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The Characterization of High-Tech Materials: Perspectives, Challenges, Trends

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Abstract. From the Stone Age on, developmental periods of mankind carry the names of materials. Materials determine the applicability of key technologies and these are in turn of major significance for the economic success and the social development in modern society. Today's high-tech materials are the consequence of an improved understanding of the structure and composition of matter and of the interplay of microstructure and minor and trace constituents. We can distinguish four basic dimensional structural categories of materials: (a) the atomic structure level; (b) the crystal, glassy or amorphous structural level; (c) the microstructural level; (d) the level of constructions. As an example, these structural levels are described in some detail for graphite, a material used extensively throughout analytical chemistry. Decisive differences at the microstructural level result in graphitic materials with very varying properties: polycrystalline electrographite, glassy carbon, and pyrolytic graphite. Examples for the use of these materials in ETAAS are discussed.

Structural features together with topochemical and trace chemical characteristics are studied today by a wide variety of analytical instrumentation and methods of modern materials analysis which can be grouped into four categories of techniques: (a) photon probe techniques; (b) electron probe techniques; (c) ion probe techniques; (d) electrical field probes.

The most important of those techniques are discussed shortly with respect to their main characteristics as lateral and depth resolution, detection sensitivity, additional bonding or structural information, depth profiling possibilities etc.

The constructions are the ultimate level of a materials structure. Structures of microelectronic components reach dimensionally into the domain of microstructure whereas constructions in heavy industry are of meter-ton dimensions. Progress in the use of materials as carriers of information is visualized by a morphological comparison of the sound tracks of conventional records with the information imprinted in optical discs.

It is important to conceive materials as dynamic systems with limited lifetime. Fatigue and recrystallization are prominent relevant phenomena which

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must be studied by microstructural and topochemical methods. Dispersion strengthened microalloys like TZM, HT-molybdenum and NS-tungsten are discussed as examples how materials can be improved with respect to their extended use under extreme conditions. Again, a thorough structural and topochemical characterization was the basis of a successful respective materials development although a multitude of relevant topochemical questions still remain to be solved.

Lifetime investigations are an essential tool of materials development as well as quality control. Relevant investigations for various tube materials for ETAAS are discussed.

Key words: atomic structure, crystal structure, microstructure, constructions, topochemistry, graphite, glassy carbon, pyrolytic carbon, microelectronics, carriers of information, refractory metal alloys, life time, recrystallization, fatigue, photon probe techniques, electron probe techniques, ion probe techniques, electrical field probes.

List of Acronyms Used

General Acronyms in the Field of Materials Science

CFC	Carbon fibre composite
CMC	Ceramic matrix composites
COST	Cooperation in science and technology
COST 503	COST-action in the field of powder metallurgy
CVD	Chemical vapour deposition
CVI	Chemical vapour infiltration
EG	Electrographite
GC	Glassy carbon
HT-Mo	High temperature molybdenum (Mo-microalloy doped with potassium silicate)
JESSI	Joint European Submicron Silicon Initiative
MMC	Metal matrix composites
MOS	Metal oxide semiconductor
NS-W	Non-sag tungsten (used for lamp filaments and evaporative metallization techniques)
PACVD	Plasma assisted chemical vapour deposition
PG	Pyrolytic graphite
PMC	Polymeric matrix composites
PVD	Physical vapour deposition
TPG	Total pyrolytic graphite
TZM	Molybdenum base alloy containing 0.5% Ti, 0.08% Zr und 0.025% C
UHP	Ultra high purity
VLSI	Very large scale integration

Analytical Technique Names

AA	Activation analysis
AAS	Atomic absorption spectrophotometry
AEM	Analytical electron microscopy
AES	Auger electron spectrometry or atomic emission spectrometry (only used in this work where it is clear that Auger electron spectrometry is not meant)
AFP	Atom force probe

ARM	Atomic resolution microscopy
ARUPS	Angle resolved UPS
ATR-IR	Attenuated total reflection infra red (spectrometry)
CTEM	Conventional transmission electron microscopy
d_B	Beam diameter
DL	Detection limit
EDX(RS)	Energy dispersive X-ray spectrometry
EELS	Electron energy loss spectrometry
EP(X)MA	Electron probe X-ray microanalysis
ERD	Elastic recoil detection
ESCA	Electron spectrometry for chemical analysis (original Siegbahn designation used if both, XPS and UPS are meant)
ETAAS	Electrothermal atomic absorption spectrometry
EXAFS	Extended X-ray absorption fine structure (spectrometry)
FE-gun	Field emission gun
FIM	Field ion microscopy
FT-IR	Fourier transform infrared (microscopy)
GDMS	Glow discharge mass spectrometry
GDOES	Glow discharge optical emission spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HREELS	High resolution EELS
i_B	Beam intensity
ICP-OES, MS	Inductively coupled plasma-optical emission spectrometry, mass spectrometry
ID-MS	Isotope dilution-mass spectrometry
IR	Infrared (spectrometry)
IRRAS	Infrared reflectance absorption spectrometry
ISS	Ion scattering spectrometry
LAMMS (LAMMA, LIMA)	Laser micromass spectrometry (and two commercial terms for respective instruments)
LAS	Classical photometry (liquid absorption-spectrophotometry)
LEED	Low energy electron diffraction
LEIS	Low energy ion scattering
LNRI-SIMS	Laser non-resonant ionization SIMS
LRI-SIMS	Laser resonance ionization SIMS
LRMA	Laser Raman micro-analysis
MEIS	Medium energy ion scattering (spectrometry)
MS	Mass spectrometry
NAA	Neutron activation analysis
NEXAFS	Near edge X-ray absorption fine structure (spectrometry)
NIR-FT	Near infrared-Fourier transform (Raman spectrometry)
NMR	Nuclear magnetic resonance (spectrometry)
NRA	Nuclear reaction analysis
OES	Optical emission spectrometry
PE	Primary electron(s)
RBS	Rutherford backscattering spectrometry
REM	Reflection electron microscopy
RHEED	Reflection high energy electron diffraction
SAM	Scanning Auger (electron) microscopy
SEM	Scanning electron microscopy
SERS	Surface enhanced Raman spectrometry
SEXAFS	Surface EXAFS

SIMS	Secondary ion mass spectrometry
SNMS	Sputtered neutrals mass spectrometry
SSMS	Spark source mass spectrometry
STEM	Scanning transmission electron microscopy
STM	Scanning tunneling microscopy
TEM	Transmission electron microscopy
THEED	Transmission high energy electron diffraction
THEELS	Transmission high energy electron loss spectrometry
UHV	Ultra high vacuum
UPS	Ultraviolet photoelectron spectrometry
WLD (-XRS)	Wavelength dispersive-XRS
XPS	X-ray photoelectron spectrometry
XRD	X-ray diffraction
XR(F)S	(fluorescence) spectrometry

The Significance of Materials to Mankind

During all of man's history, materials have been an essential feature of his culture and civilization. It is not without reason that from the Stone Age on, developmental periods of mankind carry the names of materials.

It has been said that our century will be called the silicon age and the first century of the upcoming new millenium will be the composite materials age. In the past, technological progress was gauged by how humans have used materials provided by nature. Now, equipped with greater understanding of the structure and composition of matter, material scientists in laboratories around the world create new, complex materials that are revolutionizing our times. Countries who want to stay up to date with modern key technologies have to be able to produce and handle modern materials and in many countries, material development programmes are among the most important measures to keep up with high tech developments [1, 2]. Well developed material technologies are in many cases the basis of the applicability of so called "key technologies" and these are in turn of major significance for the economic success and the social development in modern society. Some respective examples are given in Table 1.

Three main groups of materials had and still have a decisive impact on our lives: metals, ceramics and polymers. Metals are used throughout manufacturing industry and represent the basis for innumerable technological solutions. Although some of them are used by man for several millenia, state-of-the-art metals offer new properties, including greater strength, increased durability, better fabricability etc. Modern ceramics meet the most severe demands of aerospace industry, automobile industry, reactor technology. They offer a wide range of solutions for specific applications. New polymers possess superior mechanical and physical properties. Thermoplastics, thermosetting plastics, elastomers, foam plastics, membrane materials and resins are indispensable constituents of our technologies and many of them were among the early tailor-made materials for specific applications. But many other material groups like glasses, superconductors or composites are equally important and especially composites will gain paramount significance in future technologies. Table 2 tries to give an overview on some pertinent novel materials and recent developments in materials technology.

Table 1. Materials as basis for key technologies and whole branches of industry

Material	Key technology or industry
	Metals and Alloys
Steel	Mechanical engineering
	Automotive industry
Stainless steel	Chemical industry
	Food industry
Copper	Electrical engineering
Aluminium alloys	Aeronautics
NS-Tungsten	Incandescent lamps
Hard metal	Metal working and machining
Superalloys	Gas turbines, especially in aviation
	Polymers
Plastics	Packing industry; light weight and corrosion resistant
	Surrogates for metals in many applications
	Inorganic Materials
Silicon	Microelectronics
Glass and plastic fibres	Telecommunication
Gallium arsenide	Optoelectronics
	Composites
Magnetic composites	Data storage systems
Fibre reinforced composites	Aeronautics and space industry

In many cases, the technological significance of a material cannot be gauged from the profit which is connected with its production [3]. It is typical for high tech productions that the main profits lie in later steps of material processing as is shown for two typical cases in Table 3. This situation contributes to the growing economic gap between underdeveloped countries and high tech nations.

The Role of Analytical Characterization of Materials

However, what is the role of analytical characterization in modern materials development? At first sight, analytical chemists in related industries belong—together with the material testers—to the usually ill liked species of institutions who cost increasingly more money and do not—at least at first sight—contribute to a company's profits because their "products" are figures—although absolutely necessary ones—and wise advices rather than saleable products. Consequently, many firms refrain from investments into their analytical services in good times because bigger and more important investments for the production lines have to be financed and research has to be postponed for bad times. Research in such companies is, anyhow, considered to be a balloon which can be in- and deflated according to prevailing financial situations. And in really bad times, it is, of course, absolutely impossible to invest into non-profit centres like analytical laboratories.

However, it is evident that a greater understanding of the structure and composition of matter is synonymous with the evolution of a discipline dedicated to this

Table 2. Some novel materials and recent developments in materials technology

Materials category	Novel materials and/or applications (New technologies)
Metals	Dispersion strengthening of high-temperature metals and alloys (e.g. TZM, HT-Mo, NS-W, superalloys (Ni and Fe base)) Single crystal components (e.g. turbine blades, sheets) Glassy metals by rapid solidification Superplastic forming Novel coating methods for metals (PACVD, PVD, flame and plasma spraying, electroplating etc.) Intermetallics for high temperature use New superalloys by mechanical alloying Memory alloys
Ceramics	High performance ceramics: (a) Oxidic ceramics: BeO, MgO, Al_2TiO_5, Al_2O_3, ZrO_2, HfO_2, ThO_2 (b) Non-oxidic ceramics: graphite, Si_3N_4, SiC, TiB_2, TiN, TiC, Ti(C, N) BN, B_4C, AlN, ZrN, ZrB_2, CrB, CrB_2 Ceramic motor parts Ceramic prostheses Catalytic converters in cars and power stations Ceramic ball bearings Cutting ceramics Wide applications in electronics
Wear resistant materials	Hardmetals (WC-Co based, partly with mixed carbides (Ta, Nb)C, TiC) with CVD or PVD-multilayer coatings) PVD-coated high speed steel Cermets (e.g. Ti, Ta, Nb, V, Mo, W) (C, N)-(Ni, Co)-Ti_2AlC Ceramics e.g. Al_2O_3/ZrO_2 or Al_2O_3/TiC Sialon, Si_3N_4, cubic BN, polycrystalline diamond, whisker-reinforced ceramics
Composites	*Classification by the matrix components*: (a) *PMC—Polymeric matrix composites* e.g. fibre reinforced polymers (with short or long fibres, the latter ones in woven structures) *Examples*: Carbon fibre reinforced graphite (CFC) or plastic composites (b) *MMC—Metal matrix composites* *Examples*: fibre reinforced Al and Mg-alloys for aerospace applications; taylor made plastic-metal composites; Cermets and hard metals (see wear resistant materials); particle dispersion strengthened intermetallics; oxide dispersion strengthened superalloys and refractory metals (c) *CMC-Ceramic matrix composites* *Examples*: fabric reinforced SiC: with carbon fibres or SiC-fibres: C-SiC and SiC-SiC composites, usually obtained by chemical vapour infiltration (CVI).
Composites	*Classification by the composite structure*: (α) Layered composites (composite foils, plated and coated materials) (β) Particle reinforced composites or such with two skeletons penetrating each other, called cermets (e.g. Mo-ZrO_2 or wear resistant cermets) (γ) Fibre or whisker reinforced composites

