Karlsruher Institut für Technologie

Deutsche Keramische Gesellschaft e. V.

50 Years of Engineering Ceramics - From Ideas to Reality

M.J. Hoffmann

KIT – Institute for Applied Materials and
KIT Campus Transfer GmbH (KCT)

What are Engineering Ceramics ?

Definition according to VKI:
„Advanced, high-performance ceramic material that is predominantly non-metallic and inorganic and has certain useful properties”
(DIN VENV 12212)

„Stuttgart (MPI)“ Definition:
„High-performance ceramics are non-metallic, inorganic materials with an optimized microstructure. They are obtained from ceramic powders with strictly defined composition and particle characteristics under controlled conditions.“

Major Materials for „Engineering Ceramics“

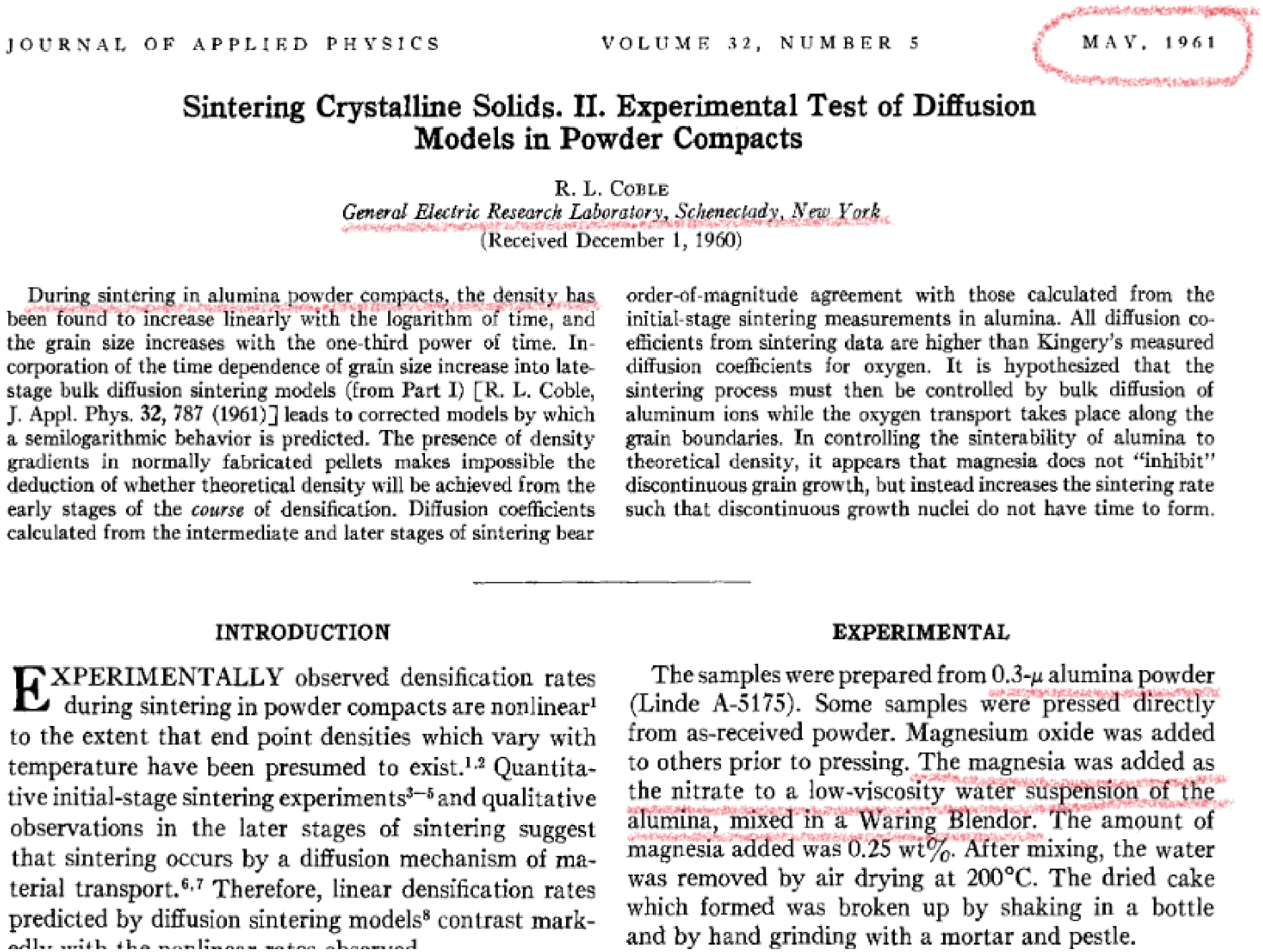
- Alumina: large-scale production since 1890 by Bayer process.
  In the 1930s-1950s mainly as used functional ceramic (insulator), later as seals or cutting tools.

- Zircona: known since 1920s, but technical useless do to the martensitic transformation during cooling.

- Silicon Carbide: discovered by Henri Moisson in 1893 in a meteor crater in Arizona. Development of a large-scale production process in 1891 by E.G. Acheson (Carborundum). Material was mainly used for grinding.

- Silicon Nitride: Synthesis of „Nitrogensilicon“ by Deville and Wöhler in 1857. First Si_3N_4-ceramic by Deeley et al. in 1961 by hot-pressing with oxidic additives.

… basic understanding of the sintering process of engineering ceramics was developed in the 1960s



JOURNAL OF APPLIED PHYSICS VOLUME 32, NUMBER 5 MAY, 1961

Sintering Crystalline Solids. II. Experimental Test of Diffusion Models in Powder Compacts

R. L. Coble
General Electric Research Laboratory, Schenectady, New York

(Received December 1, 1960)

During sintering in alumina powder compacts, the density has been found to increase linearly with the logarithm of time, and the grain size increases with the one-third power of time. Incorporation of the time dependence of grain size increase into late-stage bulk diffusion sintering models (from Part I) [R. L. Coble, J. Appl. Phys. **32**, 787 (1961)] leads to corrected models by which a semilogarithmic behavior is predicted. The presence of density gradients in normally fabricated pellets makes impossible the deduction of whether theoretical density will be achieved from the early stages of the *course* of densification. Diffusion coefficients calculated from the intermediate and later stages of sintering bear order-of-magnitude agreement with those calculated from the initial-stage sintering measurements in alumina. All diffusion coefficients from sintering data are higher than Kingery's measured diffusion coefficients for oxygen. It is hypothesized that the sintering process must then be controlled by bulk diffusion of aluminum ions while the oxygen transport takes place along the grain boundaries. In controlling the sinterability of alumina to theoretical density, it appears that magnesia does not "inhibit" discontinuous grain growth, but instead increases the sintering rate such that discontinuous growth nuclei do not have time to form.

INTRODUCTION

Experimentally observed densification rates during sintering in powder compacts are nonlinear[1] to the extent that end point densities which vary with temperature have been presumed to exist.[1,2] Quantitative initial-stage sintering experiments[3–5] and qualitative observations in the later stages of sintering suggest that sintering occurs by a diffusion mechanism of material transport.[6,7] Therefore, linear densification rates predicted by diffusion sintering models[8] contrast markedly with the nonlinear rates observed

EXPERIMENTAL

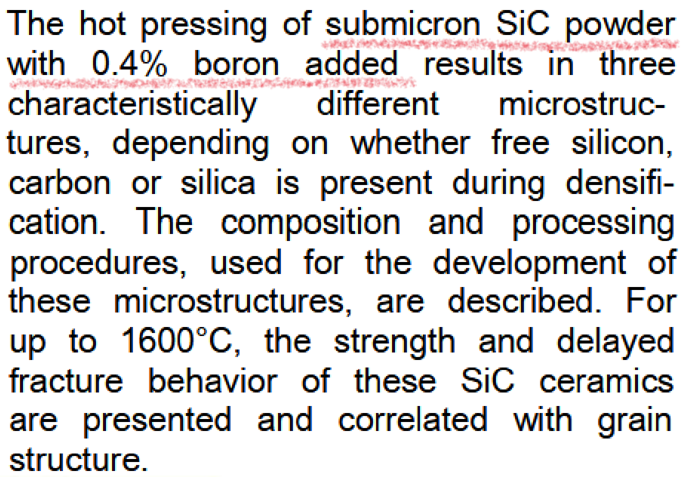
The samples were prepared from 0.3-μ alumina powder (Linde A-5175). Some samples were pressed directly from as-received powder. Magnesium oxide was added to others prior to pressing. The magnesia was added as the nitrate to a low-viscosity water suspension of the alumina, mixed in a Waring Blendor. The amount of magnesia added was 0.25 wt%. After mixing, the water was removed by air drying at 200°C. The dried cake which formed was broken up by shaking in a bottle and by hand grinding with a mortar and pestle.

American Ceramic Society Bulletin, Vol. 52, No. 12 (1973)

Strength of Boron-Doped, Hot-Pressed Silicon Carbide

SVANTE PROCHAZKA and R. J. CHARLES

General Electric Co., Corporate Research & Development, Schenectady, N. Y.



The hot pressing of submicron SiC powder with 0.4% boron added results in three characteristically different microstructures, depending on whether free silicon, carbon or silica is present during densification. The composition and processing procedures, used for the development of these microstructures, are described. For up to 1600°C, the strength and delayed fracture behavior of these SiC ceramics are presented and correlated with grain structure.

