and the body of the implant entirely coated with plasma-sprayed alumina. The head and the socket articulating surface are fabricated of dense alumina.

Seven patients at an average onset at 44 months (range 25-67) following total hip arthroplasty complained of thigh pain (absent at rest and progressively worsening with
walking) which was functionally limiting on a daily basis. The patients realized significant clinical improvement following their prosthetic hip surgery followed by recrudescent pain. Radiographic films did not show loosening of the stem. There was evidence of stress shielding of the proximal femur: thinning of the diaphyseal cortical bone and cancellous transformation were consistently noted. To eliminate the possibility of occult sepsis, scintigraphy with technetium labelled granulocytes was performed with negative results in all cases. Erythrocyte sedimentation rate, white blood cell count and C-reactive protein titres were non-contributory. Arthrocentesis for culture was performed in five cases and was negative in all.

Due to persistent symptoms unrelieved by non-steroidal therapy, these patients underwent surgical revision of the stem with intraoperative bone biopsy. At surgery the stems were all macroscopically bonded to the bone tissue.

• Histologic evaluation. For each case, sections of the bone obtained adjacent to both the smooth surface and the madreporic regions of the prosthesis were prepared. Sections of bone tissue 5 mm thick were derived from samples fixed in buffered formalin at ph 7.2, dehydrated in methanol, then embedded in methyl methacrylate and deplasticized before staining. Transverse slices of the stem 5 mm thick, at the level of the macroporous zone, were obtained with the Exact Cut® system with bore nitride, taking particular care not to damage the bone spiculae which had grown within the stem macroporosities. After fixation in methyl methacrylate, slices were ground to a thickness of 50 μm for light microscopic evaluation of bone ingrowth.

Both the deplasticized sections of the bone samples and those of the stem at the macroporous level were stained with traditional histologic methods, including Paragon (toluidine blue - basic fuchsin), modified Goldner and Von Kossa stains. A previously described method for detecting aluminium utilizing the ammonium salt of aurine tricarboxylic acid (6) with which aluminum hydroxide stains as a red band was employed. The details of these techniques have been presented in detail in a previous communication (19).

RESULTS

The histochemical tests carried out on the bone tissue adjacent to the interface both at the smooth and macroporous surfaces of the prostheses all demonstrated the presence of a non-mineralized layer, parallel to the profile of the implant. The non-mineralized layer lining the stem surface (Fig. 1) was measured in sections with both alloy and bone, resulting 106 μm + 24 μm S.D. thick (range: 68-140 μm).

The morphology of the non-calcified zone is lamellar at the light microscopic level with osteon systems typical of mature bone over most of the surface. In several cases, individual osteons appear clearly subdivided into a nonmineralized part immediately adjacent to the prosthesis, and a normally mineralized region in continuity.

In all observed cases we found on alumina coating crystallographic transformation from alpha stable phase to gamma phase, relatively less stable, and impurities in the form of Al(OH)3, which are such to permit a partial solubilization of the alumina coating.

DISCUSSION

The application of ceramics in the fabrication of total joint implants continues to receive considerable attention; reports on negative phenomena related to their use are very scarce (5, 11, 18). The first reports on the possible toxicity of aluminium appeared when in the
early 70's Berlyne (2) observed that patients suffering from chronic renal failure, treated with aluminium ion-exchange resins to correct hyperkalaemia, showed a significant increase in the plasma concentrations of this element. A similar increase was found in patients who took Al(OH)₃ antacids to control hyperphosphataemia or peptic ulcer disease. In 1971, Parsons (16) found, in the bone tissue of nephropathic patients, significant amounts of aluminium which could be related to a previous uremia and to the duration of dialysis. Dent (4) subsequently reported a case of osteomalacia due to hypophosphataemia induced by excessive intake of aluminium hydroxide. Ward in 1978 (22) and Parkinson in 1979 (15) found a correlation between osteomalacia and the aluminium content of water used as dialysate. The specific mechanism(s) for aluminium toxicity in bone remains enigmatic (13).

Lewandowska-Szumiel carried out traditional histologic tests and assays of aluminium in the bone tissue of experimental models in which alumina rods were implanted, for a period of 6-8 months. With normal histological results, he found significant concentrations of aluminium in periprosthetic tissues (11).

For the cases considered in the present study, we are not able to conclusively elucidate the mechanism(s) by which aluminium inhibits or reverses mineralization. We can only demonstrate that crystallographic transformation occurs from the stable α-phase to the relatively less stable γ-phase, and that the presence of impurities in the form of Al(OH)₃ are such that partial solubilization of the alumina coating follows in vivo.

Given the extensive world-wide use of alumina in clinical applications, the phenomenon we describe deserves careful evaluation. We have described a histologic phenomenon which appears to be related to the presence of aluminium at the prosthesis-bone interface; we did not find stem loosening but rather demineralization with residual bone apposition at the interface in the specimens retrieved at revision surgery. Results also underline the need of at least 24 months experimental validation to elucidate long term effects of new coating. We converted to the use of hydroxyapatite-coating since 1989.

