

Fritz Aldinger and Volker A. Weberruß

Advanced Ceramics and Future Materials

*An Introduction to Structures, Properties,
Technologies, Methods*



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Cover

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Preface

Chemical and physical basics paired with engineering “black box” concepts as well as practical and theoretical experience in conventional and advanced ceramics paired with unorthodox ideas for future materials are the humus of the book in hand. On the one hand, it is a guideline for students, scientists, and engineers, and on the other hand, it presents ideas for visionaries. It is the alliance of a view into the past, the present, and the future. Not more, not less. May the readers have exactly the same pleasure with the book in hand as we have had with its creation.

The book is based upon lectures/papers/posters that are held/published/presented at/from the Department Aldinger of the Max-Planck-Institut für Metallforschung (Germany) and the Chair Aldinger on Nichtmetallische-Anorganische Materialien of the Universität Stuttgart (Germany) during the past decades – joint institutions which became also known as “Pulvermetallurgisches Laboratorium (PML)”. A selection of these works is accumulated in [76]–[189]. Some of the knowledge of [76]–[189] is used as “case studies” in the book. We truly regret that it was not possible to include all works that were done at the “Pulvermetallurgisches Laboratorium (PML)” during that time. Nevertheless, we hope that most of the readers consider the selection of works presented in this book satisfactory. Furthermore, we hope that most of the readers consider our decision to discuss ceramic materials within an extended frame of reference, which also incorporates metallic materials and organic materials, satisfactory. Moreover, we hope that at least some of our readers agree with us that it is a good time to carry out first steps towards future materials paving the way to artificial gravitation technologies and energy production technologies that go beyond chemical and nuclear reactions – exactly this is what we want to do in the final chapter of the book.

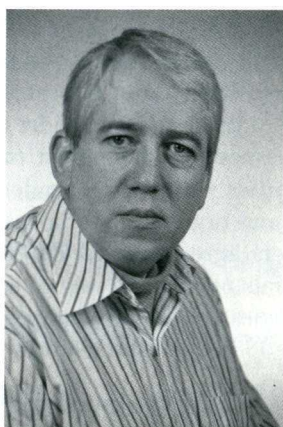
We wish to thank Dorothee Klink for the proofreading, Bernd Heinze for supplying us with nice photographs, CeramTec [71] for the abandonment of product images, microstructure images, and pictures of technical facilities, and SGL Brakes GmbH [72] for the release of images of ceramic (carbon) brake discs. Furthermore, we would like to thank Joachim Bill and Jerzy Golczewski for their valuable help. Moreover, the coauthor would like to thank Arndt Simon and Jürgen Köhler for the stimulating time at the Department Simon of the Max-Planck-Institut für Festkörperforschung.

*Fritz Aldinger und Volker A. Weberruß,
Stuttgart, January 2010.*



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Siliciumcarbid - Hochleistungskeramik

Eigenschaftsvielfalt durch Gefügedesign

Keramische Präparation und Ätzen



Ute Schäfer, Veronika Carle, Max-Planck-Institut für Metallforschung und Institut für Nichtmetallische Anorganische Materialien, Universität Stuttgart, Polymetallurgisches Laboratorium, Heisenbergstr. 5, D-70569 Stuttgart



Eigenschaftsvielfalt durch Gefügedesign

Korngestalt:

Durch die anisotropen Körner eines Plattegefüges werden Risse umgelenkt und so die Bruchzähigkeit merklich erhöht. Durch die bessere Konvergenz gibt es weniger Ausbrüche, die zum Versagen des Werkstücks oder zu erhöhtem Verschleiß führen können.

Korngröße:

Durch den kleineren Korngrößenanteil verbessert grobes Korn die Korrosionsbeständigkeit, verringert jedoch Festigkeit und Zuverlässigkeit. Speziell grobe SiC-Körner nutzen sich anisotrop ab und führen zu einem erwünschten Oberflächenreife, über das das Schmiermittel besser transportiert wird.

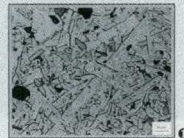
Zweitphasen:

Sie beeinträchtigen die Korrosionsbeständigkeit und - bei lokaler Korrosion - die Verschleißfestigkeit. Graphit verbessert die Nodauf Eigenschaften, ZrB₂ erhöht durch seine hohe Wärmeleitfähigkeit die Thermoschockbeständigkeit. Die Korngrößenphase in flüssigphasengesintertem SiC verringert die Hochtemperaturfestigkeit, ermöglicht aber eine hohe Bruchzähigkeit.