Table 2 (continued)

Materials category	Novel materials and/or applications (New technologies)	
Polymers	Degradable and recyclable plastics	
	Heat resistant thermoplastics	
	Membranes for separation technology	
	Conductive polymers	
	Memory polymers	
	Ultrathin foils	
Superconductors	(a) Low temperature, high field strength superconductors: NbTi, Nb_3Sn, Nb_3Al, Nb_3Ge	
	(b) Ceramic superconductors:	
	(α) Chevrel-phase, e.g. Pb Mo_6S_8	
	(β) High temperature SC: 1-2-3-superconductors, e.g. $YBa_2Cu_3O_{6.6}$	
Microelectronics materials (with special reference to refractory metals applications)	Ultrapure materials:	
	Silicon, aluminium, gold, silver	
	Ultrapure sputter targets for the formation of layers on microelectronic devices by PVD:	
	Nb	for superconducting layers and for $NbSi_2$-layers as diffusion barriers (by co-sputtering of Si and Nb)
	Ta	for superconducting layers, interconnects, capacitive layers etc.
	Mo	for $MoSi_2$ layers (by co-sputtering of Si and Mo) as interconnects or gate materials in MOS-technology
	W	for WSi_2 layers as gate material and conductive connections to the source in MOS-technology, as diffusion barrier layers, as resistivity layers etc.
	Re	as resistivity layers and contacting layers
	W10Ti	as resistivity layers and diffusion barrier layers (Pt Si/WTi/Au or Al) in MOS-technology
	TaAl	(6.7 resp. 8.75% Al) as resistivity layer
	Cr	as resistivity layers, masking layers (Cr-blanks), interconnects, protective coating against corrosion
	NiCr	as resistivity layers for film resistances (e.g. Cr60Ni)
	CoCr	as resistivity layers (e.g. Co80Cr) and floppy disc coatings
Semiconductor diode laser materials	GaAlAs	(wavelength: 750–905 nm, composition dependent)
	InGaAsP	(wavelength: 1.1–1.6 μm composition dependent)
	PbNaCl	(wavelength: 3–30 μm continuously tunable)

goal by the development of methods for bulk- and topochemical as well as structural characterization of solid-materials analysis as a special branch of analytical chemistry.

Fig. 1 gives a first overview on the wide field of analytical characterization of solid materials [4]. It lists, of course, only the most prominent methods for the different areas of solid state characterization. The diversity in structure, textures and composition of todays materials has added greatly to the complexity of the relationships between structure, composition (especially trace element concentrations) and properties and underlined our shaky knowledge in many relevant areas. As with the manufacture of many a material we are venturing also the initial stages of its char-

Table 3. Production costs and relevant increase in value for two high tech products

Tungsten filament production for incandescent lamps	Increase in value in [%]	Manufacture of microelectronic components
	0.03	Production of high purity silicon wafers
From W-bearing ore to tungsten oxide	1.8	
From the oxide to metal powder	1.9	
From metal powder to rod via direct sintering and rolling	1.6	
	5.0	Doped silicon constituents from wafer
From rod to coarse wire	5.3	
Drawing of fine wire	18.6	
From fine wire to coiled coil	70.8	
	95	Production of final VLSI microelectronic component

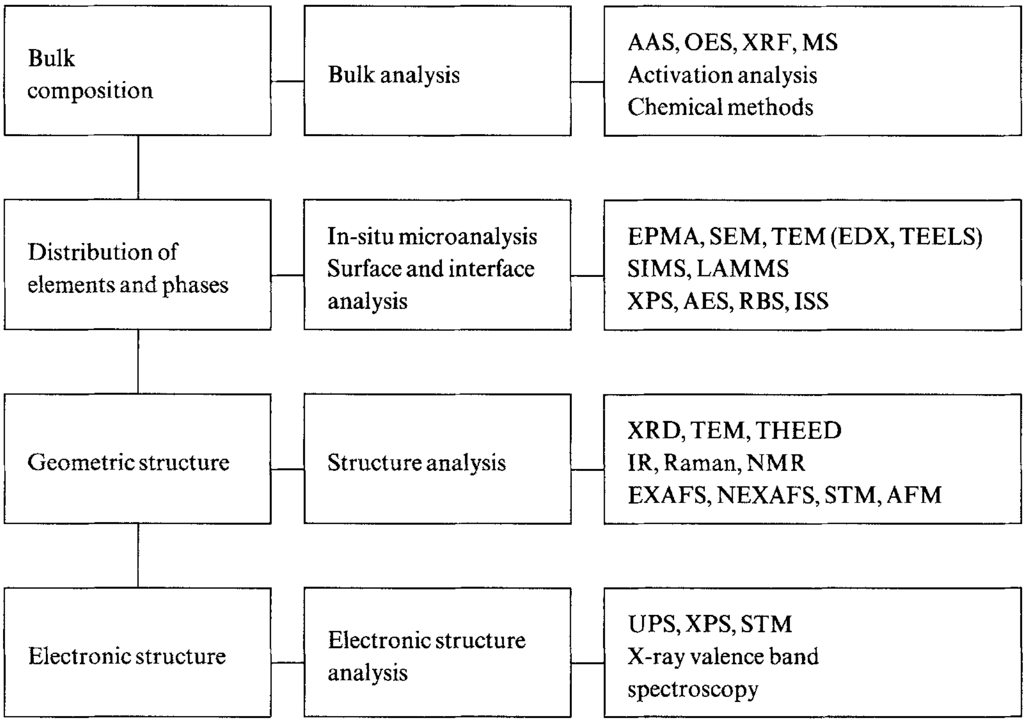


Fig. 1. Analytical characterization of solid state materials (from Grasserbauer [4])

acterization. For, as already discussed elsewhere, materials development always embraces the development of optimal ways of its characterization leading to a better understanding of its properties as well as to rational and efficient quality control measures [5].

The Four Structural Categories of Materials

If we ask for the significance of e.g. trace or topochemical characterization for this upcoming new materials age it seems important to first of all become aware of the interaction of analytical quantities with the structural and dimensional categories of materials in general. Table 4 makes us aware of the fact that there are basically four structural categories of metals and also of other materials the interaction of which is defining the gross mechanical, physical and other properties. This should be visualized by an example.

The Structural Characterization of Graphite

Graphite is chosen as an example because it is of great importance in analytical laboratories in very diverse forms and applications. It is used in the form of graphite tubes for GFAAS, as crucible material and for sample containers and apertures in X-ray fluorescence analysis, as, e.g. graphitised carbon for column fillings in HPLC, as electrode material for OES and as crucible material for the determination of gases (O, N, H) in metals and other inorganic materials by reducing fusion extraction. Glassy carbon, a novel modification of carbonaceous materials is used as electrode material in electrochemistry and as crucible material, especially in connection with microwave digestion [6]. For quite some time it was also a candidate material for ETAAS [7].

Some 30000 graphite crucibles are used for gas analysis by reducing fusion in our own laboratory together with some 1000 pyrographite coated graphite tubes for ETAAS. Furthermore, we have studied graphite extensively by morphological investigations with regard to tube lifetime and corrosion phenomena in GFAAS [8–11].

The atomic and crystal structure. As every chemist still remembers from his basic inorganic studies, the principal properties of graphite can be deduced from its specific binding situation in combination with its unique crystal structure: The sp^2-hybridized carbon atoms are combined to honey combed flat C_6-rings forming strong covalent bonds whereas the p-orbitals which stand out perpendicular to the lattice plane, overlap and form each a delocalized p_π-p_π-bond. The black colour and the electric conductivity of graphite are a consequence of this. The relatively weak bonds between the adjacent lattice planes are responsible for the low hardness of graphite and its excellent lubricating properties. However, already at this level some disorder is present in real type graphite systems inasmuch as the lattice planes are not ideally flat but exhibit a wavy structure. Hence, the layer spacings become

Table 4. The four structural categories of metals according to their characteristic dimensions

Atomic structures
Crystal or glassy structures
Microstructure
Constructions

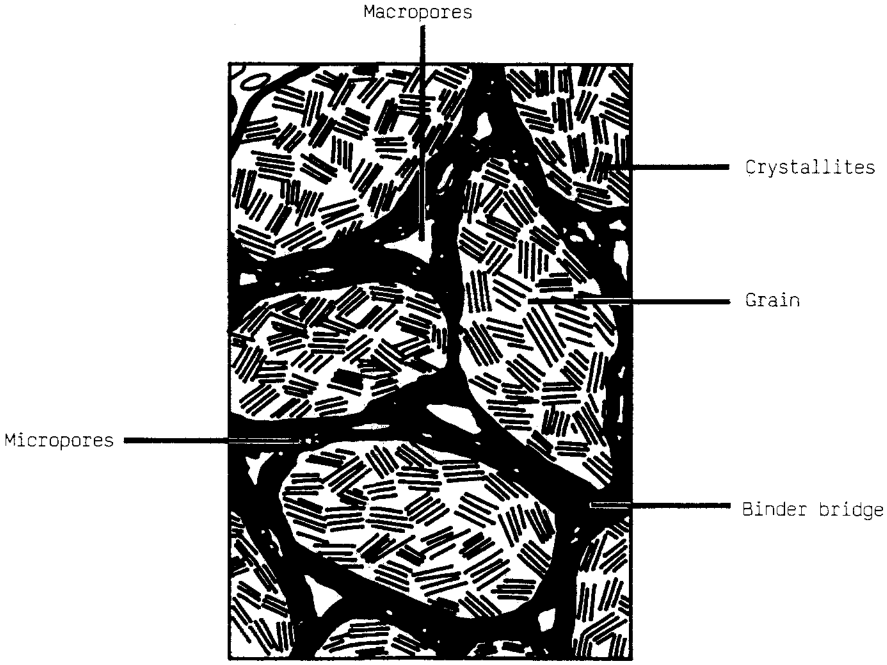


Fig. 2. Model of the microstructure of polycrystalline electrographite with carbon binder bridges and macro- resp. microporosity (from Welz et al. [8])

irregular and a number of atom defects (vacancies) within the planes are present [11].

The microstructure of polycrystalline electrographite. The industrially produced polycrystalline graphite can be imagined as being composed of a large number of such disordered tiny crystallites of 1–100 nm diameter, irregularly aggregated within grains of very varying grain size between some μm to mm. Furthermore, polycrystalline electrographite, as e.g. used for graphite tubes in GFAAS, consists of such grains which are bonded together by carbon binder bridges as shown in Fig. 2 [8]. Micropores of less than 2 nm diameter exist within these grains to a varying extent whereas macropores with diameters up to the mm-range may be found within the carbon binder bridges. It should be mentioned, however, that macropores should almost be non-existent in the high density graphites used for ETAAS and micropores in the grains, too, are much smaller than 1 nm in this case.

The microstructure of glassy carbon. In 1962, starting from phenolic resins, Yamada and Sato [12] prepared a gas-impermeable carbon which they called glassy carbon. In analytical chemistry, glassy carbon (GC) is gaining importance, e.g. as electrode material in electrochemistry [13] or as crucible material. GC is a monolithic carbon type with pronounced structural disorder and a glasslike fracture pattern. It is characterized by a very low gas permeability and a high oxidation resistance. The crystalline order of GC is very poor. The graphitic layers do not exceed a length of 5 nm in Lc direction and the layer bands are wrinkled and completely disordered as is shown in Fig. 3 [7]. Fig. 4 shows the cut through a wall of a glassy carbon tube used in ETAAS experiments [7] exhibiting macropores within the GC-matrix.