REFERENCES


Fig. 1 - Bone ingrowth inside the macroporosities of the alumina-coated stem. The picture shows the prosthesis (p), the alumina coating (a), and a bone tabeculum partly regularly mineralized (m) and partly demineralized (d) in the area in contact with the coating (Von Kossa, obj. 16x)
The problem of friction, and therefore of wear, has been known for thousands of years and yet, in spite of the various theories advanced on this complex phenomena, no one has hitherto succeeded in completely eliminating their effects.

Friction, i.e. the force opposing the relative motion of two bodies, was defined as early as 1508 by Leonardo da Vinci, who established that this force did not depend on the materials but was proportional to the normal force applied (1).

This theorem formed the basis of the theories later developed by Coulomb and Amonts which led to the present-day theories according to which friction is influenced by various factors, including pressure at the interface, temperature, roughness of the contact surfaces and slide velocity (2).

Under German standard DIN 50320/8 the wear process occurs only when all six base elements in Fig. 1 are present at the same time.

Friction is however the sum of the internal resistances opposed by the interactions between the contact surfaces. It can only be determined by the force required to overcome it, because the resistances inside the system cannot be measured, making it difficult to determine their onset.

Only when the sliding of the parts in contact overcomes the adhesion at the interface, by molecular attraction, will the body of the parts involved not be affected, no particles will be detached and consequently no wear will occur. But this is only an hypothesis because in practice there is no manifestation of friction without wear.

TEST STANDARDIZATION

For all the many criteria that have been developed to provide a useful interpretation of the results of wear tests based on the use of simulators, our present understanding of the complex phenomenon of wear allows us to state that the basic requirement is to ensure that the test system, equipment and method generates the same type of wear and the same degree of severity (3) (4). Accordingly, there should be a correlation between the real system and the simulated system.
In artificial joints, the need to carry out behaviour tests prior to implantation is now almost universally accepted, even though it is not yet compulsory. The detachment of the prosthetic elements from the bone in which the prosthesis is located is due, according to various researchers, (5) (6) (7) (8) (9) to a complex series of phenomena which may be triggered by the presence of wear particles generated during operation of the prosthesis itself. The shape and size of these particles, together with the extent of the wear, determines the intensity of the biological reaction (10). The widely used pin-on-disk machines for tribological measurements are simple and cheap, but they provide only a limited amount of information and are recommended only for an initial evaluation governing the selection of materials (11).

In order to optimize the selection of materials and the geometry of the joint it is essential that the pieces be tested under conditions that reproduce the presumed physiological conditions as closely as possible. The design of a specific simulator that furnishes load, movement, lubrication and temperature conditions reproducing those in which the prosthesis will operate once implanted is therefore essential. Unfortunately, the lack of rules establishing test parameters prevents the various research centres working on this problem from comparing their results and findings. Only when the results are obtained from the same machine is any comparison significant. Since approved rules on wear test methodology that standardize tests do not yet exist, we have taken account in this study of the recommendations contained in the draft ISO TC 150/SC4 N 21 (12). Specifically, the technical report provides indications on the testing equipment, samples and conditions.

Our aim within the EUREKA 294 programme is to evaluate the tribological behaviour over long periods (<: 10.106 cycles) of prosthesis joints using various materials, in order to select those which generate a low friction coefficient and high wear resistance. The detritus generated will be tested at a later time in order to assess the onset of possible tissue reactions.

**DESIGN OBJECTIVES**

In designing the simulator, particular attention was attached to the characteristics we considered important:

1. **Multi-station,** for the simultaneous testing of several samples. Taking the duration of one test to correspond to 10 year's walking, with a simulator cycle of one second, the continuous operation time will be 4 months. The possibility of making a simultaneous comparison of several samples subjected to the same conditions acquires significance.

2. **Ball-socket angle** according to the anatomy of ambulation. The acetabulum is situated above and at an angle to the neck of the femur. An angle of 0 to 30° can be set on the machine.

3. **Transmission of a variable and strictly controlled load** on the prosthesis elements, with the possibility of altering the load curve during the step in order to simulate different types of gait.

4. **Variation of simulated step time.**

5. **Machine stop** if the preset values exceed the defined range or if failure or fracture occurs at any workstation.
6. Closed and sealed loop lubrication circuit to prevent evaporation and contamination from outside, with circulation in a thermostat-controlled physiological solution and filter for detritus collection.
7. Constant monitoring and recording of the simulation conditions.
8. Fixing of acetabulum and femur components in such a way as to ensure the same angle of inclination for all stations, even when repositioning after removal at set time intervals to check for wear.
9. Self-centring under load of the ball in the socket.
10. Extreme flexibility in setting the parameters.

The simulator must reproduce in the joint to be tested the load, movements, speed and ambient conditions. It must be able to simulate a wide range of activities, e.g. walking, running, jumping, etc. by changing the simulation parameters so as to ensure maximum flexibility during the tests.

DESCRIPTION AND CHARACTERISTICS OF THE MACHINE

The load and joint models to which we referred are those for medium-pace walking as indicated by the Paul curves (1967) (13). The machine has nine workstations arranged in a circle. Located in the centre of it is a variable-speed motor controlled by an inverter to provide the cycle frequency. By means of a reduction gear the motor controls the movement of the nine stations, with flexing-extension (± 20) for the ball controlled by connecting rod and crank, and cam-controlled adduction-abduction (± 10) for the socket. An encoder provides the phase between the load system and the movements. The cycle time can be set from 0.5 to 2 Hz.