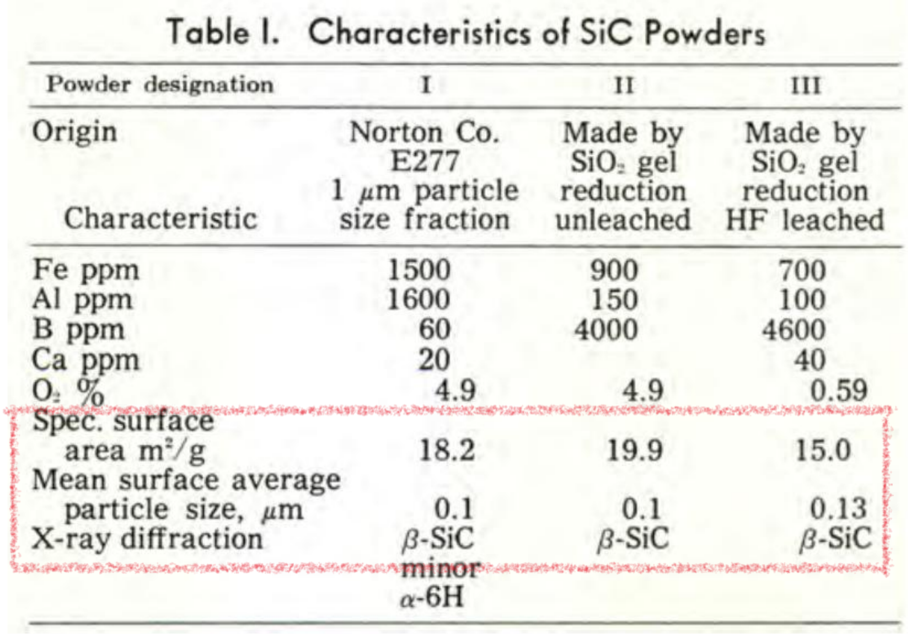
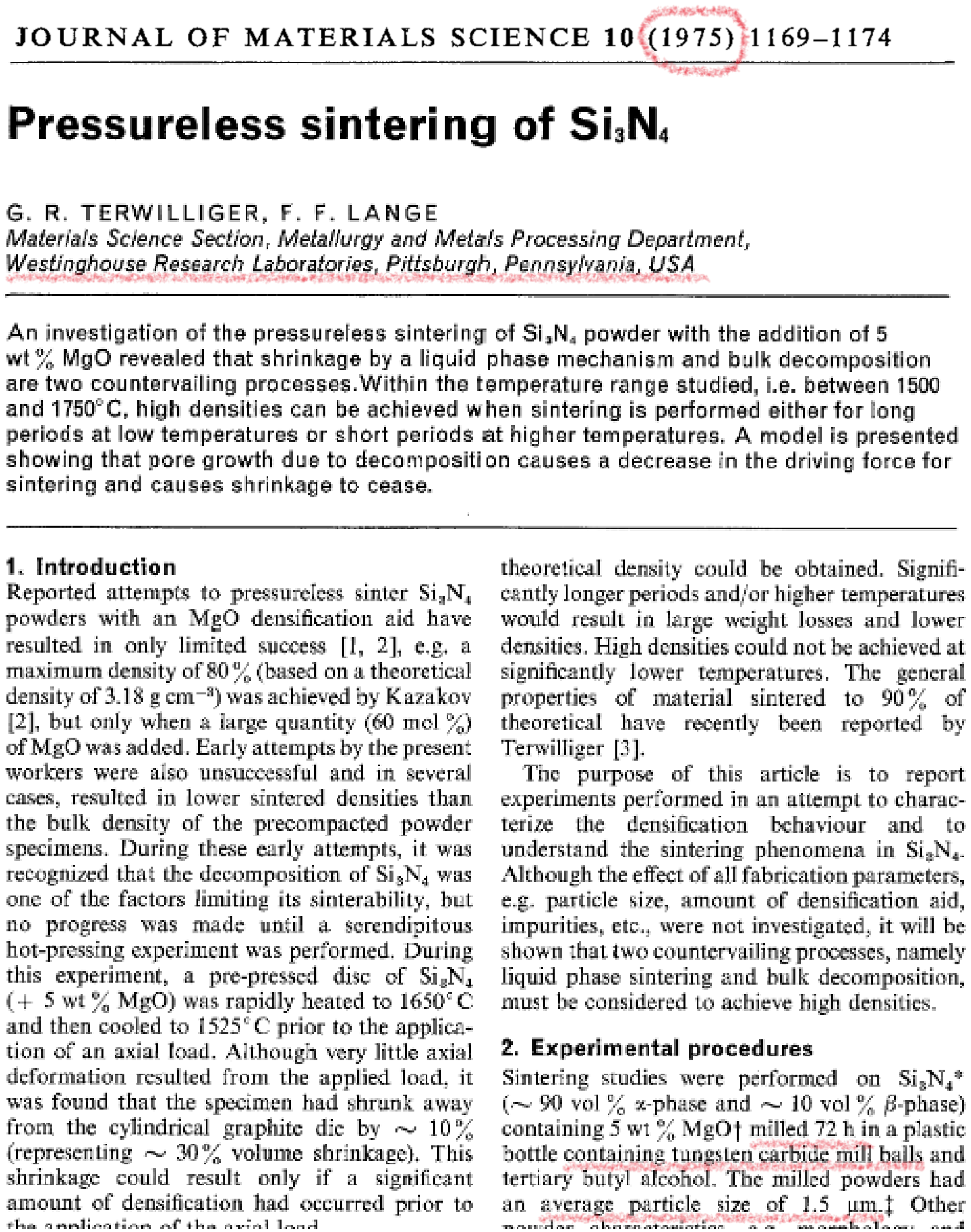


Table I. Characteristics of SiC Powders

Powder designation	I	II	III
Origin Characteristic	Norton Co. E277 1 μm particle size fraction	Made by SiO_2 gel reduction unleached	Made by SiO_2 gel reduction HF leached
Fe ppm	1500	900	700
Al ppm	1600	150	100
B ppm	60	4000	4600
Ca ppm	20		40
O_2 %	4.9	4.9	0.59
Spec. surface area m^2/g	18.2	19.9	15.0
Mean surface average particle size, μm	0.1	0.1	0.13
X-ray diffraction	β-SiC minor α-6H	β-SiC	β-SiC



JOURNAL OF MATERIALS SCIENCE 10 (1975) 1169–1174

Pressureless sintering of Si_3N_4

G. R. TERWILLIGER, F. F. LANGE
Materials Science Section, Metallurgy and Metals Processing Department, Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, USA

An investigation of the pressureless sintering of Si_3N_4 powder with the addition of 5 wt % MgO revealed that shrinkage by a liquid phase mechanism and bulk decomposition are two countervailing processes. Within the temperature range studied, i.e. between 1500 and 1750° C, high densities can be achieved when sintering is performed either for long periods at low temperatures or short periods at higher temperatures. A model is presented showing that pore growth due to decomposition causes a decrease in the driving force for sintering and causes shrinkage to cease.

1. Introduction

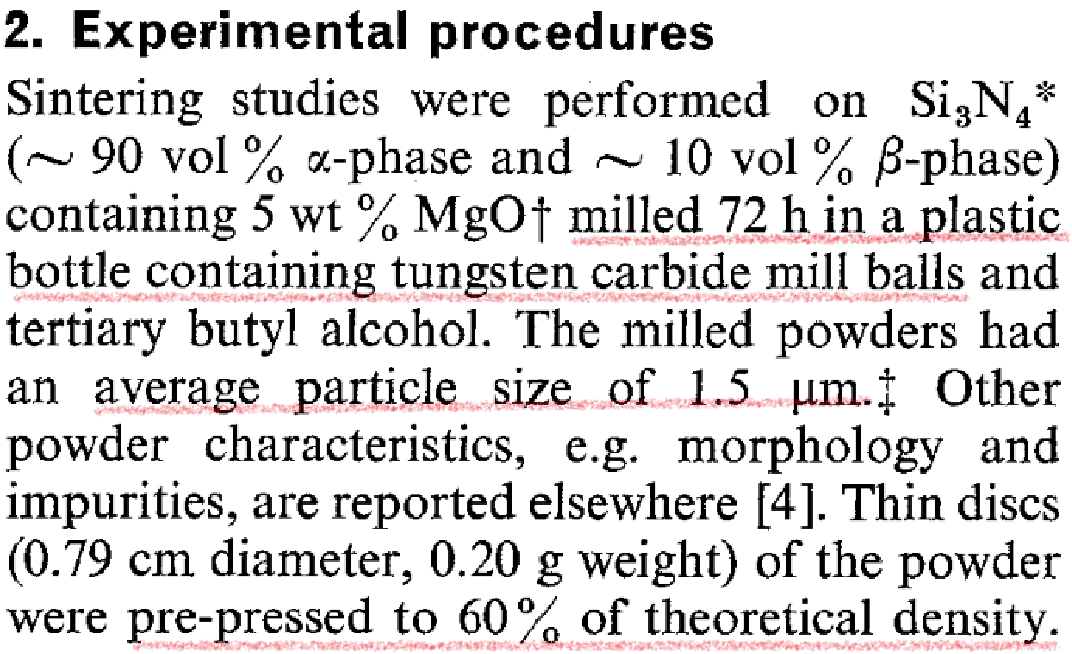
Reported attempts to pressureless sinter Si_3N_4 powders with an MgO densification aid have resulted in only limited success [1, 2], e.g. a maximum density of 80 % (based on a theoretical density of 3.18 g cm^{-3}) was achieved by Kazakov [2], but only when a large quantity (60 mol %) of MgO was added. Early attempts by the present workers were also unsuccessful and in several cases, resulted in lower sintered densities than the bulk density of the precompacted powder specimens. During these early attempts, it was recognized that the decomposition of Si_3N_4 was one of the factors limiting its sinterability, but no progress was made until a serendipitous hot-pressing experiment was performed. During this experiment, a pre-pressed disc of Si_3N_4 (+ 5 wt % MgO) was rapidly heated to 1650° C and then cooled to 1525° C prior to the application of an axial load. Although very little axial deformation resulted from the applied load, it was found that the specimen had shrunk away from the cylindrical graphite die by ~ 10% (representing ~ 30% volume shrinkage). This shrinkage could result only if a significant amount of densification had occurred prior to the application of the axial load.

theoretical density could be obtained. Significantly longer periods and/or higher temperatures would result in large weight losses and lower densities. High densities could not be achieved at significantly lower temperatures. The general properties of material sintered to 90% of theoretical have recently been reported by Terwilliger [3].

The purpose of this article is to report experiments performed in an attempt to characterize the densification behaviour and to understand the sintering phenomena in Si_3N_4. Although the effect of all fabrication parameters, e.g. particle size, amount of densification aid, impurities, etc., were not investigated, it will be shown that two countervailing processes, namely liquid phase sintering and bulk decomposition, must be considered to achieve high densities.