Porosität:

Poren verschlechtern Festigkeit und Zuverlässigkeit und sind Angriffspunkte für Materialzerstörung durch im Schmiermittel mitgeführte Partikel. Als Schmiermittelfreservoir können sie die Nodauf Eigenschaften verbessern.

Herstellung: Si-Infiltration im Grünkörper aus α -SiC und Graphit
Gefüge: Das Gefüge von SiSiC besteht aus großen α -SiC Körnern mit feinem angelagerten β -Anteil. Die helle Phase ist infiltriertes Si, das das Material porrenfrei macht, jedoch die Korrosionsbeständigkeit begrenzt.
Anwendung: Temperaturschwechselbelastete Gleitringe in Schmirz- und Ölschmierungen
Biegefestigkeit: 340 MPa
Bruchzähigkeit: 4,0 MPa $\sqrt{m}$



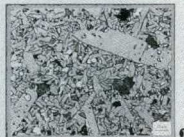
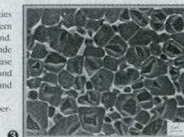
Herstellung: Druckloses Sintern, Zusatz von Al
Gefüge: SiSiC weist ein bimodales Gefüge mit anisotrop gewachsenen Körnern und einer Porosität von unter 3,5 % auf. Die voneinander isolierten Poren haben eine Größe von 20 bis 40 μm und nehmen Schmiermittel zur Verbesserung der Nodauf Eigenschaften auf.
Anwendung: Gleitlager für Industrie- und Wasserpumpen
Biegefestigkeit: 410 MPa
Bruchzähigkeit: 3,2 MPa $\sqrt{m}$

Herstellung: Druckloses Sintern mit spezieller Sinterparameter, die das Korn klein halten
Gefüge: Das Gefüge besteht aus polygon gewachsenen α -SiC-Körnern, die kleiner als 5 μm sind. Die Porosität liegt unter 1 %.
Anwendung: Wärmetauscher, Abgasabholer, Brennerdüsen
Biegefestigkeit: 450 MPa
Bruchzähigkeit: 2,5 MPa $\sqrt{m}$



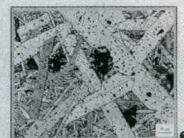
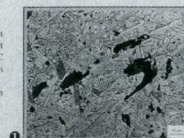
Herstellung: Druckloses Sintern von reinem β -SiC, Zusatz von B, Al
Gefüge: Das Gefüge zeigt ein feines β -Korn mit gerasteten Korngrößen. Innerhalb der β -Körner sind α -SiC-Nadeln zu sehen, die die Umwandlung zu α hat begonnen.
Anwendung: Noch nicht im Einsatz, Laborprobe.
Biegefestigkeit: k.A.
Bruchzähigkeit: k.A.

Herstellung: Flüssigphasensintern
Gefüge: LPSiC weist ein praktisch porrenfreies Gefüge aus sehr kleinen polyedrischen α -SiC-Körnern auf, die durch eine Korngrößenphase verbunden sind. Da beim Sintern die auf die Körner aufwachsende Schicht Elemente aus der flüssigen Korngrößenphase aufnimmt, sind chemische Zusammensetzung und auch das Verhalten von Randschicht und ursprünglichem Kern verschieden.
Anwendung: Lageranwendungen mit hoher Oberflächengüte und Passung
Biegefestigkeit: 600 MPa
Bruchzähigkeit: 6,0 MPa $\sqrt{m}$



Herstellung: Heißpressen, Zusatz von B, C, ZrB₂
Gefüge: Durch Bondbildung besteht das Gefüge von SiSiC-ZrB₂ aus einer Matrix kleiner, anisotrop gewachsener α -SiC-Körner mit hell erscheinenden ZrB₂-Partikeln. Das Material weist eine Porosität von 3 bis 5 % auf.
Anwendung: Dicht- und Regelgehäusen im Sanitärbereich und bei Beanspruchung in thermischen Zyklen
Biegefestigkeit: 330 MPa
Bruchzähigkeit: 3,8 MPa $\sqrt{m}$