The cyclic load at the nine stations, with a maximum value of 4000 N, while retaining a high degree of repeatability, can be varied according to different curves and applied with an angle ranging from 0 to 30° in relation to the axis of the neck of the femur.

The variability of the load is provided by hydraulic cylinders operated by proportional pressure reducing valves, with a closed loop and electronic regulator operation, while the control part is handled by pressure transducers.

The closed loop is the most rational solution for automation of the simulator since the quantity regulated is not affected by possible disturbances in the system.

The load curve is therefore strictly controlled and the instantaneous values are kept in phase with the angle of the socket for the entire duration of the test.

A quartz load-cell is fitted to the connecting rod controlling flexing-extension so as to record the friction forces between the socket and the ball.

It was decided not to reproduce intra and extra-rotatory movement on this machine so as not to make the whole system unduly sophisticated and costly at this specific stage.

The information we acquire from this experiment will be useful for the later design of a system which takes account of the third movement as well.

The data acquisition system provides continuous monitoring of the working conditions and incorporates the possibility of recording the following parameters in the last 10 cycles: the load and its position in relation to the movement of the socket; friction force; number of cycles completed; operating frequency and temperature of the work area.

The whole system is provided with a no-break power set to ensure continued operation of the microprocessor unit in the event of mains voltage drops.
A closed loop lubrication circuit, complete with filter, peristaltic pump and detritus collector tray, circulates the lubricant in the work area and keeps it thermostat controlled.

CONCLUSIONS

This study confirms the importance of the multi-station wear simulator for an extended duration comparative evaluation of hip prostheses, approximating actual operating conditions as closely as possible.

Since rules governing test methodologies for simulators do not yet exist, and while taking into account the recommendations enshrined in the ISO draft, our aim in this design has been to make the unit extremely flexible and free of all setting constraints in order to subject the prostheses to different test patterns.

REFERENCES


- 70 -
Fig. 1 - Base model of tribological system applied to hip joint.

1 - Base body (subject to wear)
2 - Opposing body (causing the wear)
3 - Intermediate substance (e.g., lubricant)
4 - Surrounding environment and temperature
5 - Load (indicated by an arrow)
6 - Motion

Fig. 2 - General view of simulator
Fig. 3 - Block diagram of electronic management
Preparazione di polveri per ceramici avanzati
formatura e sinterizzazione

G. BOVALINI, P. FASSINA, N. ZAGHINI

TEMAV - Centro Ricerche Bologna
Medicina - BO (Italy)

1. PREMESSA
I materiali per applicazioni nel settore biomedicale, come tutti sanno, devono avere delle caratteristiche e delle proprietà molto ben definite e riproducibili.
I nostri laboratori tecnologici già dal 1986 hanno iniziato lo studio di queste proprietà e hanno verificato e provato processi tecnologici, qualificati per altri impieghi, in questo settore specifico.
In collaborazione con i più avanzati gruppi italiani ed esteri del settore delle protesi biomedicali abbiamo sviluppato e messo a punto processi per la produzione su scala prototipale di materiali (polveri) e componenti in questo settore.
Il processo di produzione della polvere GSP è proprietà della TEMAV ed è stato provato e messo a punto per produrre vari tipi di polveri.
I processi di lavorazione delle polveri fino alla realizzazione dei componenti (in particolare la testa di femore) sono stati I più diversi e sono ancora in corso alcune prove di qualificazione e affidabilità.
Di seguito si presenta una breve sintesi dell'attività svolta dai nostri laboratori nell'ambito del PROGETTO EUREKA 294.

2. IL PROCESSO DI PRODUZIONE DELLE POLVERI CERAMICHE PER COMPONENTI BIOMEDICALI (PROTESI D'ANCA).
Il processo GSP, precipitazione su supporto gelante, è una tecnica tipo sol-gel, di esclusività TEMAV, sviluppato da Società del Gruppo ENI nel settore del combustibile nucleare ceramico e più recentemente applicato per la produzione di polveri o precursori ceramici avanzati.
Questo processo, a differenza dei metodi sol-gel, permette di preparare le polveri e le microsfere partendo da reagenti non costosi, sali inorganici dei metalli, e da altri reattivi di uso comune.
In particolare la tecnica GSP, come le altre metodologie sol-gel, è caratterizzata dalla possibilità di ottenere ossidi ben dispersi ed omogenei, essendo gli elementi miscelati tra loro a livello chimico anziché meccanico, ed inoltre una purezza chimica controllata (reagenti di partenza).
Le principali fasi del processo sono (Fig.1):
- Preparazione della soluzione di alimentazione per dissoluzione in acqua dei sali inorganici degli elementi e miscelazione con un addensante organico o con alcole aromatici in funzione di complessante.
- Dispersione della soluzione in gocce di dimensione controllate.
- Solidificazione delle gocce così ottenute in particelle di gel per caduta in ambiente ammoniacale.
- Invecchiamento e lavaggio in acqua.
Disidratazione per distillazione azeotropica dell'acqua.
Calcinazione.