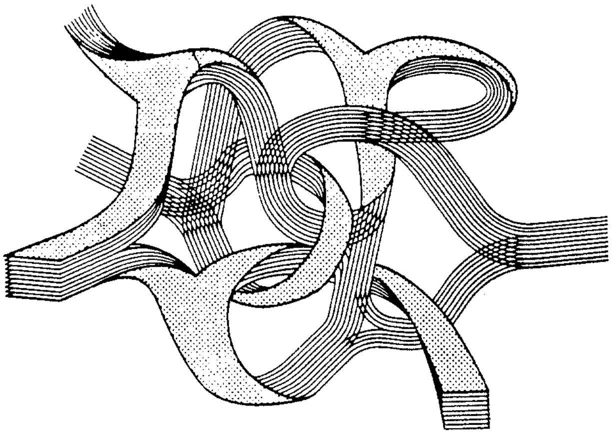


Fig. 3. Schematic structural model for glassy carbon (from Welz et al. [7])

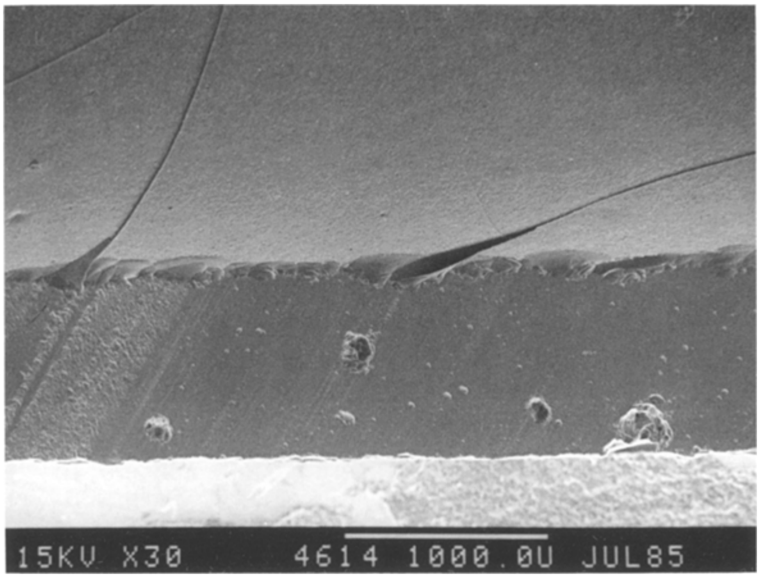


Fig. 4. Scanning electron micrograph of a cut through a glassy carbon tube of Le Carbon manufactured 1985 (CL-208-10) with macropores within the tube wall (from Welz et al. [7])

Macropores were also found all over the outer and inner tube surface. In addition, the inner tube surface was machined prior to pyrolysis which caused the formation of a surface layer with cracks [7].

The microstructure of pyrolytic graphite. Still another graphite material is (total) pyrolytic graphite (TPG) which is now generally used for platforms in the constant temperature furnace concept of AAS [10], usually together with pyrolytically coated tubes of polycrystalline electrographite. TPG has a number of properties not only desirable in ETAAS, such as low gas permeability and high chemical resistance. Comparison of tensile strength-to-mass ratios for a number of materials showed that that of PG is the highest over the entire temperature range up to 3000°C and 5–10 times greater than that of conventional EG. Thus in ETAAS, higher heating rates could be achieved by reducing the mass of PG tubes as compared to PG coated

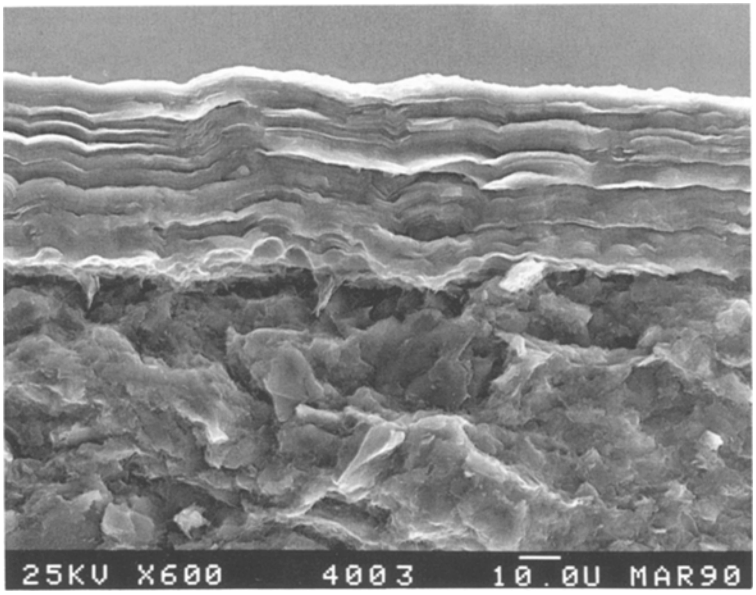


Fig. 5. Fracture surface of a new polycrystalline electrographite tube coated with pyrolytic carbon as used with Perkin-Elmer AAS instruments (from Welz et al. [10])

EG tubes. The lamellar structure of PG is shown in Fig. 5 together with that of polycrystalline EG. Fig. 5 depicts a fracture surface of a PG coated EG tube used in a Perkin-Elmer AA-spectrophotometer. The lamellar structure of PG originates in its manufacturing process: to produce TPG or PG coated tubes, the "hot wall technique" of chemical vapour deposition technology is employed where a substrate (for a TPG tube) or a EG tube (for a PG coated tube) is heated by a surrounding element while a hydrocarbon containing feed gas flows through the enclosure [10].

The carbon thus deposits by cracking of the hydrocarbon molecules as so-called continuously nucleated pyrolytic graphite. After deposition the enclosure is cooled at a controlled rate to minimize stress. It is obvious that the properties of this material are anisotropic: Thermal and electrical conductivity are much better along the lamellar structure than perpendicular to the plane of deposition.

The Microstructure of Materials and Today's Possibilities of Topochemical and Microstructural Characterization

After discussing the structure and related properties of these very different graphite materials it should be evident that the next dimensional structural phenomenon after the atomic and crystal structure—the microstructure—is very decisively influencing final material properties.

However, what is "microstructure"? Some 20 years ago, when the optical microscope was the main instrument to study the microstructure of materials, the term microstructure consequently covered all structural elements that could be detected in the optical microscope. Today, the situation has changed drastically. SEM and TEM have widened our horizons into atomic dimensions, making the detailed study of dislocation structures and the quantitative or at least semiquantitative chemical

Table 5. Principal analytical methods for the study of surface and interface phenomena and for topochemical characterization in material sciences (from Grasserbauer [4])

Photon probe techniques:
Raman spectroscopy, LRMA, SERS, IR, EXAFS, NEXFS, SEXAFS, XPS, UPS, LAMMS
Electron probe techniques:
EPXMA, SEM, AEM, THEELS, ARM, REM, LEED, RHEED, THEED, HREELS, AES
Ion probe techniques:
RBS, MEIS, ISS, ERD, NRA, SIMS, LRI-SIMS, LNRI-SIMS, SNMS, GDMS, GDOES
Electrical field probes:
FIM-atom probe, STM, AFP

characterization of phases or inclusions possible. TEM in combination with EELS and EDXRS opens new possibilities to chemically identify sub-μm dispersoids in dispersion strengthened materials [5].

AES and SAM and especially dynamic SIMS allow the study of grain boundary contaminations and the composition of surface layers or coatings [14]. Table 5 gives an overview of principal analytical methods for the study of the topochemistry in material sciences and the study of surface and interface phenomena [4]. Since all these methods use electromagnetic radiation or elementary particles (electrons, ions) as "reagents" they have been categorized as physical methods of analysis [4]. This should not lead to the assumption that chemistry is of no importance to a proper handling of these methods and to a meaningful interpretation of results. Proper sample preparation and interpretation are not feasible without a profound chemical background. These remarks seem essential because many of these methods are handled by operators trained in physics and/or electronics who are not always cooperating closely with chemists.

Table 6 gives a short description of the potential and information content of photon probe techniques and Table 7 summarizes the potential and information content of ion probe techniques. The new development of SIMS combined with advanced techniques in image analysis opens up new and fascinating possibilities of a three-dimensional stereometric study of trace and ultratrace element distribution in materials [15]. Table 8 gives finally an overview on the potential and information content of electron probe techniques. Since the majority of the techniques of Tables 6 to 8 are capable of giving topochemical as well as microstructural information and since these informations are complementary for a sound materials characterization it does not appear meaningful to separate these phenomena into two disciplines. Neither is it possible or meaningful to strictly separate surface characterization from bulk characterization since outer and inner surfaces must be considered to be among the most important discontinuities of the solid state.

We can conclude that we are today in a position to study structural and compositional details of matter from the very atomic level up to the dimensions of constructions, the ultimate level of dimensional categories of materials to be discussed later. It consequently became a bit difficult to strictly separate all four dimensional structural categories from each other. However, Table 9 tries to give an impression of the wide field of characteristic microstructural concepts and dimensions [16]. It is obvious that in some cases microstructural characteristics like

Table 6. Short description of the potential and information content of photon probe techniques (compiled from Grasserbauer [4])

Technique	Resolution		Process	Information content
	Lateral	Depth		
LRMA	1 μm	0.1 μm	Inelastic photon scattering (Stokes and anti-Stokes)	Molecular and structural microprobe; complementary info to IR about functional group vibrations, evaluation of polarization effects
SERS	1 μm	0.1 μm	As above	As above, but enhancement up to 10^6; limited to Ag, Cu, Au as substrates
NIR-FT-Raman	1 μm	0.1 μm	As above, but near IR	As above, but less fluorescence interference
FT-IR-Microscope	10 μm	1–10 μm	IR-absorption with interferometric recording of spectra	IR (0.75–1000 μm) absorption by excitation of vibrational and rotational states Molecular and functional group information
ATR-IR	Several mm	1–10 μm	Internal IR-reflection	As above: SA of polymers, catalysis, electrochemical reactions. By use of polarized light: information on orientation of adsorbates on surfaces
IRRAS	mm	1–10 μm	Angle resolved IR-reflectance measurements	Determination of complex optical properties and identification of chemisorbed species
EXAFS	ca. 20 μm	μm	Absorption of monochromatic X-rays (synchrotron radiation), several keV	“Local atomic structure probe” Measurement of atomic distances between absorbing atom and neighbours (range 6 Å)
SEXAFS	ca. 20 μm	1 nm	As above, but up to 1 keV	Accurate determinations of bond lengths of adsorbates, surface molecular studies. The polarization of synchrotron radiation allows to probe atomic distances in specific directions
NEXAFS	ca. 20 μm	μm	As above, but keV	Determination of valence states of very fine precipitates, not measurable by TEM: studies of crystal growth, nucleation, formation of interfaces

Table 6 (continued)