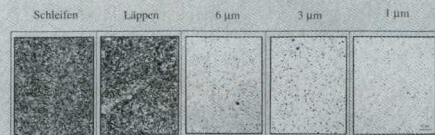
Herstellung: Druckloses Sintern, Zusatz von Al, C
Gefüge: SiSiC besitzt ein bimodales Gefüge mit anisotrop gewachsenen Körnern bei einer Porosität von ca. 8 %. Durch Zugabe von mehr als 1 % C enthält das Material Graphitpartikel bis zu 60 μm Durchmesser.
Anwendung: Einsatz bei stark druckbeanspruchten Paarungen
Biegefestigkeit: 300 MPa
Bruchzähigkeit: 3,2 MPa $\sqrt{m}$



Herstellung: Druckloses Sintern, Zusatz von Al, C
Gefüge: SiSiC zeigt ein ausgeprägt bimodales Plattegefüge aus α -SiC-Körnern mit eingelagerten Graphitpartikeln von 40 bis 60 μm Durchmesser auf. Der durch die großen Körner verringerte Gefügerinnenteil bewirkt eine erhöhte Korrosionsbeständigkeit.
Anwendung: Gleitringdichtungen in Heißwasser
Biegefestigkeit: 300 MPa
Bruchzähigkeit: 3,8 MPa $\sqrt{m}$

Keramische Präparation und Ätzen

Aufgrund des geschichteten Aufbaus der Kristallite und ihrer Verzahnung untereinander brechen keine ganzen Körner aus, sondern nur Kornfragmente, die sich beim Ätzen Schicht für Schicht glätten lassen. Bei der Endpolitur ist ein weiches Tuch mit 1 μm Diamant und langer Polierzeit nötig, um die feinsten Ausbrüche zu entfernen.



1. Murakami, kochend
- ätzt α -SiC - Korngrößen

3 g NaOH, 30 g K₂[Fe(CN)₆], 100 ml H₂O,
Ätzeit: 2 min

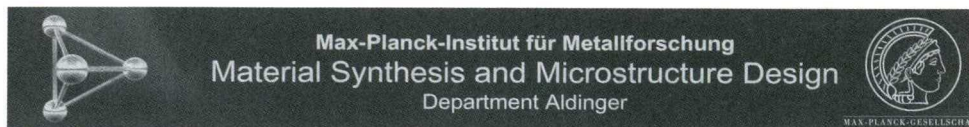
2. Salzschnelze
- ätzt β -SiC - Korngrößen

90 g KOH, 10 g KNO₃, Temperatur: 480°C,
Ätzeit: 2 min

3. Plasma-Ätzen
- nur für SiC mit Glasphase

CF₄ + O₂, im Verhältnis 1 : 1,
Ätzeit: 4 min

Silicon carbide materials.

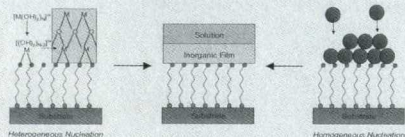


Bio-inspired Materials Synthesis

R.C. Hoffmann and J. Bill

Template-induced oxide deposition

1. Organic Modification of Substrate
2. Build-up of Thin Film
3. Formation of Inorganic/Organic-Hybrid Material

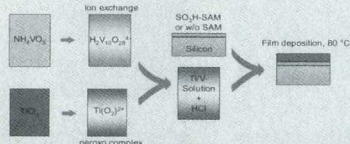


Research Objectives

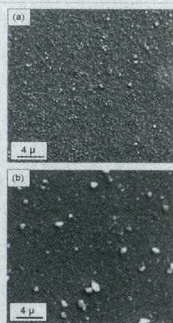
The objective of these studies is to develop strategies for materials synthesis by employing the organizational and functional characteristics of biological processes aiming to deposit ceramic-type materials from aqueous solutions at ambient conditions with respect to temperature and atmosphere. Organic templates at the surface of a substrate can induce the build up of thin films of oxides which deposit typically in nano-crystalline form, like ZrO_2 , TiO_2 , SnO_2 , V_2O_5 , similarly to biomineralisation processes.