Le microsfere ottenute hanno un'area superficiale (> 100 m²/g) e volume poroso (> 0.500 cm³/g) elevati, conservati anche a temperature di calcinazione intorno ai 500 °C. La forma delle microsfere è regolare e perfettamente sferica (Fig. 2). Le dimensioni dipendono dal metodo di spruzzatura adottato e in parte anche dalla concentrazione della soluzione di alimentazione e dalla sua viscosità.

Il processo GSP è stato sinora applicato per la produzione di ossidi di alluminio, zirconio, titanio, terre rare e ossidi misti.

Nell'ambito del progetto Eureka 294 sono state prodotte polveri di allumina, allumina - zirconia e zirconia parzialmente stabilizzata.

Nella prima fase del progetto sono state selezionate 6 differenti composizioni di polveri del sistema ossido di zirconio - ossido di alluminio a partire da polveri commerciali. Le polveri selezionate sono le seguenti:

- A 100% ossido di alluminio
- B Ossido di zirconio parzialmente stabilizzato con ossido di ittrio
- C 20% ossido di zirconio parzialmente stabilizzato con ossido di ittrio + 80% ossido di alluminio
- D 80% ossido di zirconio parzialmente stabilizzato con ossido di ittrio + 20% di ossido di alluminio
- E 40% ossido di zirconio parzialmente stabilizzato con ossido di ittrio + 60% ossido di alluminio
- F 60% ossido di zirconio parzialmente stabilizzato con ossido di ittrio + 40% ossido di alluminio

Tali polveri sono state caratterizzate mediante determinazione della composizione chimica, distribuzione delle fasi cristalline, densità apparente e compattata, area superficiale, granulometria, osservazione al SEM.

Si è studiato anche il sistema binario TiO₂-SiO₂ in vista di una potenziale applicazione come bioceramico.

A questo scopo si è proceduto alla messa a punto di un metodo di preparazione atto ad ottenere una polvere di elevata purezza e con buone caratteristiche di sintetizzabilità, requisiti indispensabili per poter utilizzare questi materiali in campo biomedico.

Nella prima fase del progetto si sono utilizzate polveri commerciali già di grado biomedico e solo negli ultimi tempi si è cominciato a caratterizzare le polveri prodotte con la tecnica GSP.

Si riporta a titolo di esempio le caratteristiche principali di una polvere di ossido di zirconio parzialmente stabilizzata con ossido di ittrio prodotta nei nostri Laboratori con il metodo GSP in Fig. 3 e Fig. 4.

In Fig. 5 viene presentato l'impianto per la produzione degli ossidi con il metodo GSP.

3. IL PROCESSO DI FABBRICAZIONE DELLE TESTE DI FEMORE IN MATERIALE CERAMICO MEDIANTE PRESSATURA ISOSTATICA A FREDDO

Le teste di femore sono state fabbricate impiegando polvere sia commerciale che polvere di nostra produzione in ZIRCONIA STABILIZZATA con il 5.5% in peso di ITTRIA.

Lo stampo, costituito da quattro parti, è in neoprene. In alcuni casi sono stati impiegati del lubrificanti a contatto con la parte interna dello stampo per permettere una migliore integrità del manufatto.
La formatura mediante pressatura Isostatica a freddo consta delle seguenti fasi:
• Riempimento dello stampo con polvere ceramica.
• Ciclo di pressatura:
  - Salita a 1000 bar in 3 minuti
  - stasi in pressione di 30 secondi
  - discesa pressione fino a 50 bar
  - discesa lenta in circa 10 minuti.

Presinterizzazione del manufatto per impartire la necessaria resistenza alle sollecitazioni meccaniche della successiva lavorazione. Si riporta un ciclo adottato per la produzione di un lotto:
- Salita a 500 °C con rampa di 38 °C/ora
- stasi a 500 °C di 3 ore
- salita a 950 °C con rampa di 280 °C/ora
- stasi a 1000 °C di 2 ore
- raffreddamento naturale in forno.

Dopo pressatura il manufatto si presenta di forma sferica. Per ridurre al massimo le lavorazioni sul sinterizzato si è cercato di ottenere la forma voluta lavorando sul presinterizzato.

I componenti vengono forati e torniti conicamente all'interno e torniti sfericamente sulla superficie esterna.

I manufatti prelavorati sono stati sinterizzati secondo il seguente ciclo termico:
- Salita a 1500 °C con rampa di 420 °C/ora
- stasi a 1500 °C di 3 ore
- discesa a T ambiente con rampa di 370 °C/ora

Durante le fasi di fabbricazione sono stati effettuati i seguenti controlli:
• Esame visivo per l'integrità del manufatto
• Verifica dimensionale e conseguente calcolo dei ritiri
• Stato superficiale
• Determinazione della densità
• Su alcuni campioni per lotto sono stati eseguiti esami distruttivi: XRD, SEM, ceramografie.

I risultati della produzione prototipale di oltre 40 componenti per lotto di materiale di partenza hanno fornito le seguenti indicazioni sulla dispersione dei dati per le varie caratteristiche di specifica:
• Analisi dimensionale (dispersione 2σ massima di 2,8% intorno al valor medio) - Densità (dispersione 2σ massima di 0,33% intorno al valor medio)
• Struttura (matrice ZrO2 - struttura integra)
• Riproducibilità e affidabilità del processo con una variabilità massima del 2.8% con un livello di confidenza del 98%.