Technique	Resolution		Process	Information content
	Lateral	Depth		
PES-techniques (*ESCA-techniques*):				
(a) XPS	100 μm (crystal) focussing) $\leqslant 10\ \mu$m (ESCASCOPE of VG, FT-lens)	Typically 5–10 atomic layers	Absorption of monochromatic X-rays and measurement of the kinetic energy of ejected photoelectrons	Qualitative and quantitative elemental analysis of surfaces ($Z > 1$; sensitivity limit ca. 0.1% (w/w) but 0.01 monolayers!) plus information on chemical bonding (by chemical shifts of binding energies) and binding energies. Depth profiles with sputtering installation possible
(b) UPS	In the order of [mm]	Several atomic layers	Absorption of monochromatic UV-radiation and measurement of the kinetic energy of ejected photoelectrons. (Excitation with noble gas discharge lamps or synchrotron radiation)	Study of electronic structures (of the valence band of solids or of bonding electrons in gas-molecules (even vibrational excited states can be resolved)) Extremely good vacuum ($p \leqslant 10^{-11}$ mbar) necessary. Study of chemisorption phenomena, adsorption, desorption (esp. with respect to catalysis)
ARUPS	In the order of mm	Single first monolayers	Same as for UPS, structural sensitivity enhancement by use of polarized radiation	Measurement of valence band emission spectra for "density of state"-calculations; very weak adsorption phenomena, e.g. of noble gases. Variation of detector angles allows to exploit directional effects in photoelectron-emission
LAMMS	1–2 μm	Several monolayers	(a) non-thermal laser desorption ($\leqslant 10^8$ W/cm^2)	Molecular information from adsorbed or chemisorbed species or from surface contaminants
	1–2 μm	In the order of μm	(b) thermal volume laser evaporation ($\geqslant 10^8$ W/cm^2)	Microanalysis for elements, some bonding and molecular information from fragmentation patterns
			Detection by TOF-MS	DL in the order of 1–10 μg/g

Table 7. Short description of the potential and information content of ion probe techniques (compiled from Grasserbauer [4])

	Resolution [nm]				
Technique	Lateral	Depth	Process	Information content	Useful yield
			Techniques based on sputtering		
SIMS	(a) Static [mm]	first ML	Sputtering with $Ar^+, O_2^+, O^-, Ga^+, Cs^+$ at 0.001 to 0.1 nm/s; TOF-SIMS	Surface studies in catalysis, gas-surface reactions, polymer analysis	
	(b) Dynamic 500–1000 e.g. Cameca IMS 1270: 50 (with Cs^+) 120 (with O)	1–5 AL	As above, but with typically 1 nm/s Double focussing MS with M/ΔM between 1000 and 100000	Only method with trace and ultratrace detection power at high lateral and depth resolution DL from ppt to high ppb-levels! Isotopic specificity High resolution and high sensitivity depth profiling possible Three-dimensional distribution analysis	10^{-2} to 10^{-6}
LRI-SIMS	1000	1–5 AL	Very complex instrumentation, single element at a time method: selective ionization of one atomic species in sputtered atom cloud by double or triple photon absorption. TOF-MS detection	Very high detection sensitivity at ppb and sub-ppb-levels, e.g. 2 ppb ^{56}Fe in Si with consumation of 0.8 AL ≈ 40 Fe atoms sputtered!	10^{-1} to 10^{-2}
LNRI-SIMS	1000	1–5 AL	Multiphoton ionization with intense pulsed UV-laser beam ($\geqslant 10^9$ W cm^{-2}) in sputtered atom cloud	As SIMS, but with DL presently still in µg/g-range	Typically 10^{-3}
SNMS	1000	1–5 AL	Secondary ionization of sputtered particles in HF-plasma above sample surface Quadrupole MS-detection	As SIMS, but with DL presently still in µg/g-range	Typically 10^{-9}
GDMS	[mm]	10–100	Ar-glow discharge for sputtering. Ionization in negative glow region Detection with double focussing MS, M/ΔM = 1000–10000	Advantages more on bulk-ultratrace analysis side than on topochemical analysis side DL in the ppt to ppb range for pin samples only!	Typically 10^{-7}

Table 7 (continued)

Technique	Resolution [nm]		Process	Information content
	Lateral	Depth		
GDOES	[mm]	10–100	As for GDMS, but with detection of atomic emission in UV/VIS-range	DL in 1 ppm range Routine method for μm layer characterization in metallurgy
			Techniques based on scattering	
RBS (HEIS)	[mm]	2–3 Measurements up to 1000 nm	α or $^4He^+$-scattering E_0 1–2 MeV Measurement of energy distribution of back scattered α or $^4He^+$-ions	Qual. and quant. elemental analysis; depth profiling by deconvolution of measured energy distribution with energy loss functions possible, however, generally poorer depth resolution than SIMS, but non destructive depth profiling! Additional structural information by channeling and blocking phenomena: study of formation of epitaxial films
MEIS	[mm]	0.3–0.4	200–600 keV	Same as above
ISS(LEIS)	[mm]	First monolayer analysis	500–600 eV He^+, Ne^+	Same as above. Adsorption studies
ERD	[mm]	First monolayer up to some μm	Elastic recoil detection of forward scattered light target atoms by bombardment with typically 3 MeV $^4He^{++}$ up to 30 MeV Si^+	Depth profiling for ^1H and ^2H with α, or H, C, N, O with Si^+

Table 8. Electron probe techniques (compiled from Grasserbauer [4])

Technique	Resolution [nm]		Process	Information content
	Lateral	Depth		
EPMA (EPXMA)	Primary E-beam: 5–50 keV ∅ 1–100 nm Excited volume: 1–5 μm^3 (pear shaped) 1–5 μm	1–5 μm	Scanning primary e-beam excites characteristic X-rays in flat, polished samples. XRS: with conventional detectors: Na – U with windowless proportional flow counters: B – U	Quantitative topochemical analysis: DL (WDS): 10–100 μg/g DL (EDS): 100–5000 μg/g Optimized for quantitative X-ray analysis
	f (Z of sample)		Quantitation after correction for absorption and enhancement (computer programmes) by use of standards possible with an accuracy of ~ 1% rel., standardless with an accuracy of 3–10% rel. as a function of matrix composition	
SEM	Primary E-beam 5–50 keV ∅ 1–100 nm		Scanning primary E-beam causes emission of: · secondary electrons (SE) · backscattered electr. (BSE) · characteristic X-rays · absorbed E can also be registered (AE) · cathodoluminescence can be observed	Topographic imaging with SE produced by inelastic scattering of PE BSE-topographic imaging with lower resolution, but with high sensitivity to Z (down to 0.1 ΔZ) SEMS are optimized for topographic imaging of rough surfaces due to high depth of field (excellent parallelity of PE beam)
	(a) SE-topographic imaging 1–5 nm (≙ magnification ~ 10^5)	1–5 nm		
	(b) BSE-topographic Z-imaging (Z-resolution: 0.1) 10–100 nm	10–100 nm		
	(c) X-ray analysis 1–5 μm as a function of Z of matrix	1–5 μm		

Table 8 (continued)

Technique	Resolution [nm] Lateral	Depth	Process	Information content
TEM	Resolution for transmitted electrons: (1) A factor of PE-energy (2) A factor of sample thickness		PE-beam generation by W, LaB_6 or field electron (FE)-guns	· Lattice imaging · Study of defects (e.g. dislocations, stacking faults etc.) · Study of dispersoids at the nm-level · Atomic structure of interfaces 3 principal imaging methods: *Bright field TEM*: Directly transmitted beam forms image: extremely thin foils are necessary for surface studies Hence: the number of applications is limited due to experimental difficulties *Dark field TEM*: The directly transmitted beam is excluded and only strongly scattered electrons form the image. Difficulty: low intensity of diffracted electrons *Reflection electron microscopy* (*REM*): Angle of beam and specimen typically 1–2°: glancing angle reflection gives rise to RHEED pattern in the back focal plane of objective lens
CTEM	PE-energy: 50–200 keV Lateral resolution for imaging: ca. 0.1–0.2 nm			
STEM	Resolution for sample thickness 100 nm and beam diameter of PE 10 nm: ca. 20 nm Resolution for sample thickness 10 nm and beam diameter 1 nm: ca. 2 nm (due to electron scattering in the sample)			
ARM	PE-energy: 400 keV–1 MeV Resolution: down to 1 Å		Cryo electron microscopy with superconducting objective lens (Nb_3Sn at $L_{He} \triangleq 4.2$ K) and cooling of specimen to same temperature to reduce radiation damage	

Table 8 (continued)

Technique	Resolution [nm]		Process	Information content
	Lateral	Depth		
X-ray nano-analysis in connection with TEM	5–30 nm at $d_B = 3$ nm and sample thickness 100–20 nm Absolute DL: 10^{-20} g Relative DL: ca. 0.X–X% (m/m) Elemental distribution imaging: lateral resolution ca. 1 nm (signal enhancement by digital image processing) Comparison of interaction volumes: Electron microprobe: $\sim 1\ \mu m^3$ TEM: sample ≠ beam ∅ excited volume 100 nm 10 nm $10^{-5}\ \mu m^3$ 10 nm 1 nm $10^{-8}\ \mu m^3$		Large area detectors (EDS) in small distance from specimen Nevertheless X-ray-nano-analysis exhibits two principal disadvantages: (a) Low collection yields (10^{-2} to 10^{-4}) (b) Low X-ray yield for light elements (B, C, N, O, ...) Therefore: analysis of transmitted electrons: EELS	XRS very important for the identification of precipitates at grain boundaries or interfaces and for sub-μm phases and inclusions
(TH) EELS	Resolution same as for X-ray-nano-analysis. Relative DL: ~3–5%. Accuracy: ~10–20% relative Especially suitable for light elements due to lacking sensitivity of EDS. High collection yields with electron spectrometers beneath thin specimen. However low signal/noise ratios and high background due to multiple elastic scattering		Imaging possible by PE-beam scanning (STEM) or stigmatic electron spectrometer: Zeiss	Qualitative and semi-quantitative information on elemental composition Position and structure of absorption edges of valence band or near valence band core levels (e.g. C-K, O-K, Si-$L_{2,3}$-ionization) contains *bonding information* Fine structure evaluation in combination with high spectral resolution (0.1 eV at 100 keV) allows to gain *stoichiometric information* for extremely small domains Sensitive detection of structural changes in nano domains possible by study of position and width of plasmon peaks

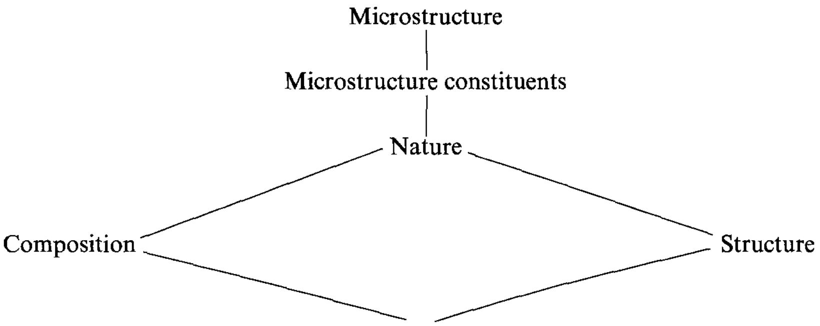
Table 8 (continued)

Technique	Resolution [nm] Lateral	 Depth	Process	Information content
HREELS (separate instrumentation, no connection with TEM)	Lateral resolution poor: mm–cm Depth resolution: monolayers		Monoenergetic electron beam focussed onto the surface of a solid-measurement of reflected electrons 2 electron spectrometers: · one for monochromatization of PE-beam (typical $E_0 = 500$ meV) · one for energy analysis of reflected electrons	Useful for studies of adsorbates on solid surfaces: · surface coverage with adsorbates · information on bonding geometry (if symmetry considerations are included in spectra evaluation) (→studies of catalytic phenomena) · thin film characterization
AES	PE-beam: 1–10 keV $d_B \geqslant 50$ nm DL ~ 0.1–1% (w/w) · low signal to noise-ratio due to very high continuum electron background (multiple scattering): registration of 1st derivative of spectrum · very high surface sensitivity; depth resolution: 0.5–5 nm		Measurement of kinetic energy of emitted Auger-electrons UHV of 10^{-10} mbar mandatory In situ sample preparation: fracturing; annealing; thin film deposition	Micro surface analysis: · elemental identification · quantitative elemental analysis · to some degree direct compound identification by evaluation of chemical shifts and line shapes · depth profiling in combination with Ar^+-sputtering
	Dependence of relative DL on beam $\varnothing$: $i_B = 10^{-9}$ A $d_B = 100$ nm rel. DL ~ 10–20% $d_B = 1$ μm rel. DL ~ 1–2%		SAM Usually performed at 10 keV to achieve small beam $\varnothing$ d min 20–50 nm: useful for SE-imaging For elemental mapping: beam $\varnothing$ above ca. 100 nm are meaningful	· SE-imaging · elemental mapping · line scans for several elements Optimization of resolution, beam current and necessary detection power. For higher sensitivity: SIMS