The aim is to understand the template process aiming to exceed the mere imitation of biological mineralization and to steer the design of new materials with tailored interfaces and nano-sized microstructures in the future.

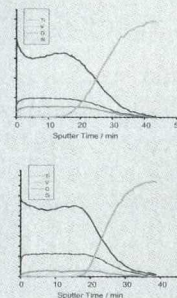
Deposition of Titania/Vanadia Nanocomposites



- Uniform and adherent films were obtained from solutions containing Ti and V species
- XPS indicates, that only TiO_2 and V_2O_5 are present in the film
- Auger depth profile reveals, that composite films of uniformly distributed TiO_2 and V_2O_5 nanoparticles were prepared
- No concentration gradient of titanium and vanadium was observed within these films.
- Zeta-potential measurements suggest, that the assembly is driven by van der Waals forces



SEM Micrographs:
As-deposited films on SO_3H -functionalized silicon wafers in 2x3 hours @ 353K from
(a) 10 mM [Ti], 10 mM [V] and 140 mM HCl;
(b) 7.5 mM [Ti], 2.5 mM [V] and 140 mM HCl.

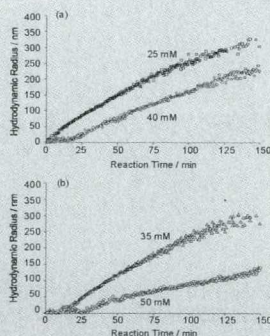


Auger Depth Profiles
Profiles correspond to SEM images.

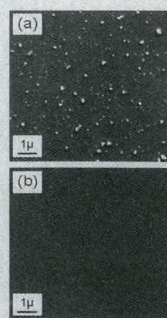
Deposition of Titania and Zincite on Polyethylene Terephthalate

The main advantage for applications, however, is the ability to coat complex shapes and the coating of temperature sensitive materials. This enables the deposition of ceramic thin films on polymers.

Titania thin films were prepared on polyethylene terephthalate substrates by hydrolysis of a peroxo complex in aqueous solutions at 333 K. Dynamic light scattering was used to monitor the particle growth in the reaction solution at various pH values. These findings were used to optimize the microstructure of the titania films by avoiding sedimentation of agglomerates and rapid depletion of the reaction solution. Films deposited on pristine PET, surface hydrolyzed PET and surface oxidized silicon were investigated by atomic force microscopy and show no significant difference in morphology



Dynamic Light Scattering
Time dependence of particle size solutions containing 10 mM Ti and various concentrations of HCl at 333 K:
(a) 25 and 40 mM HCl, (b) 35 and 40 mM HCl.



SEM Micrographs
Morphology of films grown with various concentrations of HCl at 333K:
(a) 10 mM [Ti] and 35 mM HCl;
(b) 10 mM [Ti] and 45 mM HCl.

Bio-inspired materials.

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Defining Ceramics

1. Advanced Ceramics

What would the ancient China have been without china? Imperfect! What would be the life of today without dental prostheses? Painful! What would be the space shuttle without thermal tiles? Disastrous! What would be the daily communication without mobile phones? Unimaginable! Is it thus carrying things too far that ceramic materials are objects of technologies of the past, the present, and the future? No way! But what are ceramic materials actually? Which structure do they have? How are their properties related to their structure? How are these manufactured? How are these modeled? Going somewhat beyond the conventional textbooks and the conventional monographs on modern ceramics, in the chapters that follow, an elaborate picture of modern ceramics is developed.

Going beyond the hellenic word *keramos* ("fired soil"), on the one hand, *ceramics* is defined as a name for products made out of non-metallic inorganic substances, and on the other hand, *ceramics* is defined as the art and science of making materials and products of non-metallic inorganic substances [28]. Naturally, following the standards of modern physics and modern chemistry, we want to associate the notion *non-metallic* with non-metallic energy band structures and their dependence on further constraints such as temperature and pressure, and we want to associate the notion *inorganic* with substances not showing the chemical structures of hydrocarbons. Certainly, we want to appreciate *conventional ceramics*, but we want to focus on *advanced ceramics*. We here compare with Figure 1.1, which shows the classifications, the definitions, and the terminology used in this book, and we here compare with Figures 1.2-1.13, which show some selected starting materials as well as some selected products of various branches of the ceramic industry.