La Fig. 6 mostra una testa di femore alla fine del ciclo di lavorazione.

4. CONCLUSIONI
I risultati fino ad oggi raggiunti sia nello sviluppo del metodo di produzione delle polveri che per la fabbricazione dei manufatti consiglia di proseguire sulla strada intrapresa visti anche i risultati preliminari ottenuti dalle prove biomeccaniche e meccaniche presentate dagli altri partners del PROGETTO.
GSP - PROCESS FLOW SHEET

Fig. 1

Fig. 2 - Micrografia di polvere ottenuta con il processo GSP
ZIRCONIA GSP

Polvere per sinterizzati
ZrO$_2$ - Y$_2$O$_3$ 94,5/5,5

CARATTERISTICHE

Le microsfera di ZIRCONIA GSP sono costituite da particelle di ZrO$_2$ - Y$_2$O$_3$ parzialmente stabilizzata con fase predominante tetragono e dimensione dei grani di 0,1 - 0,3 μm.

Fig. 3

Fig. 4 - Micrografia di zirconia sinterizzata
Fig. 5 - Impianto per la produzione degli ossidi con il metodo GSP

Fig. 6 - Testa di femore
Preparation and Properties of Al₂O₃-SiO₂-TiO₂ Ternary Bioceramics

M. Milosevski*, R. Milosevska*, G. Ondracek**, D. Spaseska*
Graduiertenkolleg der Arbeitsgemeinschaft Biowerkstoffe Nordrhein-Westfalen
c/o Mauerstr. 5 RWTH
D-52064 Aachen

Abstract

Al₂O₃-SiO₂-TiO₂ powders have been prepared and densified in order to produce ternary bioceramics. All materials containing different amounts of silica overcome the hysteresis effect in thermal expansion, leading usually to microcracks in sintered compacts on the basis of aluminium titanate. By different silica contents the variation of the mechanical properties is controllable and adopts with increasing silica concentrations, for example the bending strength of cortical bone. All silica containing aluminium titanate based ceramics remain free of microcracks.

* Universitet Sveti Kiril i Metodij, Tehnolosko-Metalurski Fakultet, Skopje, Republic of Macedonia
** Rheinisch-Westfälische Technische Hochschule, Institut für Gesteinshüttenkunde/ Glas, Bio- und Verbundwerkstoffe, Aachen, Deutschland

- 79 -
1. Introduction

A material becomes a biomaterial
- if it is biocompatible, meaning, that no negative interactions occur with the biosystem ("biocompatibility")
- if it provides medically relevant properties in at least one (aggregate) state ("biofunctionality")
- if it may be produced technologically as well as economically.

Interactions will take place at the interface between both, the biomaterial and the biosystem. They may occur as chemical reactions or solid solutions but characterize in any case bioactive materials. If - however - the interface remains stable without any interaction, then the implant material behaves bioinert.

The process of interaction between bioactive materials and - for example - hard tissue or cartilage is usually complex and proceeds - step by step - from the interface to its adjacent - and even far - environment. It is hardly to predict, when stability is reached and whether that state is still biocompatible. This is why bioinert implant materials represent "the safe case".

Oxide ceramics as alumina, silica or titania are the most popular bioinert materials, which, however, are altogether one-component and single phase materials. No property variation and therefore adaptation to the local needs of the biosystem is possible since their composition is fixed. In order to improve the biofunctionality it would be of interest, however, to lower the Young's modulus of elasticity or rupture strength for alumina, for instance, being both orders of magnitude higher than those of bone [14].

This is why the development of multicomponent bioceramics has been started in order to obtain those degrees of freedom to adopt properties by varying composition and microstructure. For doing so it is assumed, that bioinert components result in bioinert biomaterials and the present development is based on the system alumina-silica-titania. A ternary combination has been chosen because the favourite binary Al₂O₃-TiO₂-system always contains aluminiumtitanate in solid state (fig. 1), which expands anisotropically with temperature causing microcracks in all sintered compacts. The linear mean thermal expansion coefficients (293-1273K) of aluminiumtitanate (Al₂TiO₅) are
- for the a-axis $-3 \cdot 10^{-6}$ K⁻¹
- for the b-axis $+11,8 \cdot 10^{-6}$ K⁻¹
- for the c-axis $+21,8 \cdot 10^{-6}$ K⁻¹
which leads to the hysteresis slopes of thermal expansion and cyclic thermal treatment as shown in fig. 2.
How silica effects the thermal expansion behaviour of Al_2TiO_5-TiO_2-eutectic ceramics and wether it leads to technologically relevant improvements is subject of the following investigations.