Table 8 (continued)

Technique	Resolution [nm]		Process	Information content
	Lateral	Depth		
	$i_B = 10^{-7}$ A $d_B = 100$ nm rel. DL ~ 1–2% $d_B = 1$ μm rel. DL ~ 0.1–0.2%			
			Electron diffraction (coherent interference effects)	
THEED (with CTEM, STEM)	$E = 150$ eV $\lambda = 0.1$ nm $E = 15$ keV $\lambda = 0.01$ nm High energy of PE beam: High resolution of imaging Minimum phase size for structure analysis of precipitates: ~20 nm		De Broglie: $\lambda = \frac{h}{\sqrt{2m \cdot E}}$ Bragg angle conditions: $n\lambda = 2d \sin \vartheta$	TEM diffraction patterns: · Point patterns for monocrystalline specimens · Ring patterns for polycrystalline specimens · Stripe formed patterns for large grained or textured specimens · Diffuse circular halos for amorphous materials · Determination of lattice constants from THEED-patterns · Identification of phases
LEED and RHEED (separate instrumentation, no connection with TEM)	Monolayer sensitivity LEED: E_0 ~ 1–5 keV Study of monolayers RHEED: $E_0 > 10$ keV Study of thin films UHV necessary		*Diffraction at solid surfaces* Measurement of reflected electrons of a monoenergetic PE-beam on a fluorescent screen LEED pattern reveals the periodicity of atoms of the surface and the overall symmetry, but not the individual atomic position (periodicity is needed for reflection)	· Determination of crystalline order of the surface of a single crystal · Study of adsorption and segregation processes on surfaces or overlayers

Table 9. Characteristic microstructural concepts and dimensions



Foreign atoms Segregations in the solid solution	Metallic phases Intermetallic phases Non-metallic phases	Lattice defects 2-Dimensional · Grain boundaries · Phase boundaries 1-Dimensional · Dislocations 0-Dimensional · Vacancies
Dimensions · Concentration · Difference	Quantity	Quantity · Grain area · Dislocation density · Vacancy concentration
Extent · Spacing	Size	Area, length
Shape distribution	Shape distribution (location)	Shape distribution

lattice defects overlap dimensionally with crystal structures as well as modern constructional features of microelectronics components increasingly reach into the size domain of microstructures. Table 9 makes us aware of the utmost complexity of microstructure especially for composite materials. As was demonstrated above, the close correlation between microstructure and properties is the basis for the development of advanced and tailor-made materials with well defined and reproducible properties. The higher the requirements on a material are, the more exacting are the demands on the microstructure, i.e. the more precisely the microstructure must be tuned and kept constant in routine production. The knowledge of the microstructure and its property interactions is one of the basic topics of material science [17]. Even single crystals without grain boundaries bear diverse faults in the order of several millions per cubic centimeter. Only a hypothetical, ideal single crystal in thermodynamic equilibrium would exhibit a crystal structure with no microstructure superimposed. The properties of all real crystalline materials are determined by the ratio, size, form and distribution of ideal crystalline domains and faults, the great diversity of which is shown in Table 9.

Tables 6–8 also demonstrate that it becomes increasingly difficult to retain an overview over the wide variety of todays instrumental and methodological possibilities and tomorrows rapidly growing developments. To choose the optimal combination of methods for a given problem increasingly becomes a difficult task even for all-rounders in the field [5].

Especially for smaller industries this usually implies collaboration with a multitude of research institutions having the necessary instrumentation and expertise to operate it. And a thorough microstructural characterization increasingly becomes a question of finances, too, and in a market oriented economy, of course, also of competition. Consequently, national and continental collaborations are formed among related companies and research institutions to share the rapidly increasing costs of an explosively complex materials development the basis of which in all cases is a thorough knowledge of the structural and compositional characteristics of the materials under development. Hence, material scientists—little to their liking—find themselves caught up in global competition. As an example, the European answer to the Japanese and US challenge in the development of ultrapure materials for highly integrated circuits of microelectronic components are collaborations within the COST 503/II-action and the JESSI-project [5, 18].

Chemical Composition and Microstructure

It goes without saying that material properties strongly depend on composition. Hence from the earliest days of materials science the determination of composition has been an established practice. The statement of the acceptable range of composition usually forms the first clause of any materials specification, so that accurate bulk analysis is a necessary step in the approval of supplies as well as in production control of final materials.

However, not only the gross composition of materials influences their properties. It has been shown elsewhere which effects trace impurities can have on the properties of e.g. metals [19–21]. For the latter we can differentiate between properties which are insensitive to trace impurities, e.g. density, specific heat, thermal expansion. A second group of metal properties are directly affected by foreign atoms and, therefore, depend strongly on the foreign atom concentration. Prominent examples are the electrical and thermal conductivity at low temperatures and the transition temperature for superconductivity [22]. A third group of metal properties depends primarily on structural defects and their mobility which in turn is strongly influenced by foreign atoms. Important metal properties like plasticity, tensile strength, fracture toughness, recrystallization temperature, corrosion behaviour belong to this group [21]. For other high tech materials like advanced ceramics such rather clear relations between trace element contents and properties are yet to be developed and their analytical characterization has only recently been established [23].

It is this interplay of trace elements and the mobility of microstructural features like grain boundaries and lattice defects which often hinders clear correlations of trace element contents to mechanical properties or materials service behaviour.

An important result of a recent European collaborative study on the influence of essential trace impurities on the technology and final properties of hard metals was the following observation [24, 25]:

Clear effects of trace elements were found for initial production stages. For later stages the picture becomes more and more blurred by a rising multitude of other influential parameters.

A fairly clear correlation of dopant concentrations to final hard metal properties was only feasable in two cases: a detrimental influence of Al-inclusions in the form of oxides, silicates or calcium aluminates and of CaS-inclusions could be established. The observed inconclusiveness of much of the technological testing of relevant test specimens as to the influence of dopants rather reflects the developmental state of the art of these tests and the great complexity of influences especially of trace elements in combination with microstructural features rather than the absence of specific influences of dopants or impurities.

This finding can be generalized: Clear correlations of the impact of impurities on mechanical properties and material behaviour in actual service are not yet established for most high tech materials. Contrary, a safe control of microstructure is often not possible at the time being for many a high tech material and a better control of property variations is presently the theme of numerous development programs in the high tech field. A prerequisite of such endeavours is, of course, a rigorous observance of chemical (very often trace and topochemical) specifications.

Constructions

The last structural category to be shortly discussed are constructions or the geometry of the final part made out of a material for a certain purpose. It, too, has a decisive influence on the behaviour of a material in service. One of the most prominent examples is the paramount significance of the cutting geometry of hard metal cutting inserts for the machining of metals [26, 27]. Another example is the influence of sample geometry and surface finish for mechanical testing. For brittle materials, designers of constructions must be aware of the fact that there is a loss of strength with increasing component size which has to do with the distribution of defect sizes influencing fracture statistics [33].

Structures in microelectronics components. By far the most intricate constructions of a whole symphony of high tech materials are today packed into ever smaller highly integrated systems of the microelectronics industry. For minimum integrated circuit geometries of the new megabit generations of the late 80ies (1 M, 4 M) and the early 90ies (16 M, 64 M), dimensions of structural building elements for the first time shrank into the submicron regime approaching the wavelength limits of visible light and thereby necessitating completely new technologies in chip production [28, 29]. This is one of the greatest challenges for the wide field of structural and topochemical characterization and much of the relevant recent development was triggered by the pressing needs—and the great financial strength—of the microelectronics industry and its suppliers of basic materials and components. Parallel to the dimensional miniaturization, purity requirements for involved materials—also refractory metals and their silicides—reached levels which were considered utopian only several years ago [5, 30, 31].

Fig. 6 tries to visualize the constant trend of miniaturization of microelectronics components and the critical defect sizes which require routine inspection [29]. Of

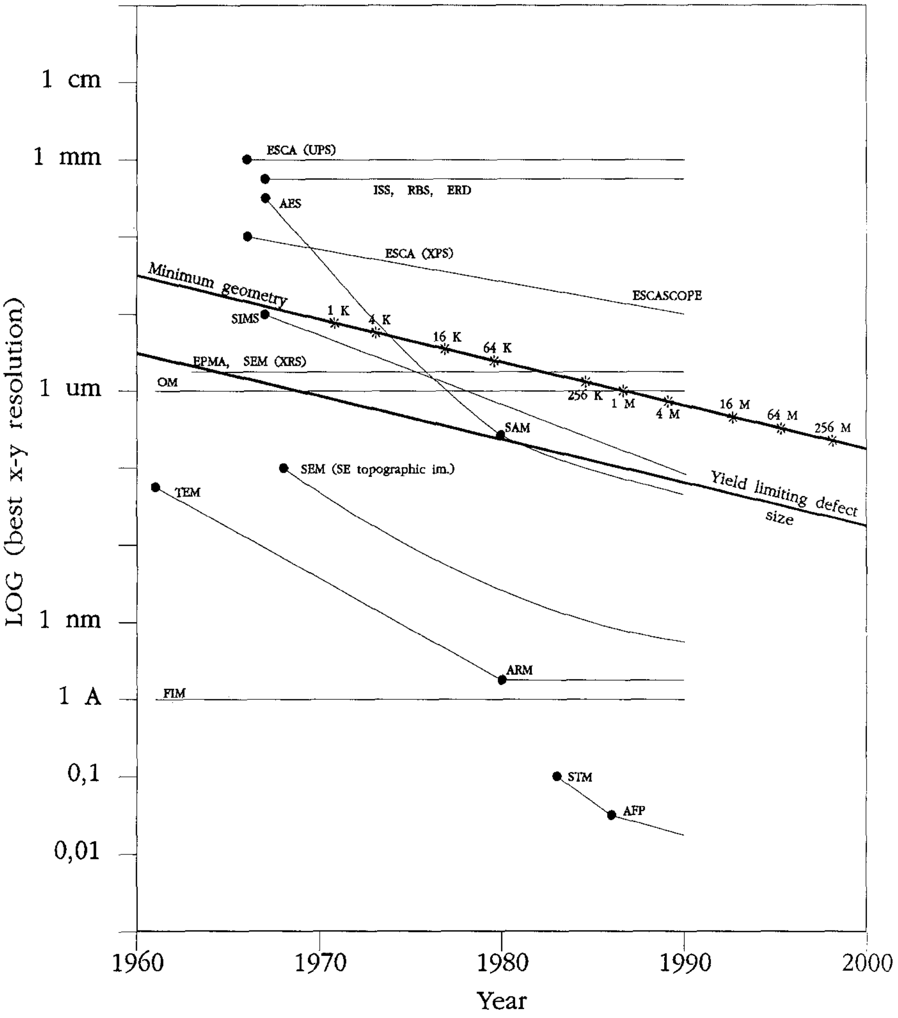


Fig. 6. The steady trend of miniaturization in microelectronics and most important analytical methods for defect and particulate impurity inspection (from Shaffner [29])

course, particulate impurities of the same size as the critical defects have to be kept away in production at large—a task which still awaits a solution for particles below 0.1 μm relevant to 4 M and higher integrations. Fig. 6 also shows the most important instrumentation together with relevant advancements in lateral spatial resolution.

Materials as carriers of information. It appears worth mentioning here also a property imposed in materials which increasingly becomes important for complex high tech systems: Materials are made carriers of information. This is nothing very new and even modern man made information systems appear quite rudimentary and bold if compared to the biological information systems the most prominent example of which is the genetic code laid down in chromosomes. However, progress can be visualized, e.g. by a comparison of the "geometry of information" of traditional and modern audio-systems.