2. Experimental procedures

Sintering studies were performed on Si_3N_4* (~ 90 vol % α-phase and ~ 10 vol % β-phase) containing 5 wt % MgO† milled 72 h in a plastic bottle containing tungsten carbide mill balls and tertiary butyl alcohol. The milled powders had an average particle size of 1.5 µm.‡ Other powder characteristics, e.g. morphology and



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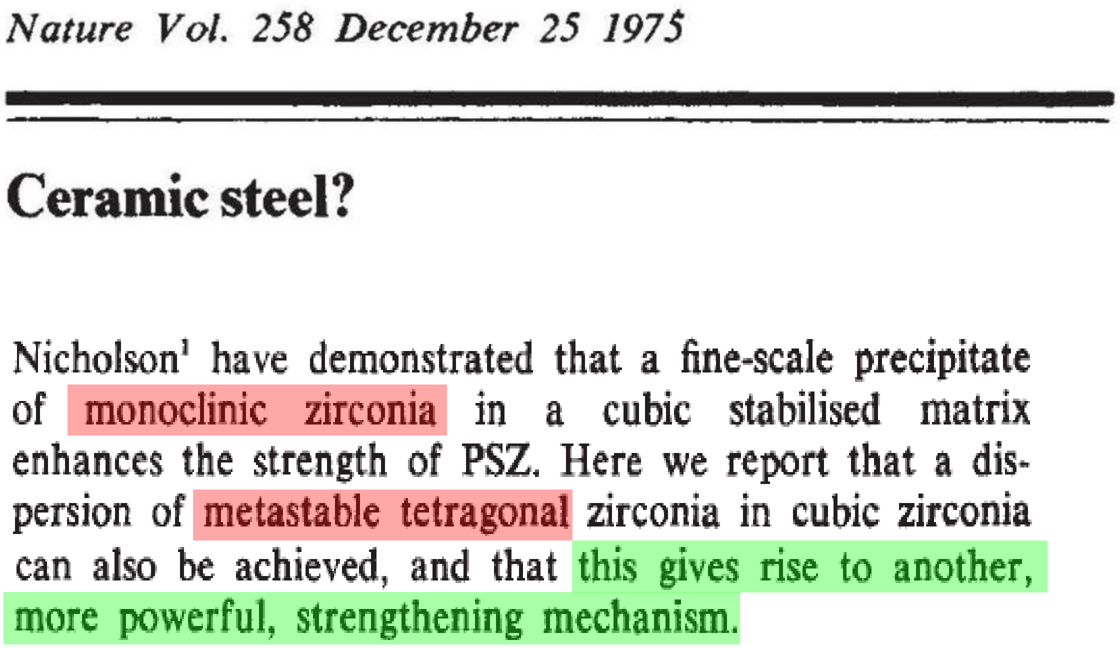
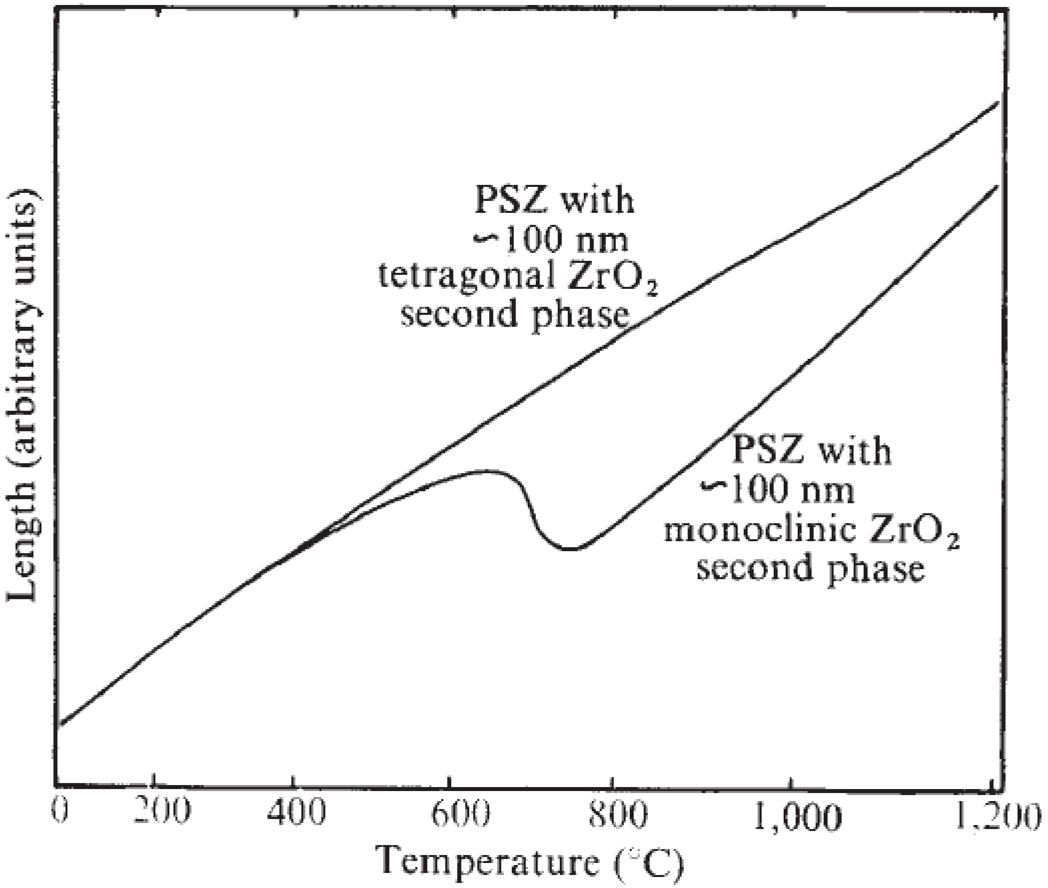
Partially Stablized Zirconia (PSZ)



Nature Vol. 258 December 25 1975

Ceramic steel?

Nicholson[1] have demonstrated that a fine-scale precipitate of monoclinic zirconia in a cubic stabilised matrix enhances the strength of PSZ. Here we report that a dispersion of metastable tetragonal zirconia in cubic zirconia can also be achieved, and that this gives rise to another, more powerful, strengthening mechanism.



R.C. Garvie, R.H. Hannink, R.T. Pascoe, CSIRO Melbourne

Common Features in the Early Development Stage of Engineering Ceramics

- Availability of **purer and synthetic powders** provided by the chemical industry instead of the mining industry

- Impact of modern **process engineering** to obtain fine-grained starting powders with high sintering activity (solid state sintering)

- Strong interest in Japanese and U.S. **power companies** in new materials for high-temperature applications

- Rapidly increasing **interdisciplinary research** between ceramists, metallurgists, physicists, chemists, process engineers, mechanical engineers

Research Activities in Germany

- TU Berlin:
  The Technical University of Berlin appointed in 1972 **Hans Hausner** as full professor for the Chair of Ceramics at the newly founded Institute of Non-Metallic Materials

- DFVLR Köln-Porz (now: DLR Köln):
  DFVLR appointed **Wolfgang Bunk** in 1970 as Director of the Institute for Material Science

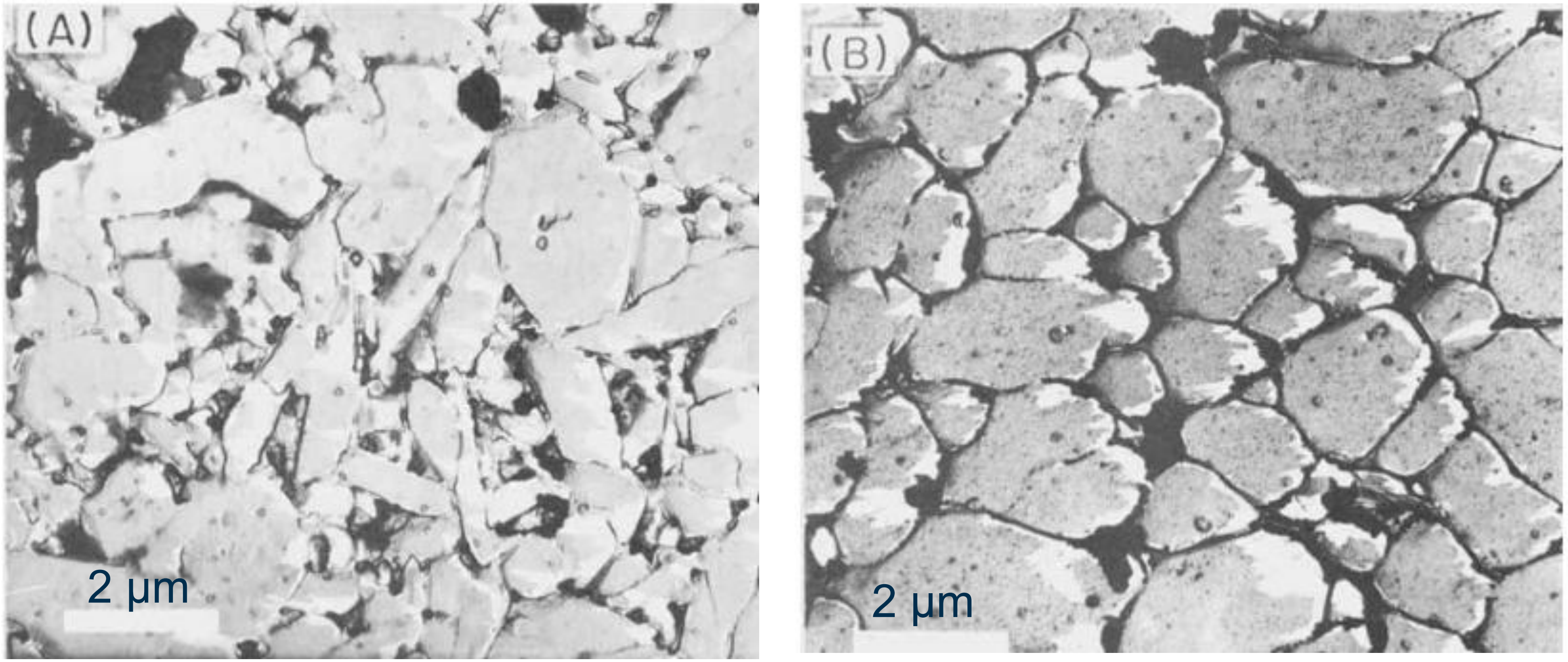
- Nuclear Research Center Karlsruhe / TH Karlsruhe (now: KIT):
  In 1965, appointment of **Fritz Thümmler** as Director of the Institute for Materials and Solid State Research (IMF I)

- MPI for Metals Research in Stuttgart
  In 1968, **Günter Petzow** took over the management of the newly founded Powder Metallurgical Laboratory (PML)

Advances in science using silicon nitride ceramics as an example

First microstructures of hot-pressed silicon nitride ceramics

Terwilliger and Lange, J.Am.Ceram.Soc. Vol.57 [1] 1974



Terwilliger densified Si_3N_4 with 5 wt.% MgO and discovered already the impact of the polymorphism of the starting powder (α/β-ratio).

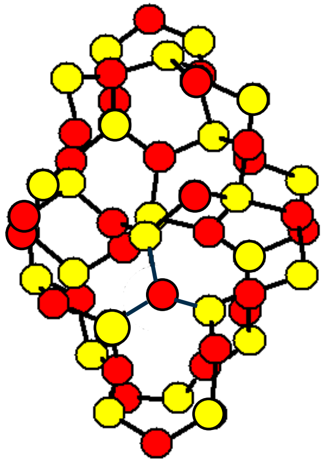
However, the presence of the liquid phase limits high-temperature resistance

The exploration of solid solutions between Si_3N_4 and Al_2O_3 (sialons)

The chemist K.H. Jack (UK) had analysed the crystal structure of α- und α/β-Si_3N_4 at the beginning of the 1970s and developed a vision of what would become in a new field of ceramic science:

"Oxygen replaces nitrogen in α-silicon nitride to a limited extent, but further replacement seems possible if network silicon atoms are replaced by aluminium or by another substituent of valency lower than silicon. Furthermore, replacement of network silicon by aluminium would allow accommodation of other metallic cations in the silicon nitride structure in a manner similar to that occurring in crystalline silicates and in glasses. There seems a good possibility of developing a completely new range of nitride and oxynitride materials based on the Si–Al–O–N system.