2. Preparation and sintering of Al_2TiO_5-TiO_2-SiO_2 powders

The low-melting Al_2TiO_5-TiO_2-eutectic (79,7 w/o Al_2O_3 +20,3 w/o TiO_2; compare fig.1) has been selected to be the basis component because its thermal expansion hysteresis is less expressed than that of pure aluminium titanate (compare fig. 2). Different amounts of silica (3, 5, 10, 20, 30 w/o) have been mixed with the eutectic, which was produced in a first step as shown in fig. 3. The as-produced eutectic powder is two-phased (fig. 4) and has been combined in a recent step with silica via tetraethylorthosilicate (TEOS) providing Al_2TiO_5-TiO_2-SiO_2 powders as given in fig. 5. Compacts (60x4x4mm) have been pressed and sintered according to the scheme in fig. 6, the sinter density of which versus the SiO_2-content passes a maximum (at 5w/o SiO_2) when sintered
as given in fig. 7. From the x-ray analysis after different thermal treatment it is evident, that the material is three-phased (Al$_2$TiO$_5$-mullite) below 1700 K (fig. 8). Sintering at higher temperatures ($\leq$ 1625k) results in higher porosities (fig. 9) which also increases by increasing SiO$_2$-content (fig. 10). Technologically most important however is the absence of microcracks in all SiO$_2$-containing microstructures!

3. Technologically relevant properties of ternary Al$_2$O$_3$-SiO$_2$-TiO$_2$ ceramics

Youngs modulus of elasticity, the bending strength and the compressive strength as well as thermal expansion have been measured using the three-point bending test for Youngs modulus and the bending strength. In analogy to fig. 7 the mechanical properties versus SiO$_2$-concentration all pass a maximum (95 w/o Al$_2$TiO$_5$-TiO$_2$ eutectic + 5 w/o SiO$_2$; figs 11-13), if - and exactly only if - the material has been sintered at 1573 K (compare figs. 14-16). At higher SiO$_2$-concentrations (>5 w/o SiO$_2$) the mechanical properties decrease approaching in the case of the bending strength - for instance - values close to these for cortical bone [14].

The structural reason for these effects are subject of current constitutional investigations supported, however, already by the result, that ternary Al$_2$TiO$_5$-SiO$_2$-TiO$_2$ ceramics do not undergo thermal expansion hysteresis (fig. 17), may therefore be sintered without microcracks and do have a reversible mean linear thermal expansion coefficient.

Fig. 2: The hysteresis of thermal expansion of Al$_2$TiO$_5$ (above) and Al$_2$TiO$_5$-TiO$_2$-eutectic (below) as a function of temperature and cycling
Fig. 3: Schematic diagram for obtaining Al₂TiO₅-TiO₂ mixtures

Fig. 4: x-ray analysis of eutectic Al₂TiO₅-TiO₂-powder

× Al₂TiO₅

□ TiO₂
Fig. 5: SCAN micrograph of Al$_2$TiO$_5$-TiO$_2$-SiO$_2$ powder with different SiO$_2$-content
eutectic $\text{Al}_2\text{TiO}_5$-$\text{SiO}_2$-powder + water ($\text{H}_2\text{O}$:powder=10:1 w/w)

tetrakis(propyl)thiollate
$\left(\text{C}_5\text{H}_11\text{O}_4\text{Ti}\right)$ + isopropanol
hydrochloric acid (0,5 molar)

mixing: 20 min
$\left(\text{TEOS/ISOPROPANOL/H}_2\text{O/HCl}=1:5:2:1\text{ ml}\right)$
+ neutralization ($\text{NaOH}$, pH=5,5)

mixing: 30 min ($\text{pH}=7$)

grounding: attritor mill; 1500 r/min, 1h

drying: 263 K, 3h

grounding: achat mortar, 1h
$\left(\text{Al}_2\text{TiO}_5\right)$-$\text{SiO}_2$-$\text{TiO}_2$-powder: particle size 0,1-1µm

cold pressing: 10kN/cm$^2$

sintering: 1573 K, 3h

Fig. 6: Schematic flow diagram of the process of $\text{Al}_2\text{TiO}_5$-$\text{TiO}_2$-$\text{SiO}_2$
preparation

Fig. 7: Sinter densities of $\text{Al}_2\text{TiO}_5$-$\text{SiO}_2$-$\text{TiO}_2$-pellets with $\text{Al}_2\text{TiO}_5$-$\text{TiO}_2$-
eutectic component as $\text{SiO}_2$-concentration functions
(sintering temperature 1573 K)
Fig. 8: X-ray-analysis of Al$_2$TiO$_5$-(75.7 w/o)-SiO$_2$(5 w/o)-TiO$_2$(19.3 w/o)-
ceramic ("TIASIL") after sintering at different temperatures (given in

diagram)
  x Al$_2$TiO$_5$       • TiO$_2$       △ mullite
Fig. 9: Microstructures of Al₂TiO₅-(75.7 w/o)-TiO₂ (19.3 w/o)-SiO₂ (5 w/o)-components sintered at different temperatures (magnification 80x)
Fig. 10: Microstructures of $\text{Al}_2\text{TiO}_5$-$\text{TiO}_2$-$\text{SiO}_2$ ceramics with increasing $\text{SiO}_2$ content (magnification 80x)

Fig. 11: Young's modulus of elasticity of $\text{Al}_2\text{TiO}_5$-$\text{SiO}_2$-$\text{TiO}_2$ ceramic with constant eutectic $\text{Al}_2\text{TiO}_5$-$\text{TiO}_2$-ratio but varying $\text{SiO}_2$-content
Fig. 12: The bending strength of Al$_2$TiO$_5$-SiO$_2$-TiO$_2$ ceramic with constant eutectic Al$_2$TiO$_5$-TiO$_2$-ratio but varying SiO$_2$-content

Fig. 13: The compressive strength of Al$_2$TiO$_5$-SiO$_2$-TiO$_2$-ceramic with constant eutectic Al$_2$TiO$_5$:TiO$_2$-ratio but varying SiO$_2$-content
Fig. 14: Young's modulus of elasticity of Al$_2$TiO$_5$ (75.7 w/o) - SiO$_2$ (5w/o) - TiO$_2$ (19.3 w/o) - ceramic ("TIASIL") in dependence on the sintering temperature.