We should already here appreciate that advanced ceramics meets the highest demands of present technologies. For instance, many ceramic materials are extremely resistant against abrasion! For instance, many ceramic materials are extremely resistant against heat! For instance, depending on further constraints such as temperature and pressure, ceramic materials can be insulators, ceramic materials can be conductors, and ceramic materials can be semi-conductors. Dear reader, ceramic materials even can be ferroelectrics without which the performance of present communication technology would be more than poor. Dear reader, the hip joint endoprotheses that are shown in Figure 1.10 are implants meanwhile doing their job in hundreds of millions of human bodies worldwide! Isn't this a feat?

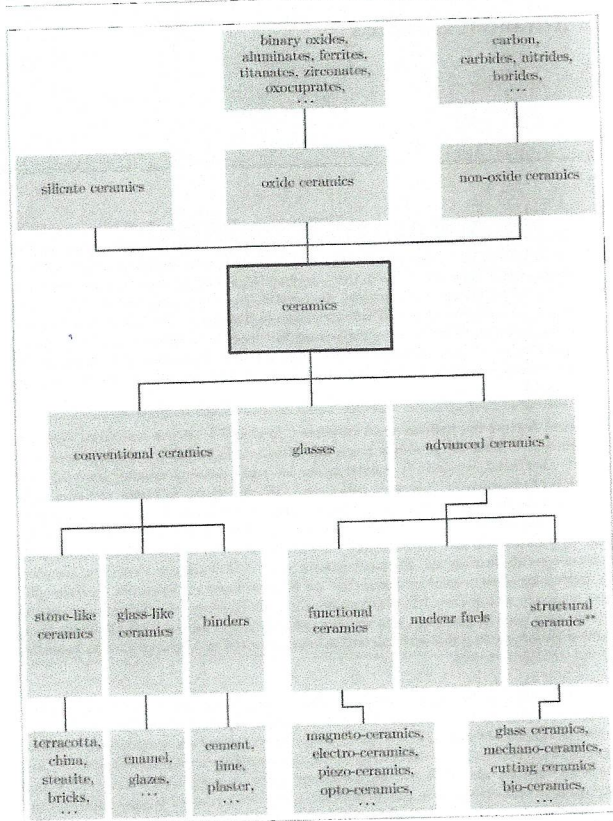


Figure 1.1. Classifications, definitions, and terminology. * frequently noted as "fine ceramics" (Japan) or "Hochleistungskeramik" (Germany). ** frequently noted as "engineering ceramics" (USA, GB) or "Ingenieurkeramik" (Germany).

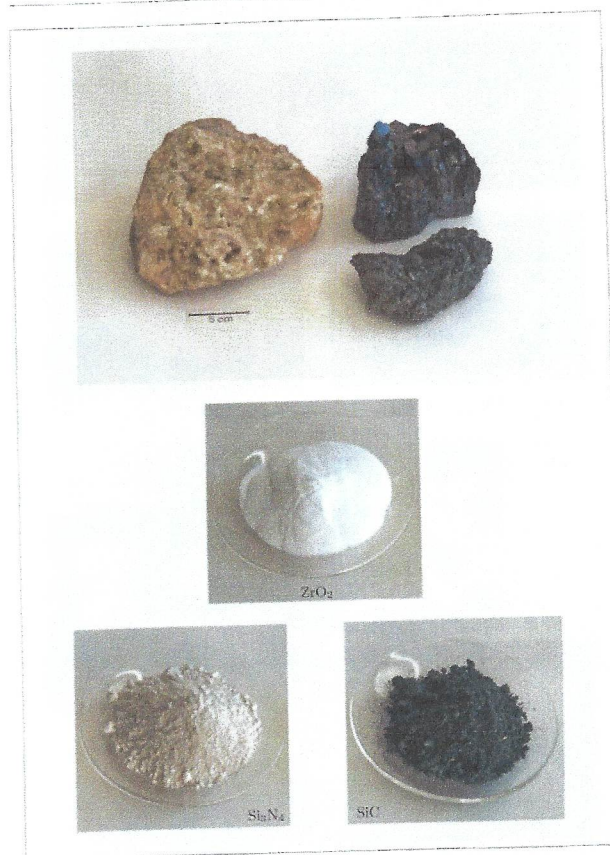


Figure 1.2. Mineral stones and powdered artificial non-metallic inorganic materials.