Research report in 1968



α-Si_3N_4

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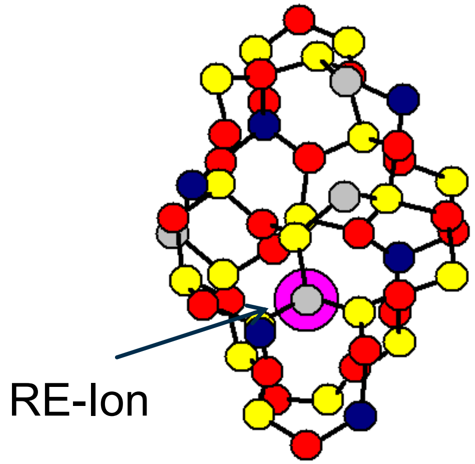


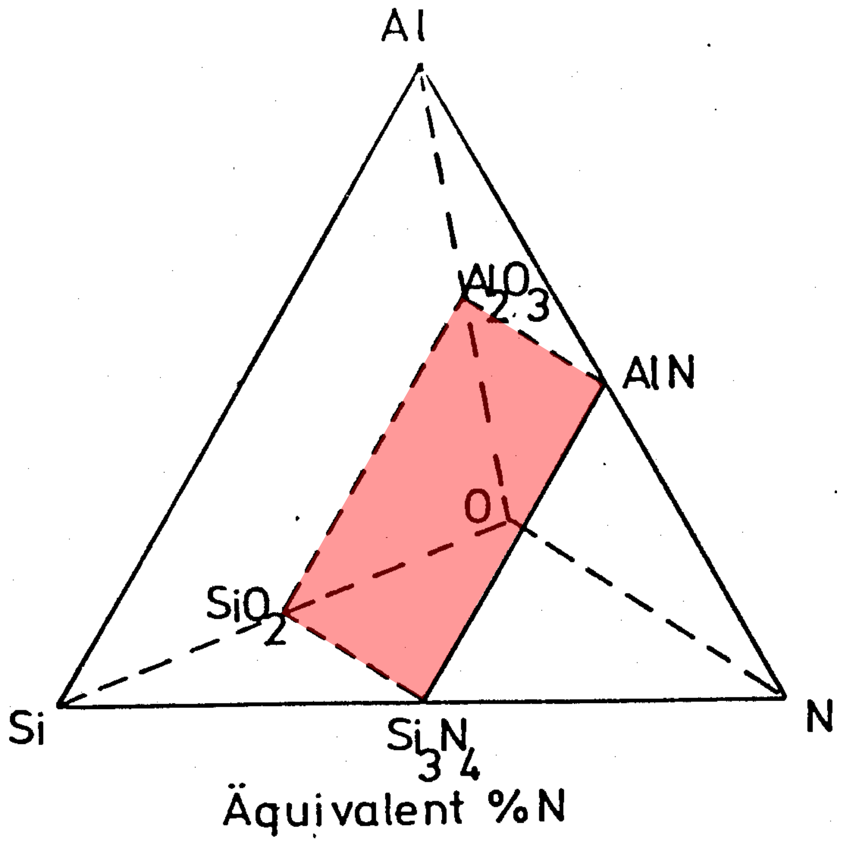
α-Sialon

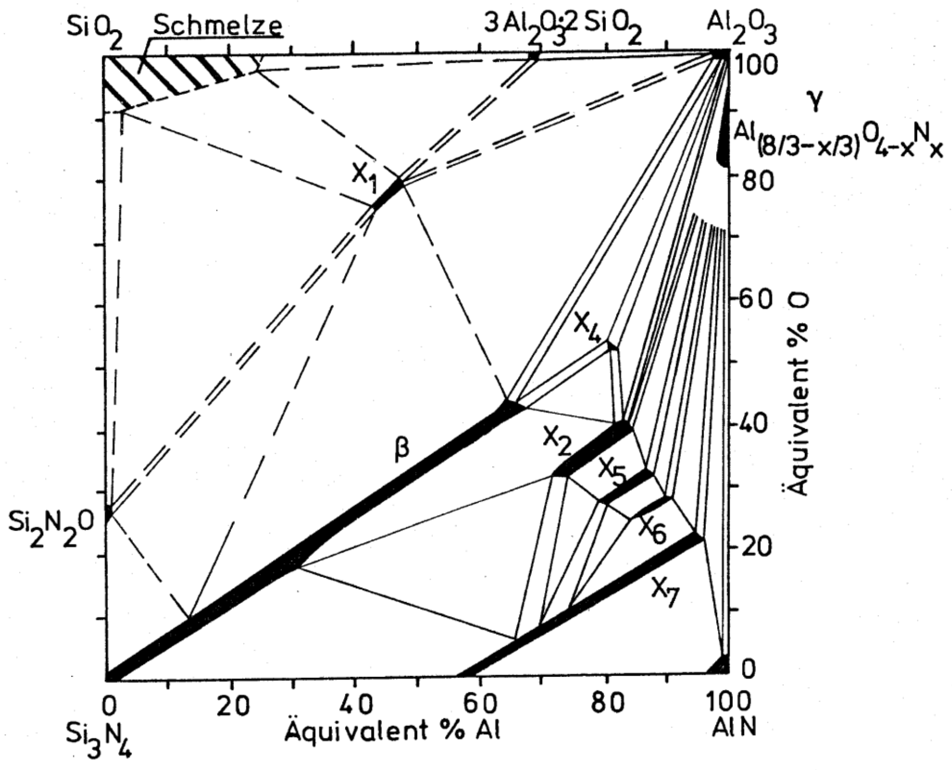
Si^{4+} → Al^{3+}

N^{3-} → O^{2-}

+ RE^{3+} (cavity)

Petzow`s team in Stuttgart explored the phase diagrams of sialons

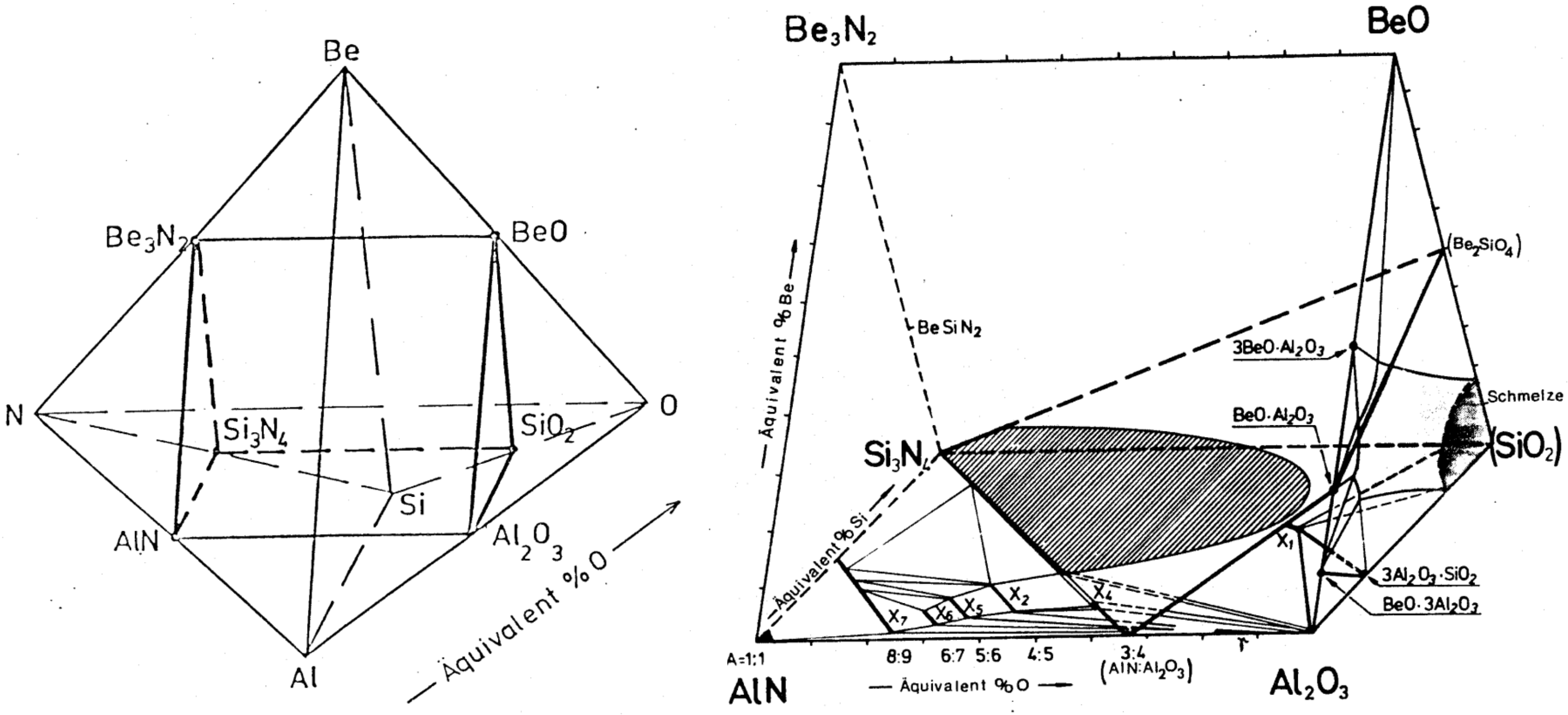




Gaukler, Lukas, Petzow: J. Am. Ceram. Soc., Vol.58 [7-8] 1975

→ Representation as a reciprocal salt system with concentrations in eq%

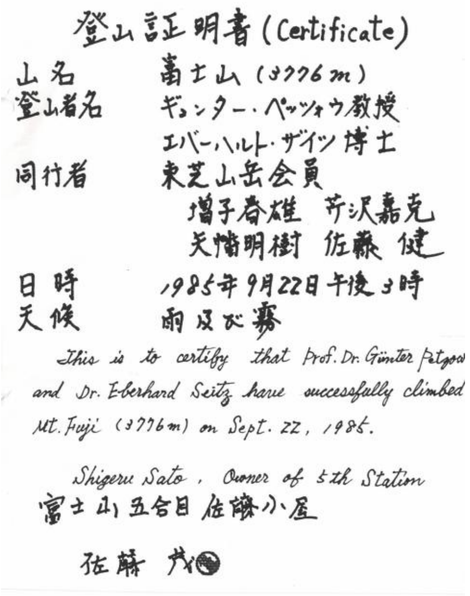
Petzow`s team in Stuttgart explored the phase diagrams of sialons



L. Gaukler, Ph.D. thesis University of Stuttgart, 1976

→ Representation of the 5-component system Be-Si-Al-O-N as reciprocal salt system

German „Ceramic Pope“ became famous in Japan



登山証明書（Certificate）

山名	富士山（3776 m）
登山者名	ギュンター・ペッツォウ教授 エバーハルト・ザイツ博士
同行者	東芝山岳会員 増子春雄　芹沢嘉克 矢幡明樹　佐藤 健
日時	1985年9月22日午後3時
天候	雨及び霧

This is to certify that Prof. Dr. Günter Petzow and Dr. Eberhard Seitz have successfully climbed Mt. Fuji (3776 m) on Sept. 22, 1985.