Fig. 15: The bending strength of Al$_2$TiO$_5$ (75.7 w/o) - SiO$_2$ (5w/o) - TiO$_2$ (19.3 w/o) - ceramic ("TIASIL") in dependence on the sintering temperature.
Fig. 16: The compressive strength of Al$_2$TiO$_5$-(75.7 w/o)-SiO$_2$(5 w/o)-TiO$_2$ (19.3 w/o)-ceramic ("TIASIL") in dependence on the sintering temperature

Fig. 17: Thermal expansion of Al$_2$TiO$_5$-(75.7 w/o)-SiO$_2$(5 w/o)-TiO$_2$ (19.3 w/o)-ceramic ("TIASIL")
4. References

1. Bartsch, C.
   Wird Keramik die Welt erobern?
   Magazin Neue Werkstoffe 1 (1987) 6

2. Demaestry, P.; Giachello, A.; Martingo, C.; Majani, C.;
   Influence of some oxides on the thermal characteristics of stochiometric Al₂TiO₅
   Elvesier, Publ. Co (199 )

   Festigkeitsuntersuchungen an Granulaten
   Keramische Zeitschrift 45-6, (1993) 321

   Effect of additives on several properties of aluminium titanate ceramics

5. Kranth, A.
   Keramische Werkstoffe
   Umschau 11 (1983) 337

6. Lang, S.; Fillmore, C.; Maxwell, J.
   The system BeO-Al₂O₃-TiO₂ phase relation and general properties of three component
   porcelains
   J. Res. Nat. Stds.48(4) (1952) 298

7. Milosevski, M.; Schulz, B.
   Preparation, characterization and diffusivity of Al₂TiO₅ in: Ceramics and Metals
   (D. Kolar, M. Kosec, J. Krawczynski, eds)
   KFA-INF Jülich report on bilateral seminars (1987) 195

8. Milosevski, M.; Milosevska, R.; Ondracek, G.; Spaseska, D.
   Preparation and properties of Al₂TiO₅-SiO₂-TiO₂ ternary bioceramics
   in Biomaterials (I.Stamenkovic, J. Krawczynski, eds.) KFK-INT Jülich Report

9. Milosevski M; Ondracek G.; Schüller M.; Zabicky J.; Zevin L.;
   New Sources for Oxide Ceramics : on the preparation of ultrafine, high pure oxide
   ceramic powders,
   in Thömmeßen M.(ed.), Deutsch-Israelische Zusammenarbeit Materialforschung,

10. N.N.
    Alumina 4-titania powder by vapor phase reaction
    New Materials, Japan 4 (1987) 4

11. Olvies R.C.; Roy R.; Osborn E.F.;

12. Qian, O.; Phya, Y.; Hamano, K.; Nakagava, Z.
    Effects of excess alumina on microstructure of aluminium titanate ceramics prepared
13. Stamenkovic, I.; Ondracek, G.
Preparation and thermal expansion of Al$_2$TiO$_5$-TiO$_2$ sintered bodies
in: Ceramics and Metals (D. Kolar, M. Kosec, J. Krawczynski, eds) KFA-INT Jülich
report on bilateral seminars (1987) 81

14. Stamenkovic, I.; Ondracek, G.; Gasic, M.
Sintering behavior of titanium and alumina intermixed and premolten powders
in: Contemporary Inorganic Materials—Progress in Ceramics, Metals and Composites (G.
Ondracek, D. Vöhringer, eds) KFA-INT Jülich report on bilateral seminars (1985) 135

15. Walzer, P.; Henrick, H.; Langer, M.
Ceramic components in passenger car Diesel engines
Materials and Design 7 (1986) 75

16. Willman G.;
Für die Orthopädie bewährte keramische Implantatwerkstoffe
Sprechsaal 126-6 (1993) 384
previously published in this series

Joint German-Indonesian Seminar on R&D Activities using the MPR-30
Jakarta, August 19-21, 1985
GERMAN-INDONESIAN COOPERATION
ISBN 3-89336-011-5

Joint German-Indonesian Seminar on Public Acceptance, Waste-Management, and Nuclear Safety
Jakarta, October 7-9, 1986
GERMAN-INDONESIAN COOPERATION
ISBN 3-89336-012-3

VIIIth German-Yugoslav Meeting on Materials Science and Development: Ceramics and Metals
edited by Drago Kolar, Marija Kosec and Johanna Krawczynski
Brdo pri Kranju, May 18-21, 1987
GERMAN-YUGOSLAV COOPERATION
ISBN 3-89336-001-8