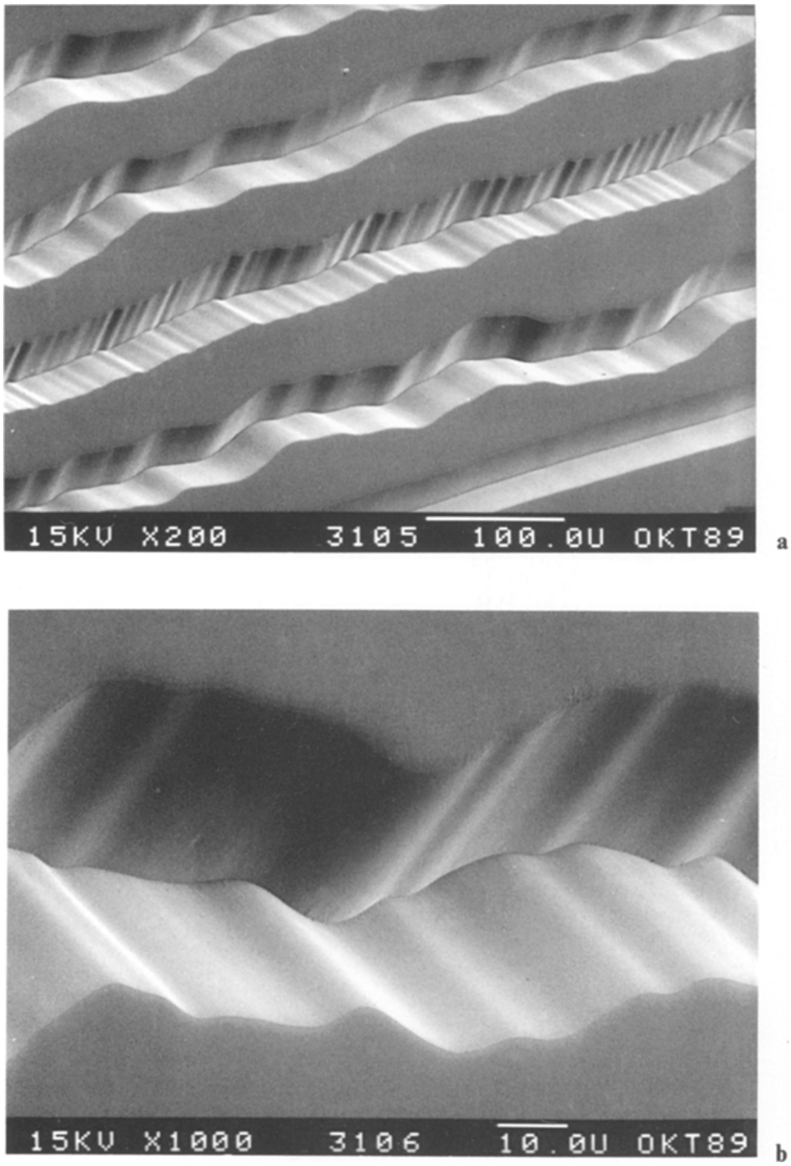


Fig. 7. Morphology of sound tracks on a conventional record at two magnifications: **a**: × 200 and **b**: × 1000

Fig. 7 shows the morphology of sound tracks of a conventional record at two magnifications.

Fig. 8 demonstrates the vast gain in information volume of a modern compact disk, again at two magnifications, the lower one being identical to the higher magnification of Fig. 7.

Optical disks at the time being resemble the medium of highest information density with structures in the 100-nm to 1-μm region determined by the wavelength of the light used for imprinting. The great drawback of optical disks is, of course, their irreversibility as compared to magnetic carriers (tapes, discs or cards).

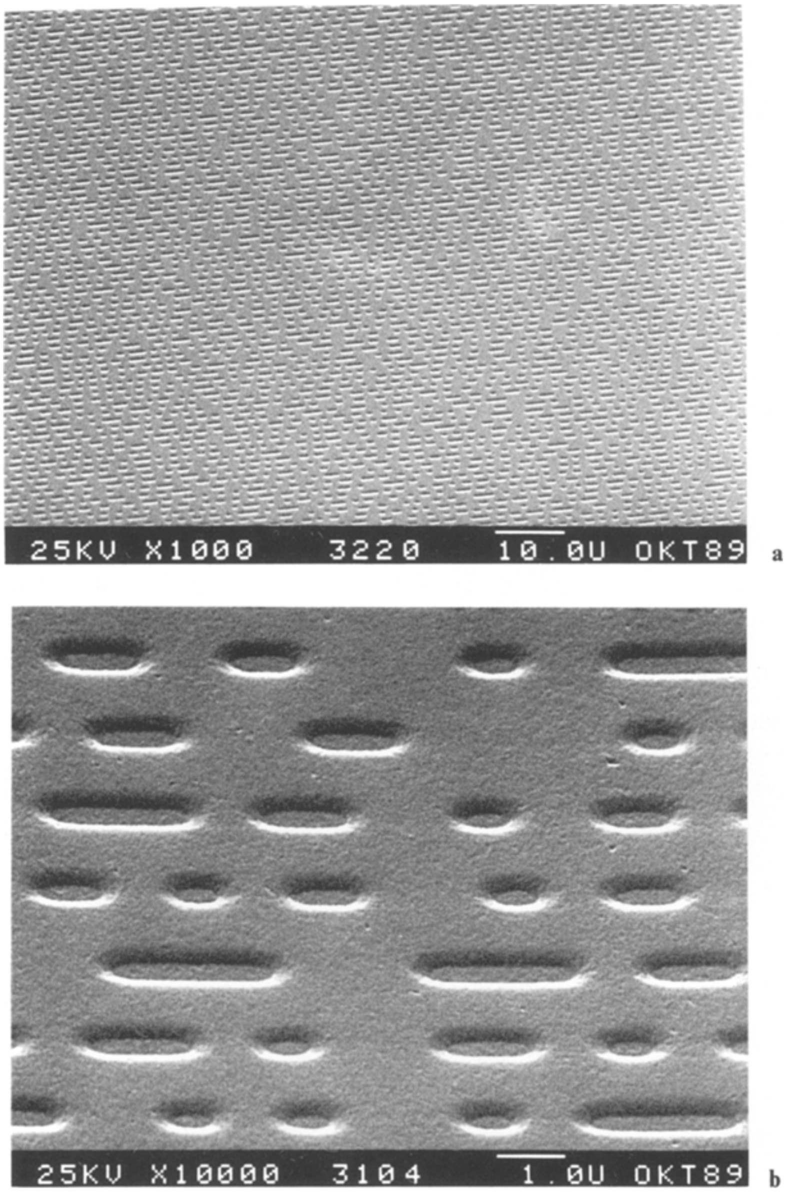


Fig. 8. Morphology of sound tracks on a modern compact disc at two magnifications: **a**: × 1000 and **b**: × 10000

Materials Are Dynamic Systems with Limited Life Time

On April 28, 1988, an Aloha Airlines jet liner lost the roof of the forward cabin at 7200 m altitude. A flight attendant was killed and 65 passengers were injured. The 19 year old plane was heading from Hilo, Hawaii, to Honolulu performing its 89681st flight. The reason for the accident was a phenomenon very well known to material scientists: fatigue. The repeated stress of thousands of take offs and landings caused the growth of tiny cracks at rivet holes. These cracks, though small enough to escape visual inspection, led to the disaster.

What does this story have to do with analytical chemistry? Inclusions, for a long time objects of intensive topochemical and morphological investigations [32] are among the most frequent sources for crack initiation in metallic as well as in ceramic materials.

Practically all materials must be viewed as dynamic systems with a limited life time especially in many high tech applications which is usually synonymous with extreme conditions.

The Recrystallization of Refractory Metals and Alloys

Another prominent example for such a dynamic system is a refractory metal in high temperature use and under corrosive attack as e.g. a tungsten tube assembly in a modern ETAAS-instrument [34, 35].

Fig. 9 shows new upper and lower tube parts with shiny and smooth surfaces and with slits to promote constant temperature conditions [36].

Fig. 10 shows the enlarged surface of parts which have been used until intercrystalline cracks terminated the tube life. Recrystallization changed the materials structure drastically. Crystals grew by several orders of magnitude into the 10- to 100-μm range thereby vastly reducing the grain boundary surface from ca. 100 m^2/g to ca. 0.1 m^2/g. Consequently, grain boundary contaminants are greatly enriched and brittleness increases proportionally. Again the combined structural and topochemical changes lead to a decisive deterioration of mechanical properties and to a limited service life.

Recrystallization not only of refractory metals is also decisively influenced by the purity level. Fig. 11 shows the recrystallization domains of pure molybdenum and two of its microalloys—TZM and HT-molybdenum [37]. For pure molybdenum, it is demonstrated how the increasing material purity in the last years from about 99.80% to 99.95% has lowered this recrystallization domain which in practice frequently has negative effects in various applications [38]. This is one of the rare examples that—besides many positive effects—the much more stringent purity demands of today also can exert some unfavourable influences on important material characteristics. The consequence of this phenomenon for refractory metals is the trend to the readdition of specific impurities for dispersion strengthening, i.e. the fabrication of so called "microalloys" with the very much higher recrystallization domains e.g. shown in Fig. 11 for TZM and HT-Mo sheet and wire.

TZM is a molybdenum alloy with 0.5% Ti, 0.08% Zr and ca. 250 μg/g C and O, respectively [39]. By precipitation of fine dispersoids the alloying elements give rise to both solid solution hardening and dispersion hardening. The finely dispersed oxides and carbides prevent the undesirable grain growth at relatively low recrystallization temperature [40]. Of course, this also implies

- a better high temperature strength,
- a better high temperature creep resistance,
- a reduced tendency to heat deformation,
- a better weldability,
- a better corrosion resistance,
- a reduced tendency to embrittlement.

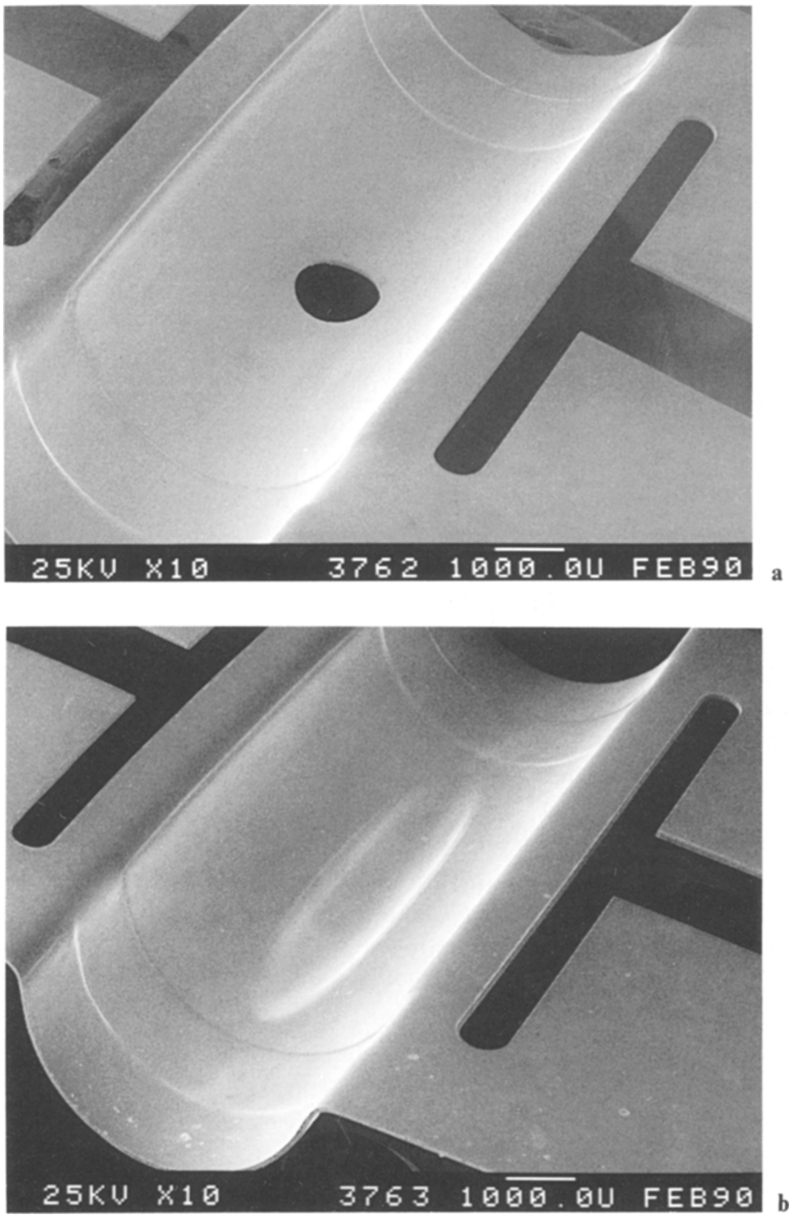


Fig. 9. Upper (**a**) and lower (**b**) tube parts of the tungsten tube assembly for the new WETA-ETAAS device (from Ortner et al. [36])

TZM is the most widely used Mo-alloy. Its share of the total annual production of molybdenum metal and alloys ranges between 5 and 15% in the Western world [44].