Shigeru Sato, Owner of 5th Station

富士山五合目 佐藤小屋

佐藤 茂

Statement from the National Academy of Sciences (USA) / 1983-84:

Japan is the leading country in the research and development of advanced ceramics for diverse applications in microelectronics, motors, various types of sensors, as cutting ceramics, for power generation, and even for orthopedics.

Japanese ministries (notable MITI) ensured continuity of funding and shared research infrastructure, something less present in the U.S.

Political boundary conditions in the 1970s

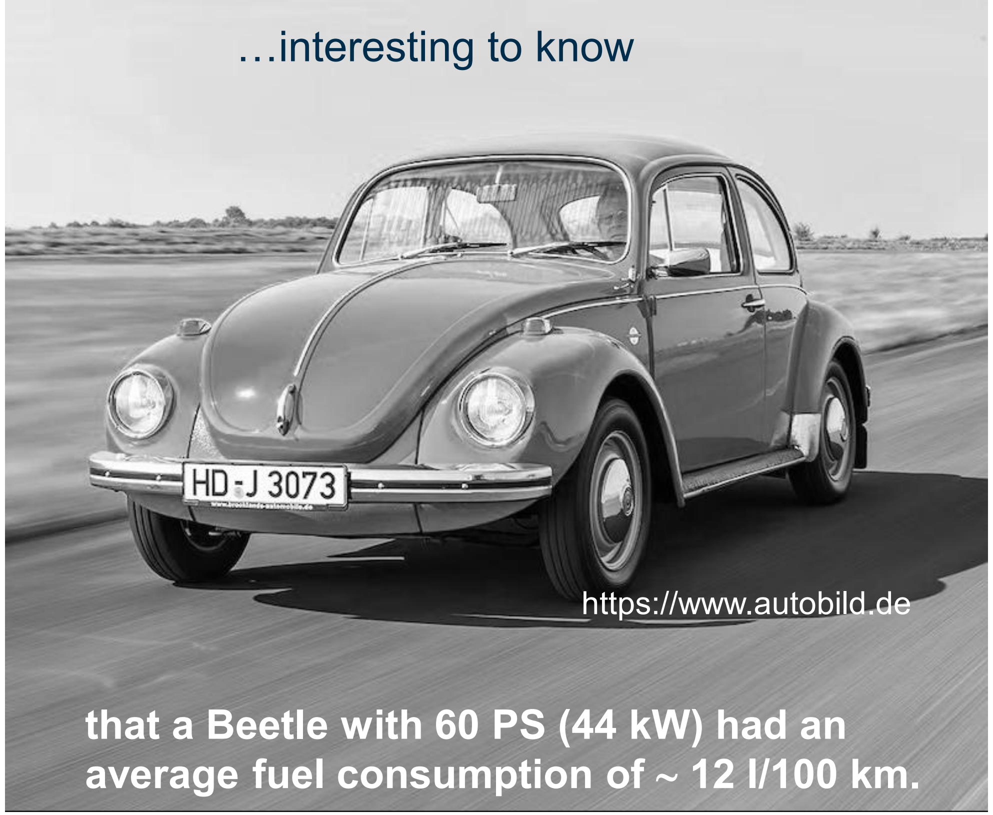
…the oil crisis in 1973

25. November 1973

Autofreier Sonntag in der BRD

© picture alliance / dpa

…interesting to know



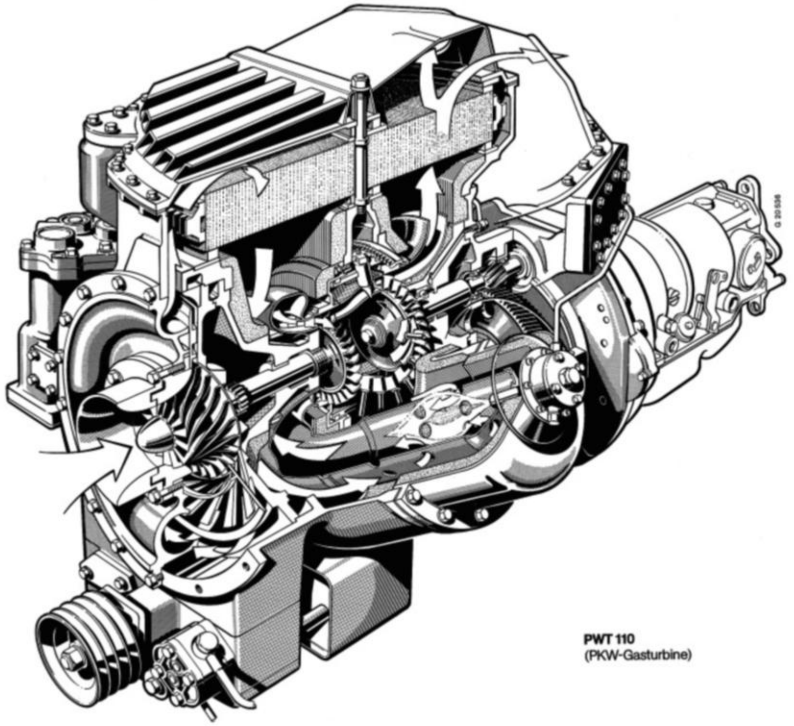
https://www.autobild.de

that a Beetle with 60 PS (44 kW) had an average fuel consumption of ~ 12 l/100 km.

BMBF-project (1978): „Forschungs-Personenwagen“ taking into account the specified guidelines regarding energy and resource conservation, environmental friendliness, safety, economic efficiency and utility value.

The Gas turbine of Daimler-Benz

Source: Daimler-Benz AG, Press Department



The prerequisite for building a gas turbine (110 kW output) with low fuel consumption was the development of highly heat-resistant, ceramic turbine wheels. Real-life conditions for the Daimler gas turbine: 1250°C and 60,000 rpm.

Source: Daimler-Benz AG, Press Department

Outcome of a trip to the Far East by a Baden-Württemberg business delegation in April 1984

PM: Lothar Späth
(1978-1991)

→ 10.000.000 DM for clean rooms

Shell construction PML, 1985

...but there was a need to find funding for the ceramic research

A BMBF-project could be established within the framework of the „Matfo“-program (03 M 2012 B) with the title:

„Development of thermally and mechanically highly stressed ceramic materials with high reliability as a basis for high-performance components for engine and turbine construction”

- Partners: Bayer AG, Daimler AG, MTU, Höchst AG, BMBF
- Financial Volume: 17 Mill. DM
- Financing: Industry (50%)
  BMBF (50%)

Entwicklung von thermisch und mechanisch hochbeanspruchten Keramikwerkstoffen mit hoher Zuverlässigkeit als Grundlage für leistungsfähige Bauteile für den Motoren- und Turbinenbau

1986 – 1992

Max-Planck-Institut für
Metallforschung
Bayer - BMFT-PLR - Daimler - Höchst - MTU

What has driven further development of high-performance ceramics?

government funding programs (e.g. DFG priority program, many state funding programs)

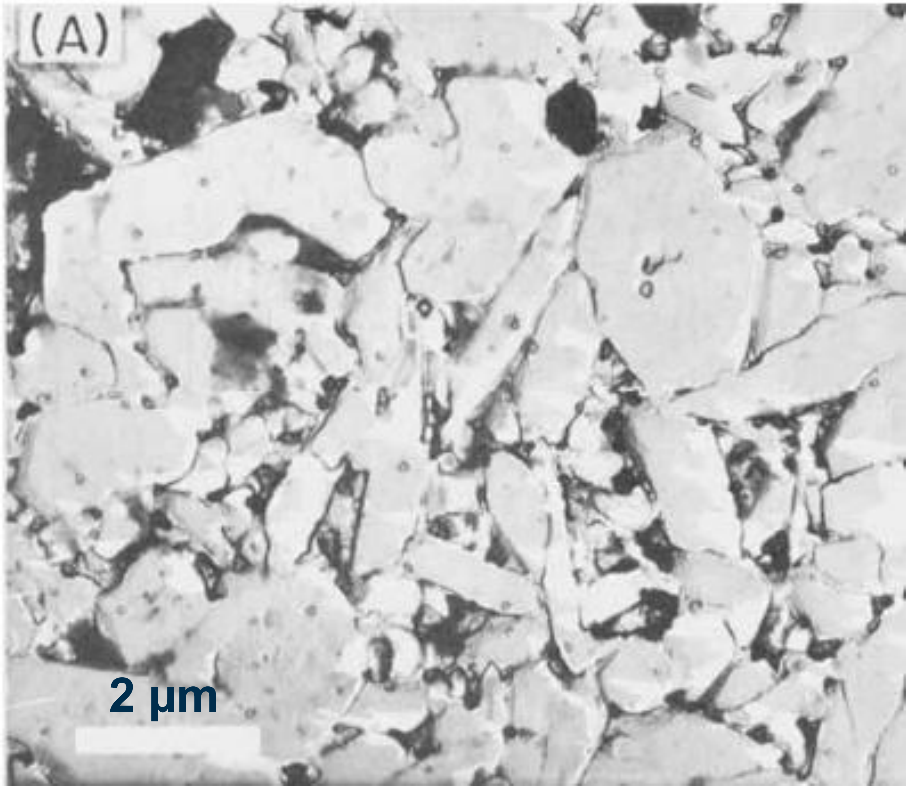
> 20 „Professorships in Ceramics“ in the D-A-CH-region (1985-2000)

Formation of strong scientific networks nationally and internationally

What was the impact from other scientific disciplines?