Proceedings of the Fourth Workshop on Two-Phase Flow Predictions
edited by M. Sommerfeld and H. Zeisel
Erlangen, October 21-23, 1987
GERMAN-YUGOSLAV COOPERATION
ISBN 3-89336-002-6

IInd Workshop on Process Automation
Darmstadt, November 2-6, 1987
GERMAN-YUGOSLAV COOPERATION
ISBN 3-89336-003-4

Ist German-Yugoslav Meeting in the Framework of the Bilateral Project Development of Innovation Structures in Yugoslavia
edited by G. Bräunling and V. Matejić
Innovation Consultancy Centers
Plitvice, September 5-7, 1988
GERMAN-YUGOSLAV COOPERATION
ISBN 3-89336-024-7

Proceedings of the 8th Winter School on Proteinases and their Inhibitors: Recent Developments
edited by E. Auerswald, H. Fritz and V. Turk
Tiers, March 8-12, 1980
GERMAN-YUGOSLAV COOPERATION
ISBN 3-89336-020-4

Second German-Greek Workshop on Materials Research for Information Technology
edited by G. Kaiser and H. Wenzel
Jülich, May 22-23, 1989
GERMAN-GREEK COOPERATION
ISBN 3-89336-018-2

Seminar Fertigungsplanung und -steuerung
zusammengestellt von
Burghild Wienecke-Toutaoui, Rolf Albrecht
Split, 7. und 8. Juni 1989
GERMAN-YUGOSLAV COOPERATION
ISBN 3-89336-025-5

IXth German-Yugoslav Meeting on Materials Science and Development: Emerging Materials by Advanced Processing
edited by Wolfgang A. Kaysser, Jutta Weber-Bock
Hirsau/Stuttgart, April 16-19, 1989
GERMAN-YUGOSLAV COOPERATION
ISBN 3-89336-026-3
Bilateral Seminars of the International Bureau

1. IInd German Yugoslav Meeting in the Framework of the Bilateral Project
   Development of Innovation Structures in Yugoslavia
   Innovation Management
   Plitvice, October 18-20, 1989
   edited by Vlastimir Matejić
   GERMAN-YUGOSLAV COOPERATION

2. IInd Workshop on Plasma and Laser Technology
   Cairo, February 21-28, 1990
   edited by E. Hintz
   GERMAN-EGYPTIAN COOPERATION

3. Seminar on Emissions and Air Quality
   Thessaloniki, October 9, 1990
   edited by N. Moussiopoulos, D. Kaiser
   GERMAN-GREEK COOPERATION

4. 5th Workshop on Two-Phase Flow Predictions
   Erlangen, March 19-22, 1990

5. IInd Workshop on Plasma and Laser Technology, Volume 2
   Cairo, February 21-28, 1990
   edited by Ph. Mertens, B. Schweer (1991)
   GERMAN-EGYPTIAN COOPERATION

6. 2. Brasilianisch-Deutsches Symposium für Naturstoffchemie
   2. Simposio Brasileiro-Alemao de Produtos Naturais
   herausgegeben von G. Habermehl (1991)
   DEUTSCH-BRASILIANISCHE ZUSAMMENARBEIT

7. 3rd German-Greek Workshop on
   Materials Research for Information Technology
   Thessaloniki, September 26 – 27, 1991
   GERMAN-GREEK COOPERATION

8. Egyptian-German Springschool and Conference
   Particle and Nuclear Physics
   Cairo, April 11-19, 1992
   GERMAN-EGYPTIAN COOPERATION

9. Seminar on Monitoring and Modelling in the Mesoscale
   Thessaloniki, September 27, 1991
   edited by N. Moussiopoulos, G. Kaiser (1992)
   GERMAN-GREEK COOPERATION
10 3rd Workshop on Process Automation  
GERMAN-SLOVENIAN COOPERATION

11 Course on Medical Aspects of Nuclear and Radiation Accidents  
Cairo, April 11-16, 1992  
GERMAN-EGYPTIAN COOPERATION

12 Egyptian-German Spring School and Conference  
Particle and Nuclear Physics, Volume 2: Contributed Papers  
Cairo, April 11-19, 1992  
GERMAN-EGYPTIAN COOPERATION

13 Indo-German Workshop on  
High Pressure Technology-Engineering  
Pune, January 3-4, 1992  
GERMAN-INDIAN COOPERATION

14 6th Workshop on Two-Phase Flow Predictions  
Erlangen, March 30 - April 2, 1992  
edited by M. Sommerfeld (1993)

15 3rd Workshop on Plasma and Laser Physics  
Ismailia, October 3-7, 1993  
edited by Ph. Mertens (1994)  
GERMAN-EGYPTIAN COOPERATION

16 Utilization of the Low Active Waste Incinerator  
Facility (LAWI) for Research and Development Work  
Cairo, December 11-12, 1993 (1994)  
GERMAN-EGYPTIAN COOPERATION

17 8th SIMCER International Symposium on Ceramics  
Biomaterials – Special Meeting of the Project EUREKA 294  
Rimini, November 10-12, 1992  
edited by I. Stamenković, J. Krawczynski (1994)  
GERMAN COOPERATION with the University "Sv. Kiril i Metodij", Skopje