HT (= high temperature) molybdenum is doped with potassium silicate similar to non-sag (NS)-tungsten [41–43]. As for NS-W, a strong directionally accentuated deformation and certain intermediary heat treatments are necessary to develop the pronounced fibrous structure which is stabilized by the formation of fine K-silicate filled bubbles at the grain boundaries. Fig. 12 shows these rows of bubbles which form in the direction of the deformation. They are the cause of the directional grain

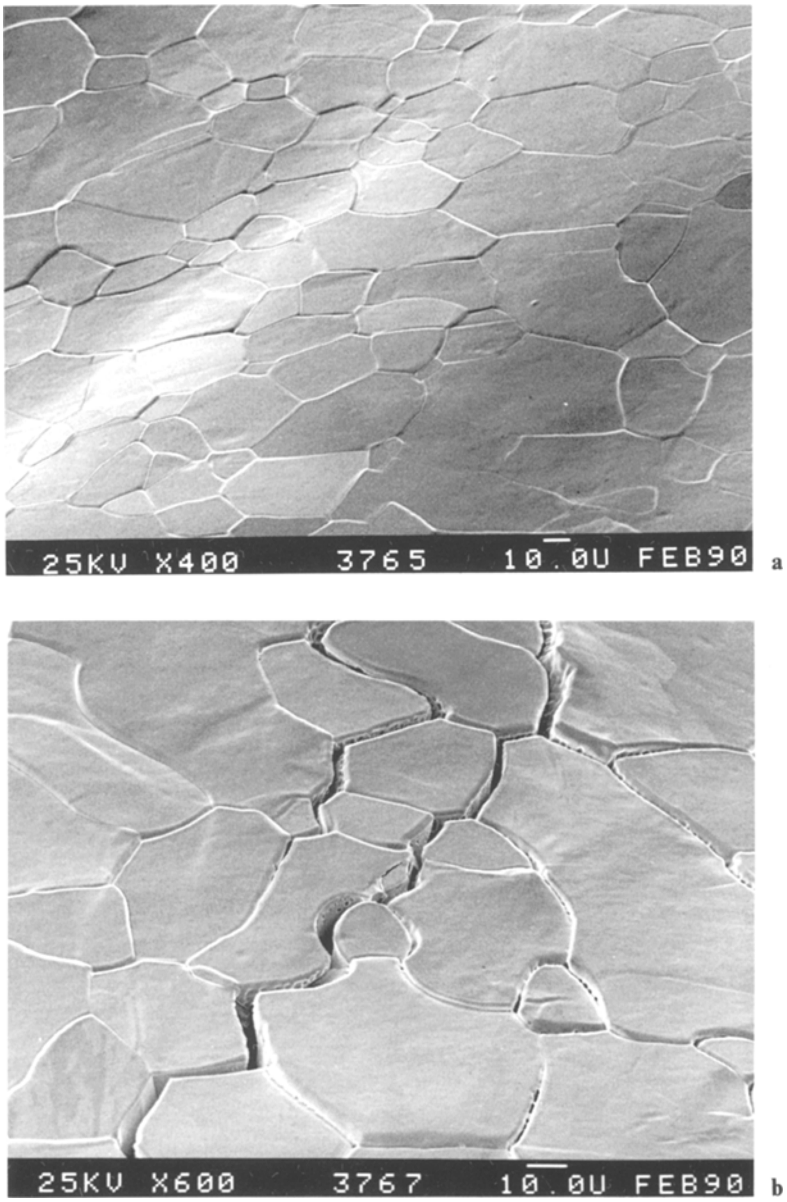


Fig. 10. Enlarged surface area of a used tungsten tube assembly demonstrating the phenomenon of recrystallization (**a**) and failure due to intercrystalline crack formation and grain boundary loosening (**b**). The assembly was subjected to 250 analysis cycles at an atomization temperature of 3000°C for the analysis of Mn-traces in sea water

growth during recrystallization and lead to the typical elongated recrystallized grain structure which is also visible in Fig. 12.

On account of the necessary high deformation to develop the fibrous structure only wires and relatively thin sheets can be produced from HT-molybdenum. On the other hand, the unsurpassed formability of the K-silicate as compared to the much harder and more brittle dispersoids of TZM make it the best dispersoid for the manufacture of fine wires and sheets. Consequently, HT-Mo wires find wide-

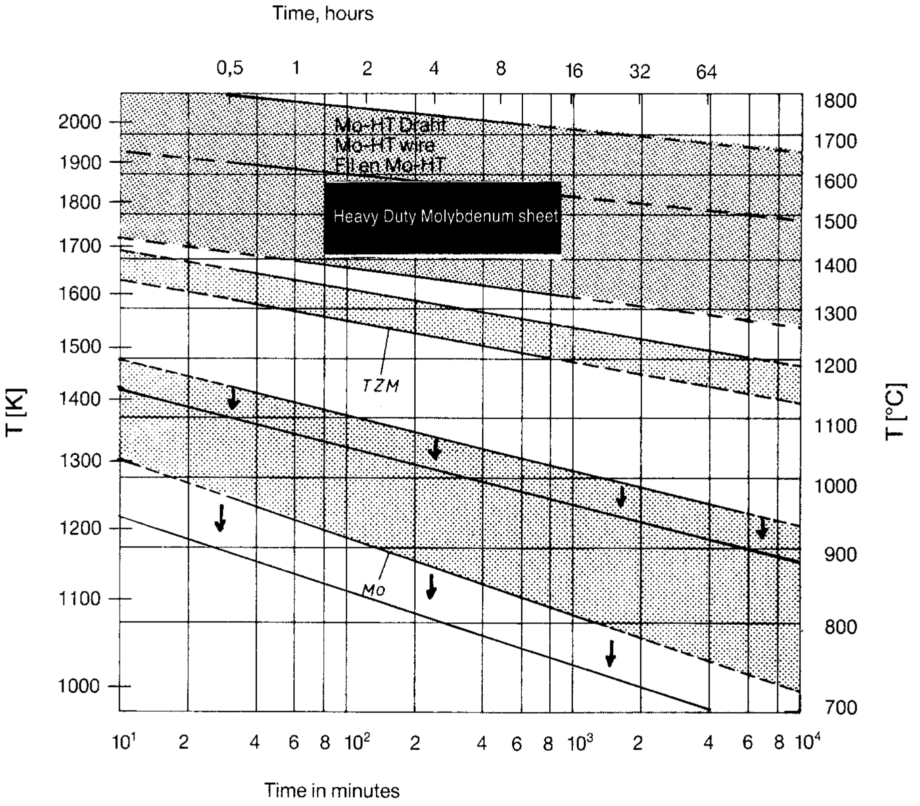
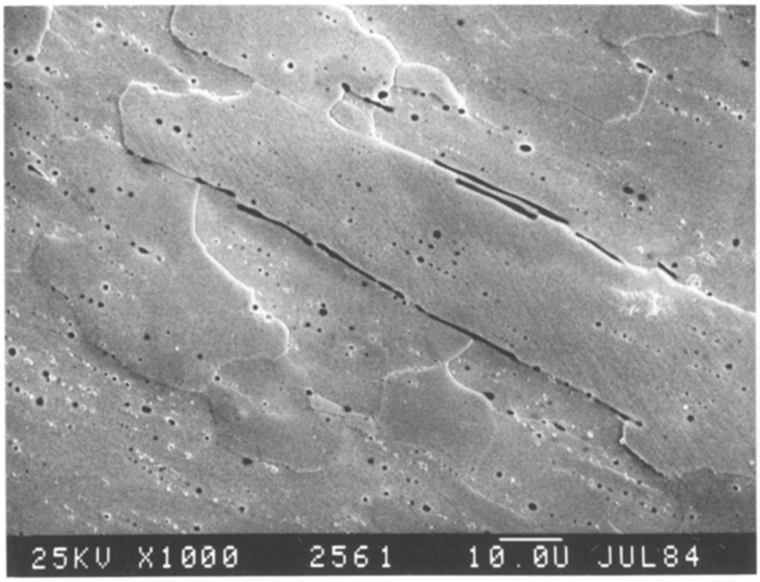


Fig. 11. Recrystallization of fully dense pure molybdenum, TZM and HT-molybdenum (sheet, deformation: 95%; wire, deformation: 99.98%) in relation to time and temperature. Lower and upper limits represent the onset and completion of recrystallization, respectively (from ref. [37])

spread applications as support wires for incandescent filaments of NS-tungsten or thoriated tungsten used in bulbs for car and motorcycle headlamps which have to be resistant to mechanical shocks and vibrations at highest temperatures. The same applies to HT-Mo tape (elliptically etched) sealed into glass of iodine bulbs. HT-Mo is also used as structural parts in electronic tubes subjected to thermal stress and used in special heavy duty applications.

In TZM, a part of the dispersoids (mainly the oxides) are formed during early production stages from the added titanium and zirconium hydrides and exhibit a rather coarse particle size distribution (dispersion strengthening). A much finer dispersoid part is then formed during sintering (solid solution strengthening). Fig. 13 shows a TEM-micrograph of a subgrain boundary in TZM with carbide precipitates of about 5-nm diameter in the longitudinal axis. Since the dispersoids in TZM are already formed in early production stages and during sintering at the latest, no further deformation is necessary for the development of the final structure as is the case for HT-molybdenum. Hence, also large parts up to 5000 kg can be produced as, e.g. large dies for the isothermal forging of Ni-based superalloys and titanium based alloys for the aviation industry [45]. The significantly higher recrystallization domain of HT-Mo as compared to TZM is yet unclear. It probably is related to different dispersoid coarsening mechanisms at high temperatures [38]



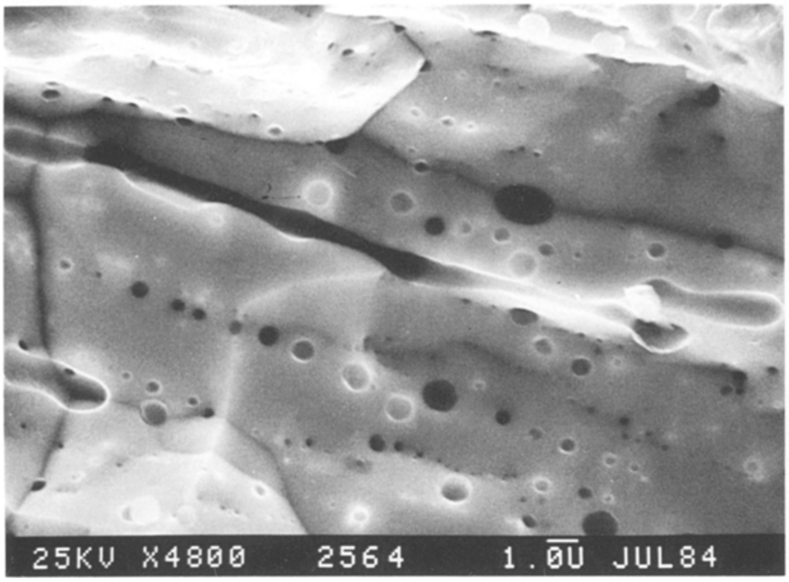


Fig. 12. Microstructure of recrystallized K-silicate doped HT-molybdenum at two magnifications: **a**: × 1000, polished section; **b**: × 4800, fracture micrograph

and is still subject of intensive investigations, mainly of a comparative nature with a new generation of molybdenum alloys with deformable rare earth oxide dispersoids which also exhibit elongated grain structures after respective forming [42–44].