→ Advances in microstructural characterization (e.g. silicon nitride)

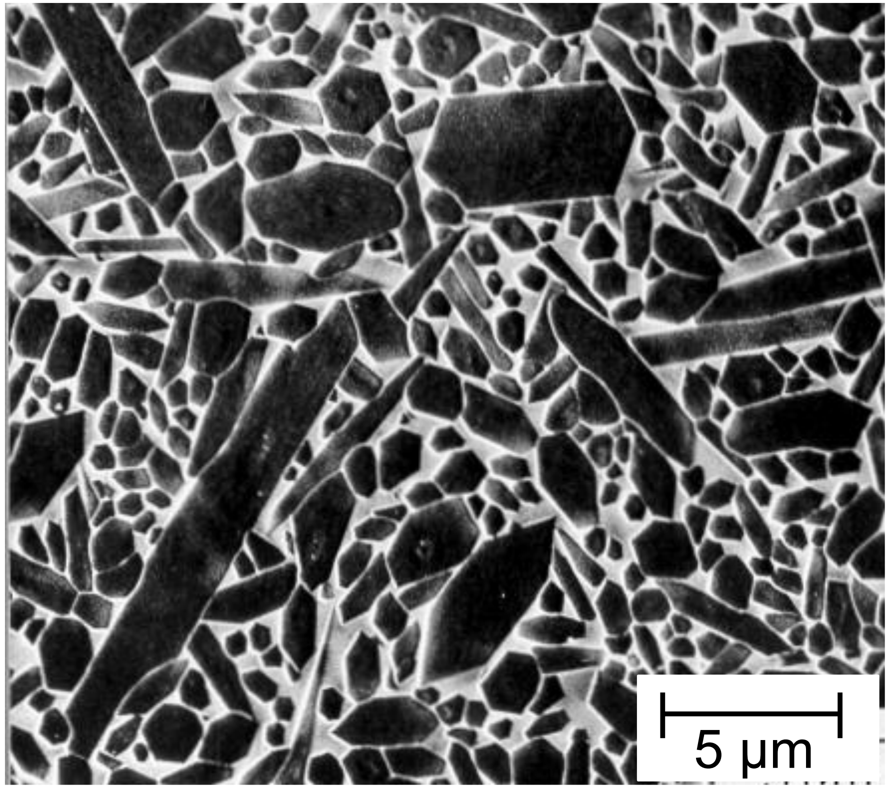
1974



chemically etched

Terwilliger and Lange, JACS, Vol.57 [1] 1974

mid 1980s



plasma etched

Hoffmann, IAM-KWT

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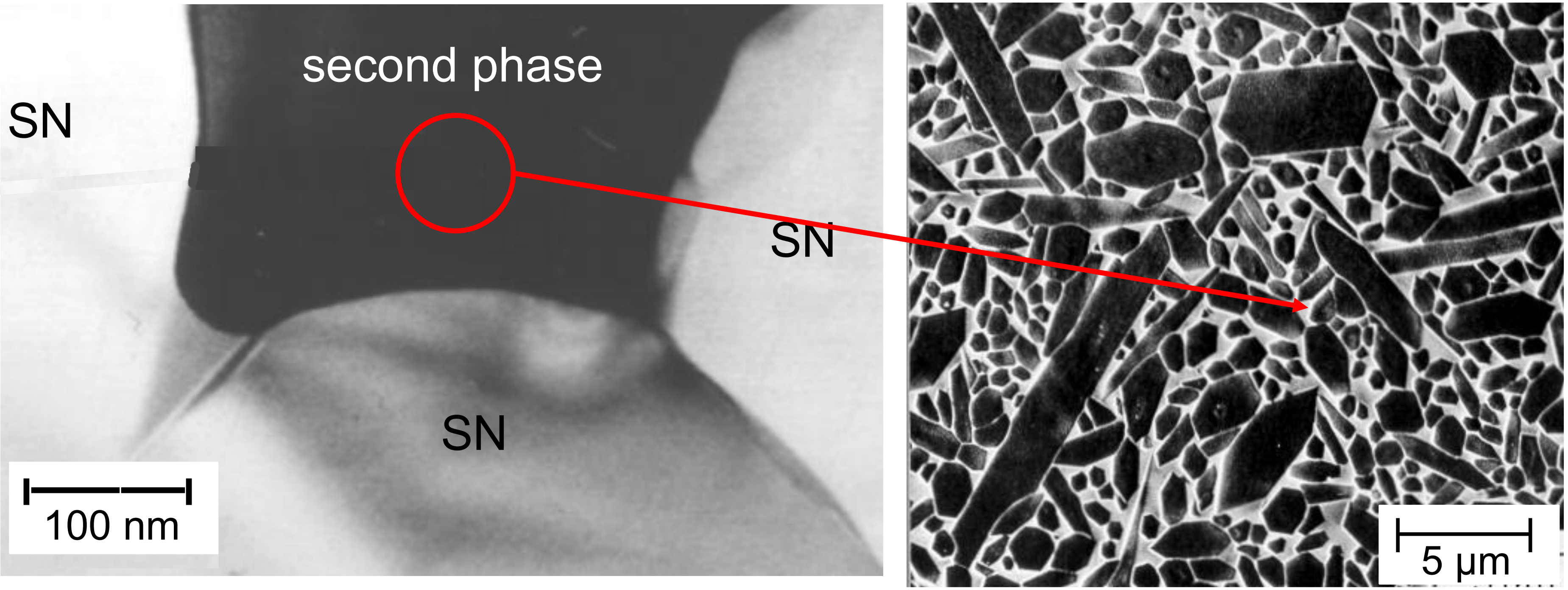
mid 1980s

mid 1980s

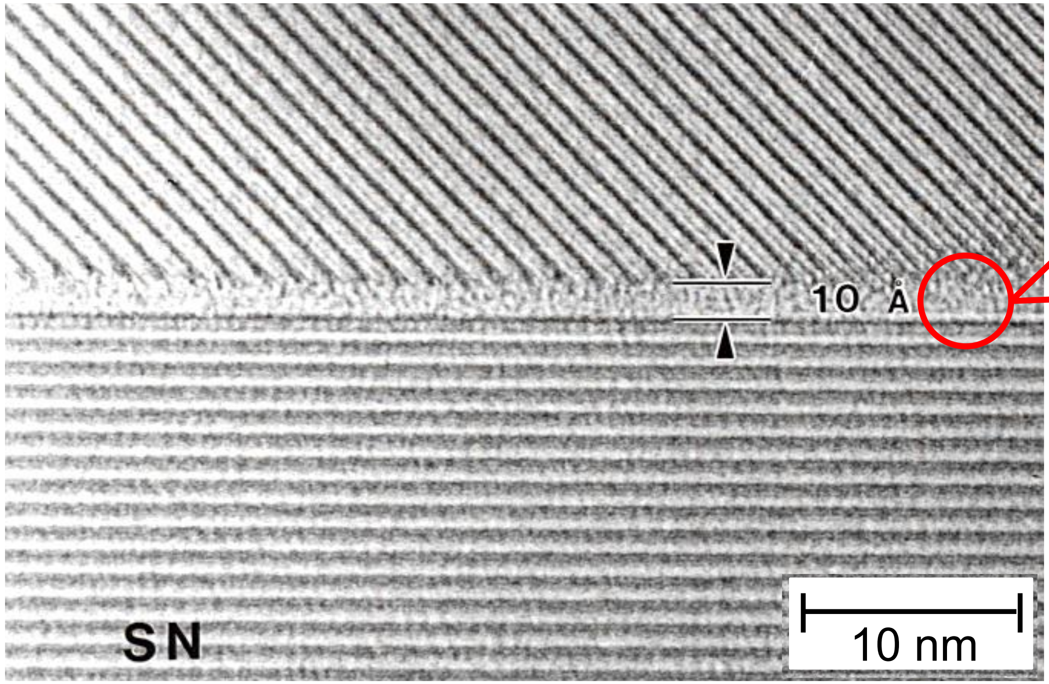


TEM analysis of the triple junctions

What was the impact from other scientific disciplines?

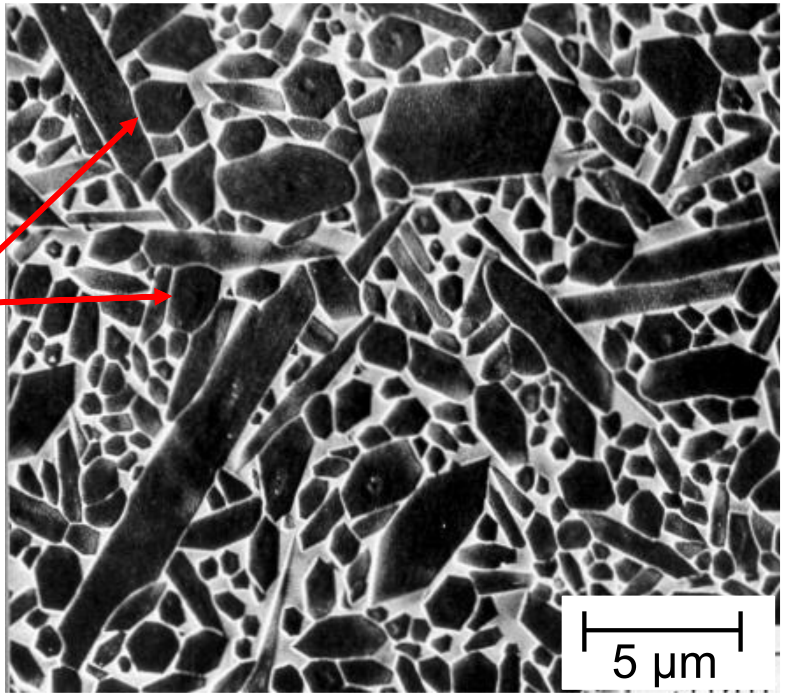
→ Advances in microstructural characterization (e.g. silicon nitride)

mid 1990s



measurement of the thickness of grain boundary films

mid 1980s



plasma etched

H.-J. Kleebe et al. (1993)

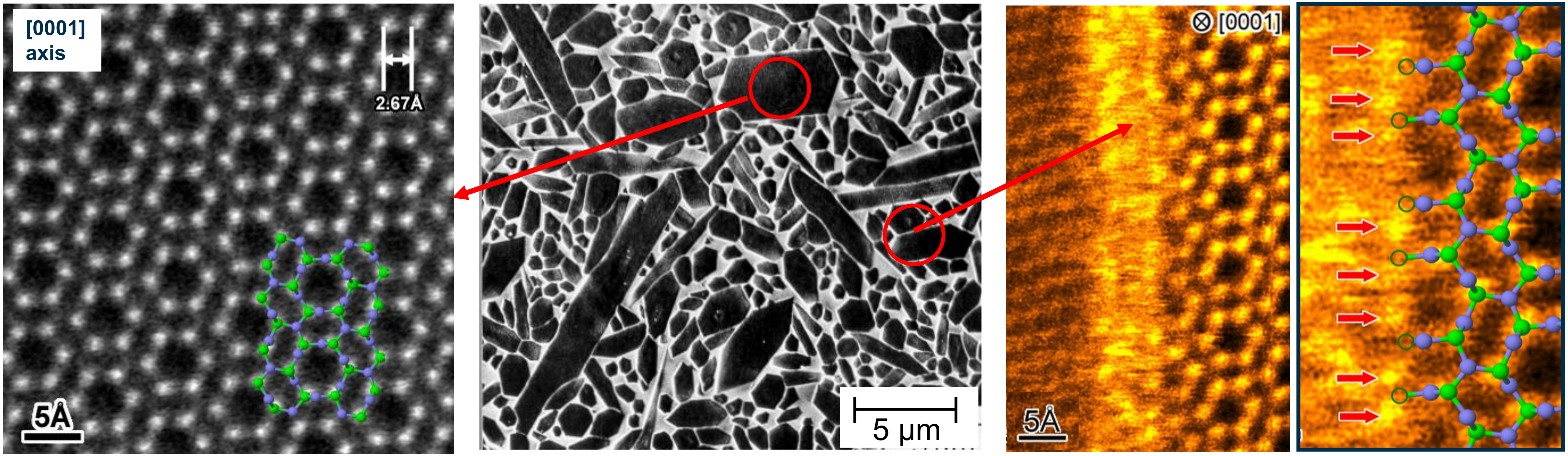
What was the impact from other scientific disciplines?