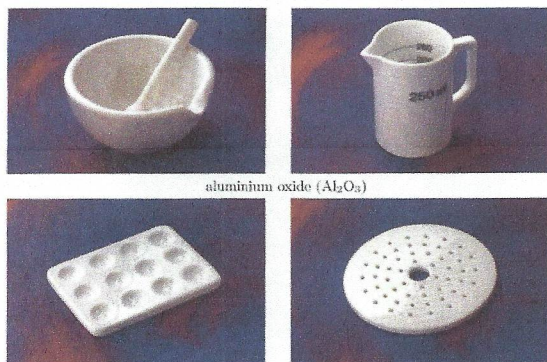
aluminum oxide (Al_2O_3)

Figure 1.3. Laboratory ware.

images kindly provided by CeramTec

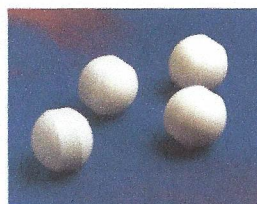
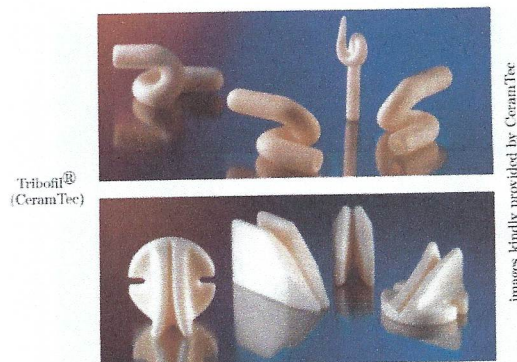
magnesium silicate
($\text{Mg}_3\text{Si}_4\text{O}_{10}$ hydroxide: stentite)aluminum oxide (Al_2O_3)

Figure 1.4. Grinding balls.

Tribofil®
(CeramTec)

images kindly provided by CeramTec

Figure 1.5. Textile machinery components. Pigtails (top) and oiler guides (bottom).

ZN 101 B
(CeramTec)TZP (ZrO_2 , Y_2O_3 stabilized)

images kindly provided by CeramTec

Figure 1.6. Ceramic cutters. Scissors (top) and knives (bottom).



Figure 1.7. Components for industrial machinery and industrial facilities. SSiC: sintered SiC. SSiC: Si-infiltrated SiC.

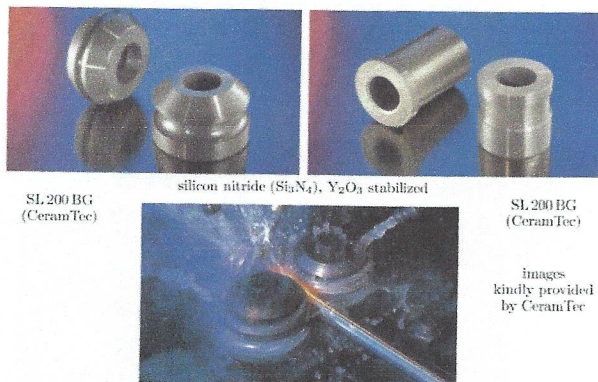


Figure 1.8. Welding rollers (top) and their application (bottom). The lower picture shows a facility for pipe welding.

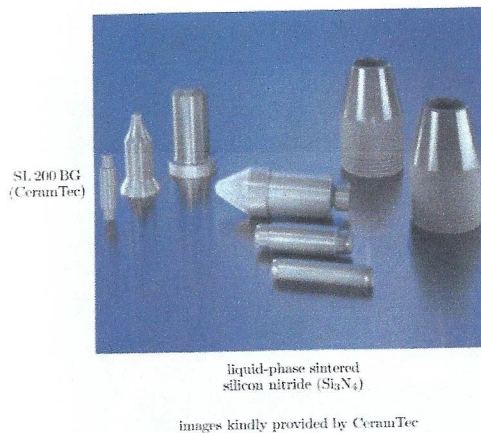


Figure 1.9. Centering pins for welding processes (top) and their application (bottom). The lower picture shows a facility for metal active gas welding.