→ Advances in microstructural characterization (e.g. silicon nitride)

mid 2000s

mid 1980s

mid 2000s



Z-contrast microscopy of Si_3N_4 lattice

HAADF images give information of atoms adsorbed at in Si_3N_4 interface

Shibata et al., Nature (2004)

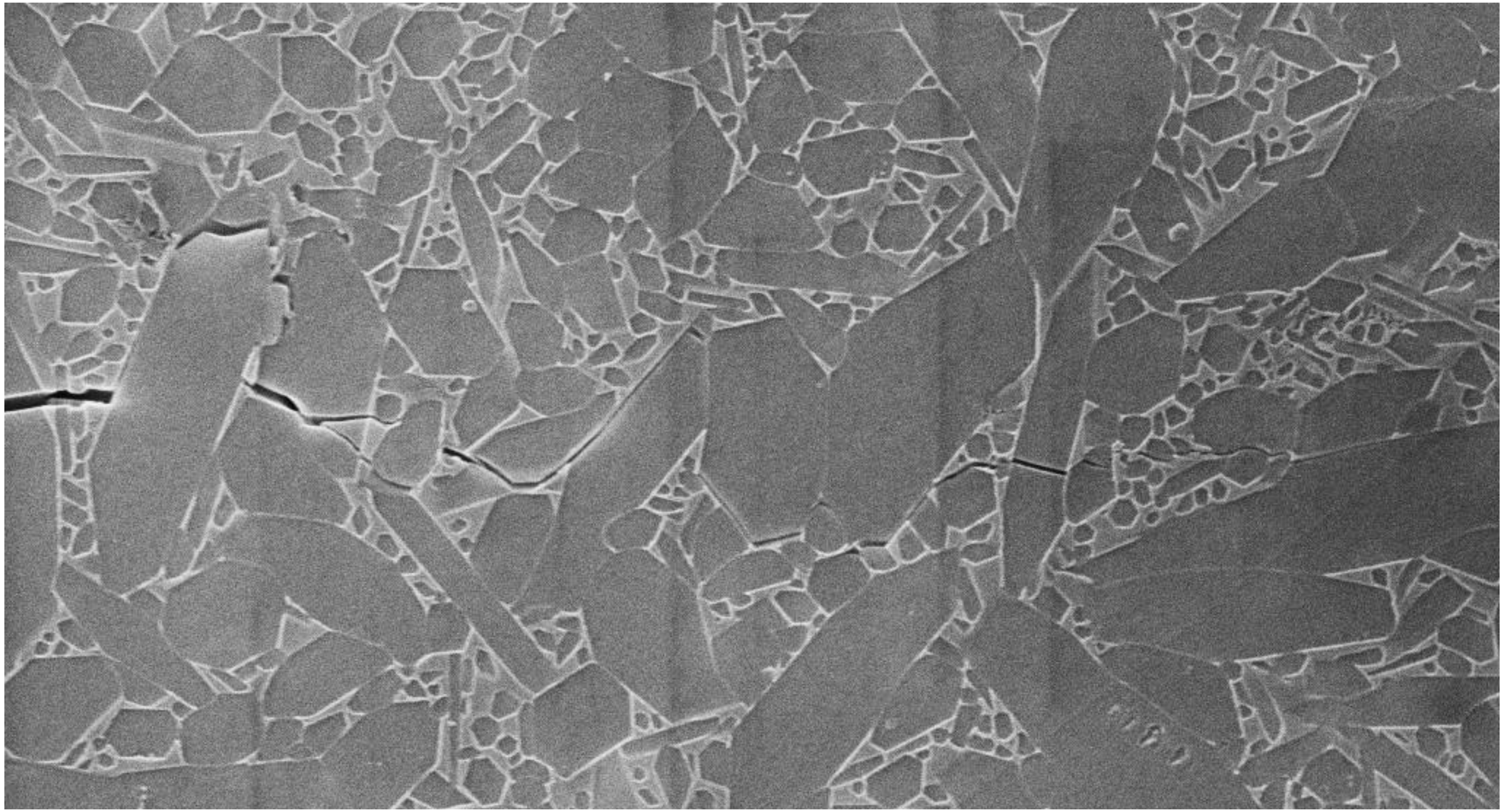
What was the impact from other scientific disciplines?

→ Progress in fracture mechanics

- 1920: Birth of fracture mechanics with A.A. Griffith´s fundamental work on “The Phenomena of Rupture and Flow in Solids”. G.R. Irwin developed later (1940s-1950s) the concepts of stress intensity factor K and the fracture toughness.
- 1970s: First systematic research on „Fracture Mechanics of Ceramics“, published in a book series edited by Bradt, Evans, Haselman, and Lange.
- In the following decades, new experimental methods were developed to gain a fundamental understanding of subcritical crack growth, fatigue, creep, thermal shock, transformation toughening, microcrack toughening, R-curve behavior, etc.

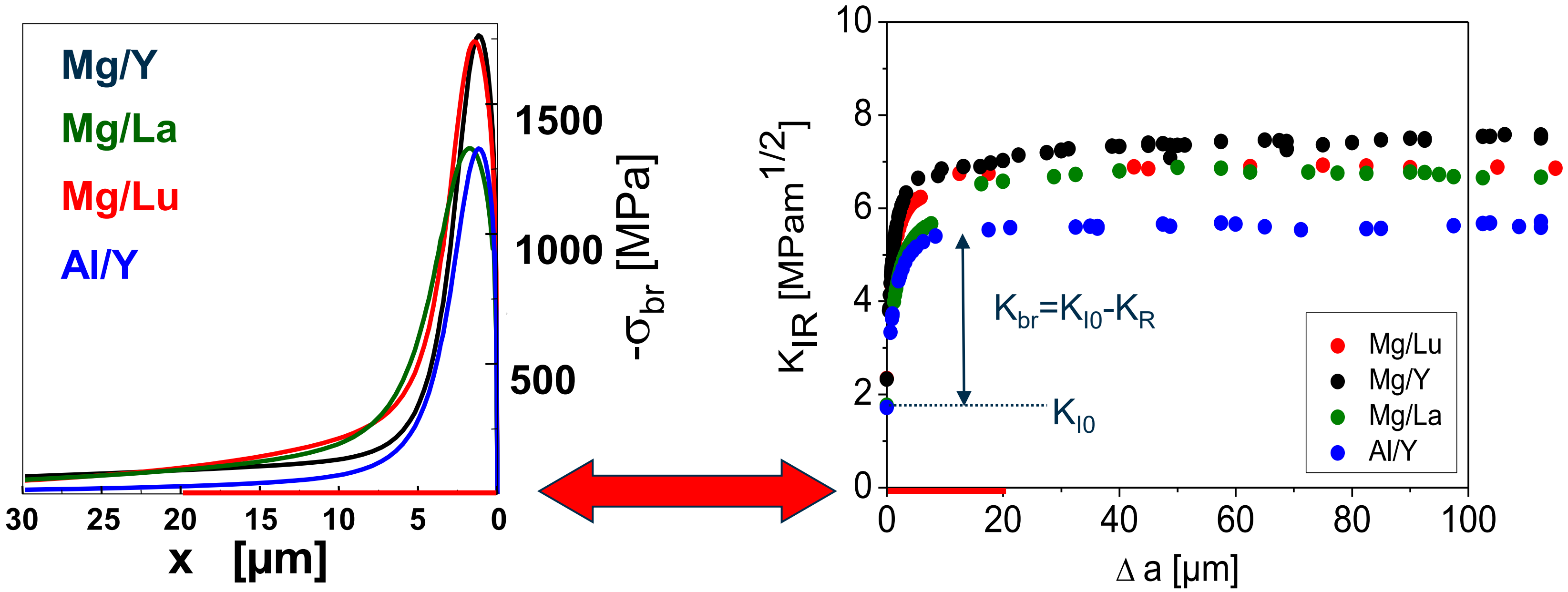
Combine different length scales to understand the material properties

→ In-situ observation of crack propagation in a Si_3N_4-ceramic



Combine different length scales to understand the material properties

→ Characterization of R-curves of different Si_3N_4-ceramics



$$K_{br} = \int_0^a h(x,a)\sigma_{br}\left[\delta(x)\right]dx$$

By combining experiments and theory, the different material behavior can be explained

Fünfschilling et al., J Mat Sci., 2009

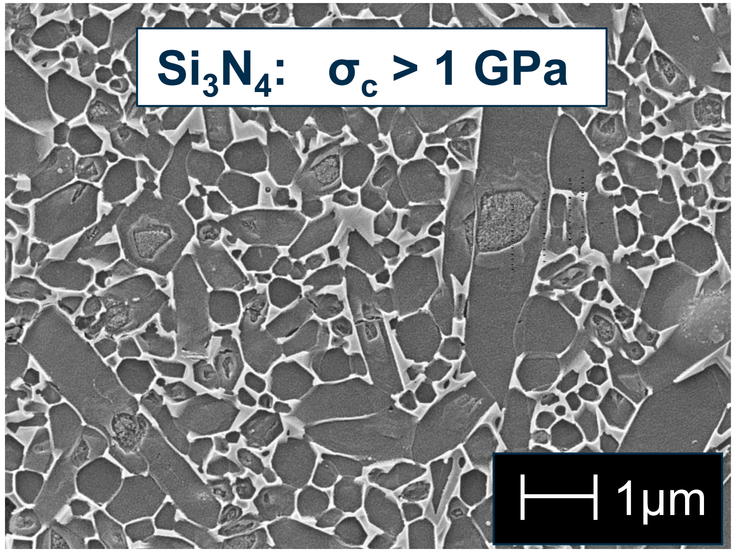
Link between Materials Data and Real Applications (State of the art)

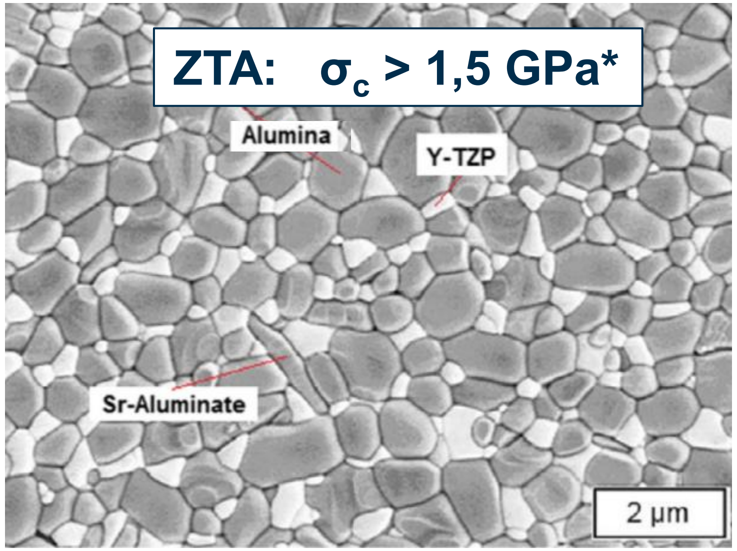
- **Material data** for reliability assessments for specific applications are available or can be determined using known methods.

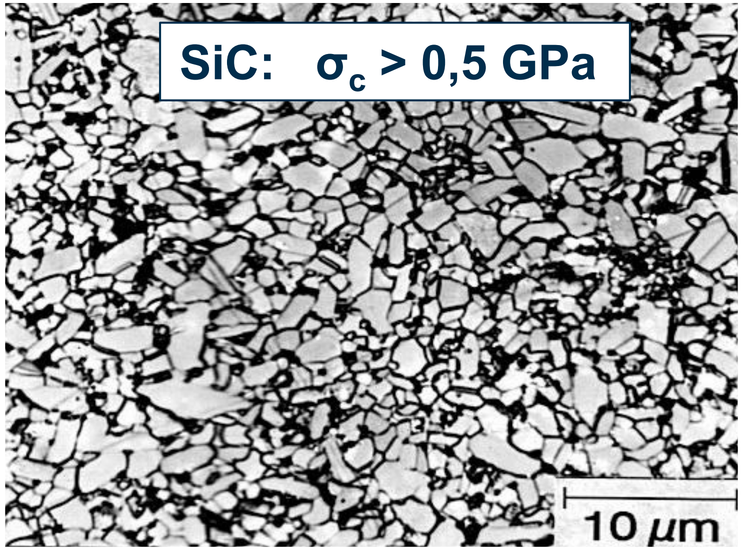
- Locally occurring **load scenarios** in ceramic components under application conditions can be determined using **FE simulations**.

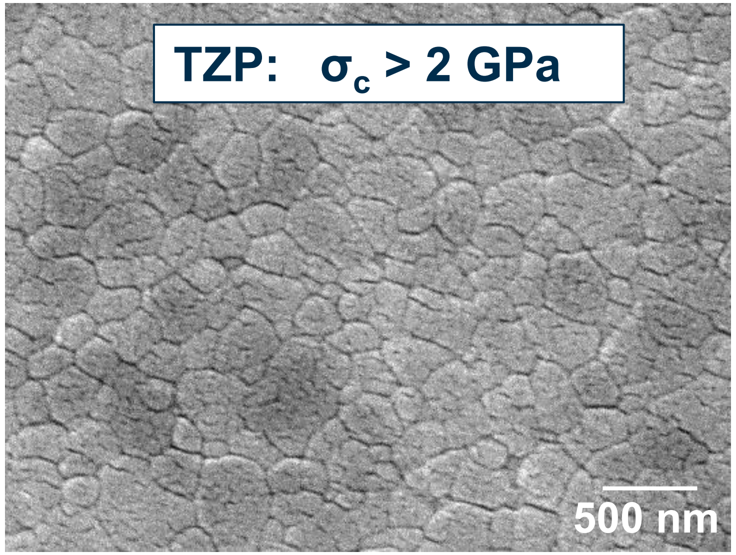
- By using “Stau” – a computer program developed by Munz et al. at FZK (now KIT) or “CARES” developed by NASA, the **failure probability of a multiaxially loaded monolithic ceramic component** as a function of time in service **can be predicted**.

High-strength ceramics are available for a wide range of applications


Si_3N_4: σ_c > 1 GPa

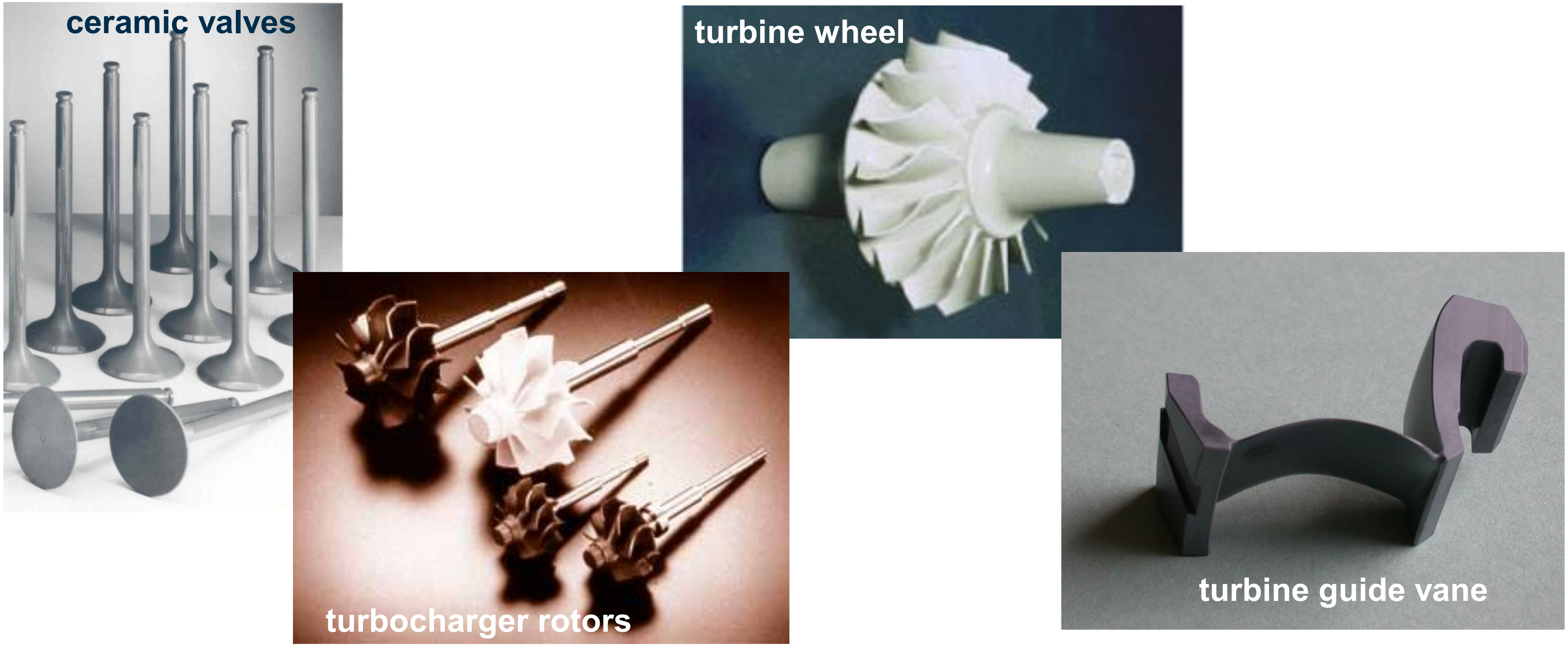

ZTA: σ_c > 1,5 GPa*


SiC: σ_c > 0,5 GPa


TZP: σ_c > 2 GPa

*Chevalier et al., J. Am. Ceram. Soc., 2020; 103: 1482-1513

High-temperature resistant ceramic for engines and turbines



None of these components have ever been mass-produced, but has that meant ceramic science has failed? The answer is NO!

Did you expect 50 years ago applications like these?

Si_3N_4-ceramics as substrate in power IGBTs (courtesy Niterra)

hip joint from ZTA (Biolox delta)

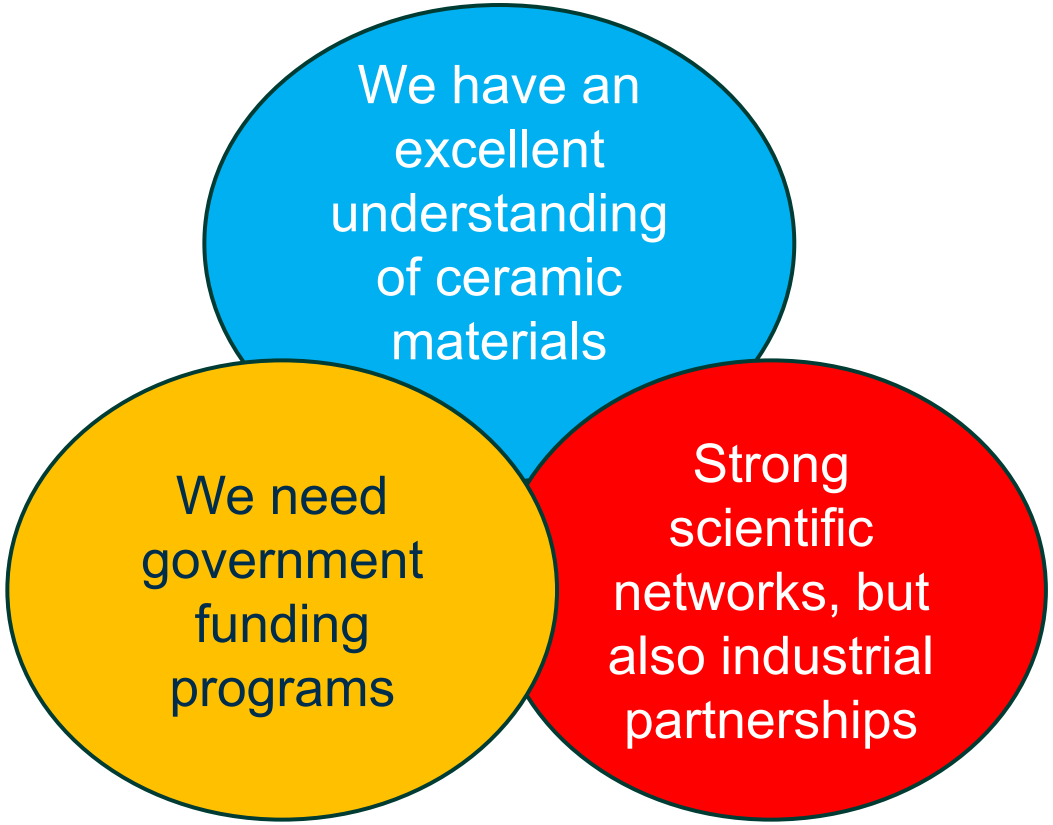
calibrating welding rolls (courtesy FCT)

tooth brackets from translucent Al_2O_3

colored dental crown from ZrO_2

courtesy Ivoclar

“Outlook for the next 50 years”



We have an excellent understanding of ceramic materials

We need government funding programs

Strong scientific networks, but also industrial partnerships

Fraunhofer
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Fraunhofer-Institut für Keramische Technologien und Systeme IKTS

Jahresbericht
2024/25