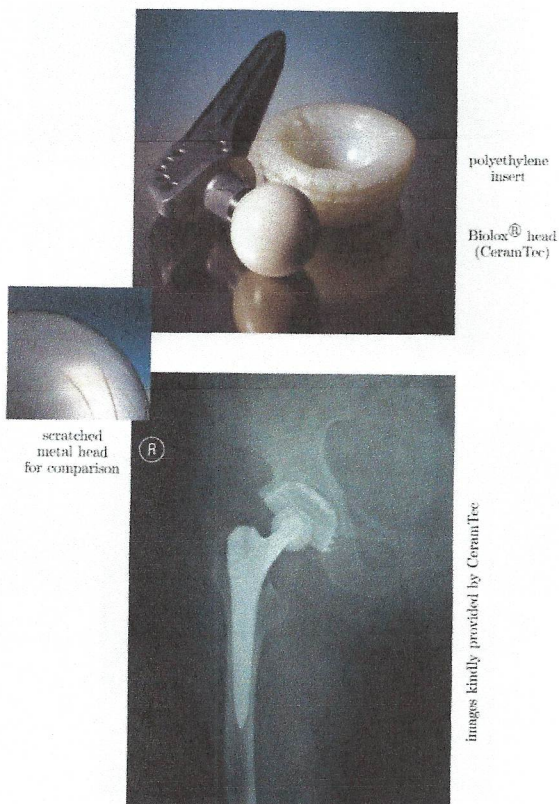


Figure 1.10. Hip joint endoprosthesis (top) and its application (bottom).

image kindly provided
by FHG/IWM [191]

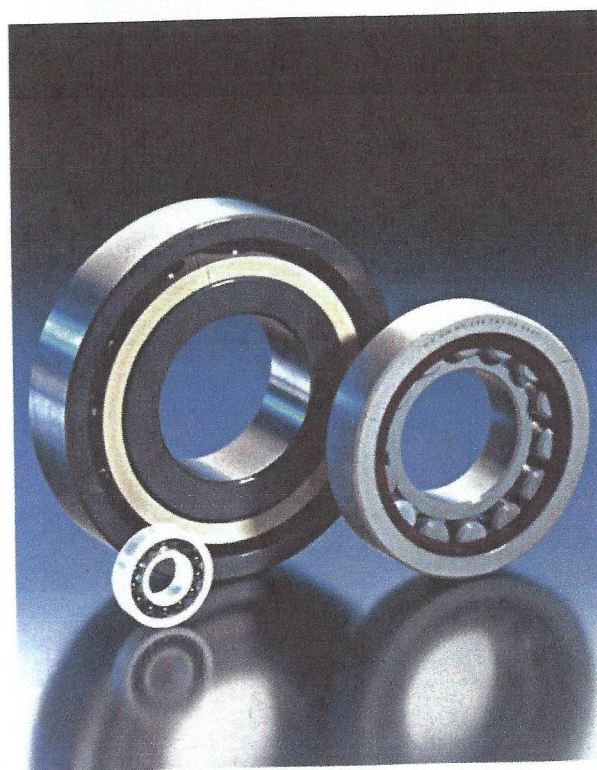
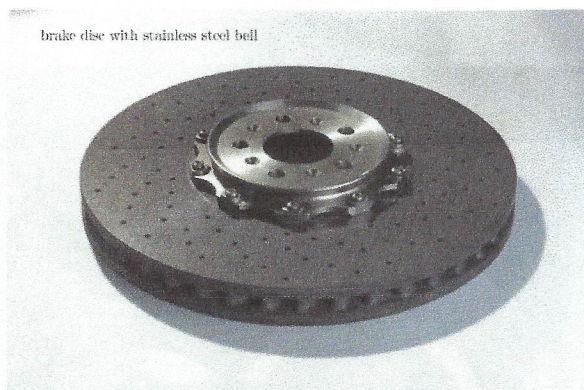


Figure 1.11. Ball (roller) bearings.

brake disc with stainless steel bell



images kindly provided by SGL Brakes GmbH

brake disc with titanium bell

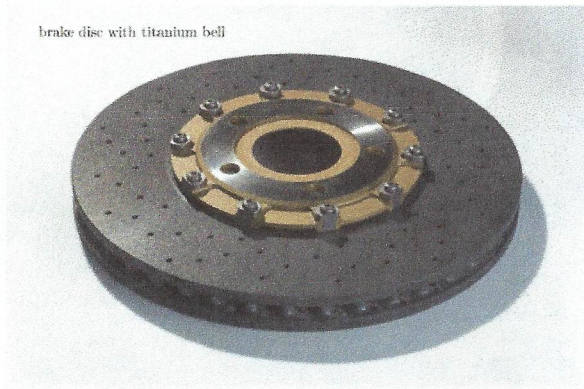


Figure 1.12. Ceramic (carbon) brake discs.

taken from the VAWsc picture archive

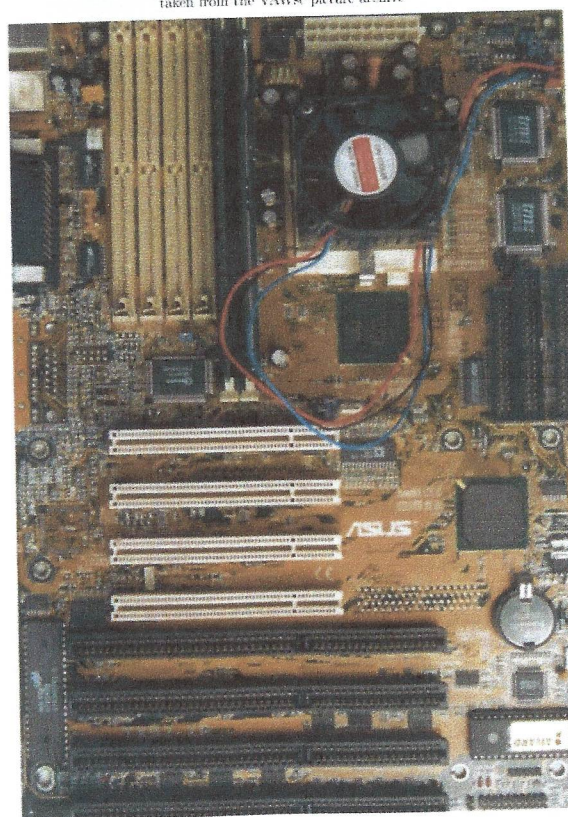


Figure 1.13. PC motherboard with chip carriers.

Going beyond advanced ceramics, in the final Chapter 5, first steps towards new fields of materials research are carried out. The following first introductory remarks already here should be useful. On the one hand, a branch of research is started up dealing with the question "How must materials be structured and how must their technical environment be structured that these can be used as the material basis for an oscillatory system generating a measurable oscillatory gravitational field, so to speak, as the material basis for a gravitational laser?" On the other hand, a branch of research is started up dealing with the question "How must materials be structured and how must their technical environment be structured that these – fundamentally going beyond nuclear techniques and matter-antimatter destruction – can be disaggregated into radiation, which in turn can be used as starting point for new types of energy plants, new types of spacecraft propulsions, and new types of matter conversion techniques?" For this purpose, a self-consistent network of model conceptions is launched, which some colleagues may consider as a direct extension of the Ginzburg-Landau theory of superconductivity [20] or as a semi-classical approach to quantum systems comparable to the Wigner-Main approach to quantum systems [34, 35, 64], however, which could turn out to be the true nonlinear extension of conventional quantum mechanics [63], on all accounts, which works without any known restrictions, and which firstly can supply us with much more information about the principles that govern the constitution, the stabilities, and the instabilities of materials than the methods of thermodynamics and the methods of quantum mechanics can do, and which secondly can supply us with paths to these new fields of materials research. Certainly, it goes far beyond the scope of this book to develop these new fields of research in great detail already here. However, the first steps towards this goal indeed are taken here.

Why do we think that a book about advanced ceramics is the adequate place for such first steps? Well, on the one hand, in the framework of advanced fuels such as nuclear fuel rods, ceramic materials play an important role so that we expect that ceramic materials will also play an important role in our more advanced context. Well, on the other hand, wanting to gain an access to artificial gravitation, it should not be the worst choice to depart from materials with a relatively high mass density and a relatively low free charge carrier density, promising us high gravitational radiation and low electromagnetic radiation, as it is the case for a lot of ceramic materials. Anyway, departing from advanced ceramics of the past and the present, let us also point into the future of materials.