A multitude of "topochemical questions" also remain to be solved. To mention just a few:

— A detailed study on the chemistry of bubble formation in HT-molybdenum would be necessary in order to clarify the exact composition of the K-silicate bubble fillings. The question whether some of the K-silicate disintegrates into

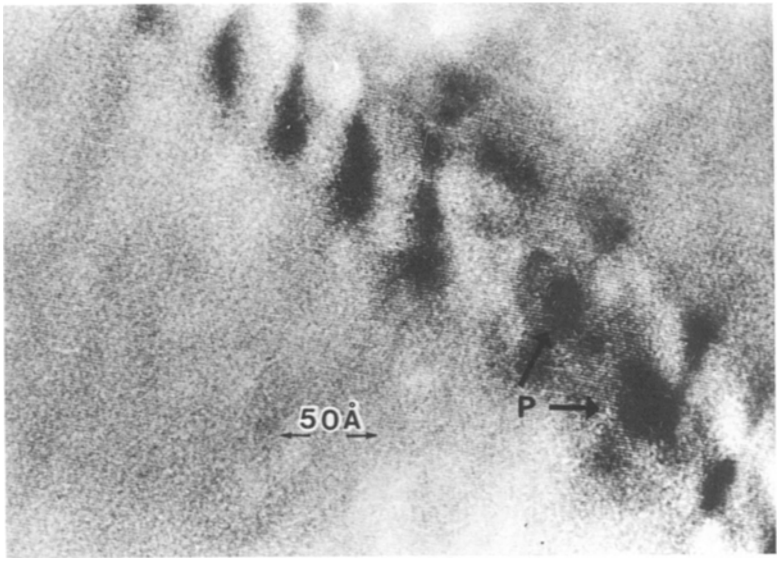


Fig. 13. TEM-micrograph of a subgrain boundary in TZM with carbide precipitates with particle diameters of 1–10 nm

possibly metallic K (like in NS-W) and SiO_2 and a possible subsequent reduction of SiO_2 to Si and formation of Mo-silicide dispersoids is yet unanswered.

— A detailed study on the particle size distribution and the three-dimensional distribution of Ti- and Zr-carbides and oxides in TZM and possible grain boundary enrichments in the matrix molybdenum with carbon and/or oxygen would be important for a better understanding of many related phenomena.

These examples should demonstrate the interplay of topochemistry and microstructure for modern high tech materials which necessitates the close multidisciplinary collaboration of chemists, physicists, material scientists, construction engineers etc. for many intriguing advancements in tomorrow's material development.

Lifetime Investigations for Graphite Tubes in ETAAS

As a typical example of lifetime investigations for high tech materials in actual use in analytical chemistry, relevant work on various tube materials for ETAAS can be mentioned. Extensive experiments with uncoated and PG coated polycrystalline EG tubes, PG platforms, TPG tubes and GC tubes as well as with tungsten tubes were carried out [7–11, 34, 35, 49, 50]. These investigations focussed on two main topics:

(a) the observation of morphological changes until final tube damage by scanning electron microscopy,
(b) the study of changes of the analytical signal with rising numbers of analysis cycles and the attempt to correlate these changes with morphological alterations of (a).

Some of the most interesting conclusions should be mentioned:

— It is necessary to distinguish between an analytically useful tube lifetime and the total lifetime of a tube until final tube breakage which is caused by progressive wall thinning in the case of graphite or by crack formation due to recrystallization in the case of tungsten.

The analytically useful tube or tube assembly lifetime (with platform) was defined by Welz et al. [8, 11] as the number of firings which can be made until the analytical signal drops to 80% of its initial value and/or the relative standard deviation begins to deteriorate significantly. The analytically useful lifetime was typically found to be shorter when measurements were in peak height rather than in integrated absorbance.

Total lifetime for TPG- and GC-tubes is significantly longer than for uncoated or PG-coated EG-tubes. However, the analytically useful lifetime was, in most instances, significantly shorter than that of PG coated EG tubes with or without PG platforms. The latter combination gave the best analytical performance over an extended period of 300 to 600 firings under most of the conditions investigated. This was in spite of severe corrosion of the tube and the PG-tube coating. The secret behind this unexpectedly good performance was the secondary coating of the platform and exposed polycrystalline graphite by redeposition of vapourized carbon mainly of the binder bridges of the EG. This apparently resulted in a kind of a "self-healing" process which is peculiar to the tube- and platform combination.

Conclusion

Technological progress is closely linked to the evolution of materials. Todays tailor-made materials are the consequence of an improved understanding of the structure and composition of matter. The interplay of structure and composition is a very complex one and four principal structural categories can be distinguished: the levels of atomic and crystal structures in which the basic properties of a material are inherent; frequently, however, variations in microstructure might lead to a wide variety of properties for a material of a given chemical composition, atomic and crystal structure. As an example of relevance to analytical chemists, the microstructural variations of graphite are elucidated which result in so diverse materials as polycrystalline electrographite, glassy carbon and pyrolytic graphite. All these materials are extensively used in a wide range of analytical instrumentation, especially in ETAAS.

In many cases, impurities interact with microstructural features and the influence of trace elements on material properties cannot be understood without knowledge of this interplay. It is, therefore, necessary to study microstructural features in close combination with a thorough trace- and topochemical characterization of a material in order to understand the impact of impurities on material properties.

An overview is therefore attempted on the wide range of today's analytical instrumentation which allows a thorough materials characterization from the atomic to the constructional level of a material. Methods for the topochemical characterization and for the study of surface and interface phenomena can be grouped into four categories: photon probe, electron probe, ion probe techniques and electrical field probes. Knowledge on their basic characteristics like lateral and depth resolution, detection limits, their further information contents, e.g. on structural or bonding details, depth profiling capabilities etc., is an indispensable tool for the analytical chemist active in materials characterization.

The ultimate level of a materials structure, the constructions might reach dimensionally from the domain of microstructure as in the case of microelectronics up to the meter-ton dimensions for heavy industry. As an example of the latter, the molybdenum alloy TZM is described in some detail which is used in the form of large dies for the production of superalloy turbine blades for the aviation industry. Other examples of the morphological characterization of constructions concern the use of plastic materials as carriers of information.

Finally, it is important to be aware of the fact that materials are dynamic systems with limited lifetime. Fatigue and recrystallization of metals are prominent relevant examples. Again these phenomena must be studied by microstructural and topochemical methods in order to develop strategies to prevent or reduce such phenomena which might otherwise hinder the proper use of a material for a given purpose. Dispersion strengthened microalloys like TZM, HT-molybdenum, NS-tungsten have been developed along these lines for extreme applications like, e.g. the use of NS-tungsten in incandescent lamps as coiled coils with wire diameters down to 10 μm which are operated at 70 to 95% of the melting temperature of tungsten! Life time investigations are an essential task of quality control of constructions in technical use. As an example again of interest in analytical chemistry, lifetime investigations for graphite tubes in ETAAS are discussed.

Hopefully it could be demonstrated that the study of the solid state adds a new dimension to the analytical characterization as compared to liquids and gases: topochemistry and structure analysis. The lower the concentration of a constituent in a solid matrix, the more likely is its heterogeneous distribution. A homogeneous distribution of minor and trace constituents is rather exceptional especially in crystalline materials. Due to the complexity of microstructure, interactions of trace elements with microstructural features are manifold, too. This is all the more so since trace elements can be present in a crystalline material in a variety of topochemical situations: from interstitially or substitutionally "dissolved" states to coherent and incoherent segregations and on to grain boundary precipitates, pore fillings or heterogeneous impurities and inclusions. It should also be mentioned that no material is known to the authors which does not exhibit a dependence of some of its properties on the content of some minor or trace elements.

Furthermore, ultrapurity and effects of ultratraces (at the sub-μg/g-level) play an increasingly important role for many high tech materials and relevant examples are not limited to microelectronics applications. The complexity in materials development is further increased by modern composite materials with a wide spectrum of different phases, fibres, whiskers, dispersoids, bubbles, pores which can contribute to the special design of a tailor-made material for a specific application. No doubt, this complexity needs the instrumental potential and the knowledge and expertise of materials analysts to a rising extent for a fruitful future materials development as well as for a competent quality control of high tech constructions.

References

[1] F. R. Güntsch, *VDI-Berichte* **1990**, *797*, 3.

[2] R. Stickler, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 4* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1990, p. 273.

[3] B. Schönwald, J. Kuhn, *Technische Mitteilungen Krupp* **1989**, *2*, 55.

[4] M. Grasserbauer, *Surface and Interface Analysis* (Lecture manuscript), TU Vienna, 1989.

[5] H. M. Ortner, P. Wilhartitz, *Fresenius' J. Anal. Chem.* **1990**, *337*, 686.

[6] L. B. Gilman, W. G. Engelhart, *Spectrosc. Int.* **1990**, *2*, 16.

[7] B. Welz, G. Schlemmer, H. M. Ortner, W. Birzer, *Spectrochim. Acta* **1990**, *45B*, 367.

[8] B. Welz, G. Schlemmer, H. M. Ortner, *Spectrochim. Acta* **1986**, *41B*, 567.

[9] B. Welz, A. J. Curtius, G. Schlemmer, H. M. Ortner, W. Birzer, *Spectrochim. Acta* **1986**, *41B*, 1175.

[10] B. Welz, G. Schlemmer, H. M. Ortner, W. Birzer, *Spectrochim. Acta* **1989**, *44B*, 1125.

[11] B. Welz, G. Schlemmer, H. M. Ortner, W. Wegscheider, *Prog. Analyt. Spectrosc.* **1989**, *12*, 111.

[12] S. Yamada, H. Sato, *Nature* **1962**, *193*, 261.

[13] W. E. van der Linden, J. W. Dieker, *Anal. Chim. Acta* **1980**, *119*, 1.

[14] M. Grasserbauer, P. Wilhartitz, H. M. Ortner, E. Kny, *Int. J. Refract. and Hard Met.* **1986**, *5*, 30, 88, 135.

[15] M. Grasserbauer, collaboration with Plansee, sponsored by the Austrian Ministry for Science and Research.

[16] F. Jeglitsch, *Pract. Metallogr.* **1989**, *26*, 389.

[17] G. Petzow, *Ber. Bunsenges. Phys. Chem.* **1989**, *93*, 1, 1173.

[18] K. H. Knapp, *Techn. Rundschau* **1989**, *35*, 199.

[19] H. M. Ortner, *Erzmetall* **1982**, *35*, 555, 613.

[20] H. M. Ortner, in: *Analysis of High Temperature Materials* (O. van der Biest, ed.), Appl. Science Publ., New York-London, 1983, p. 1.

[21] H. M. Ortner, W. Blödorn, G. Friedbacher, M. Grasserbauer, V. Krivan, A. Virag, P. Wilhartitz, G. Wünsch, *Mikrochim. Acta [Wien]* **1987**, *I*, 233.

[22] K. K. Schulze, *J. Met.* **1981**, *33*, 33.

[23] J. A. C. Broekaert, T. Graule, H. Jenett, G. Tölg, P. Tschöpel, *Fresenius' Z. Anal. Chem.* **1989**, *332*, 825.

[24] H. M. Ortner, P. Wilhartitz, B. Lux, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 4* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1990, p. 279.

[25] H. M. Ortner, P. Wilhartitz, M. Grasserbauer, A. Virag, G. Friedbacher, *Final Report of COST*, 503/I, Group 2, Project A-3, 1988.

[26] W. Schedler, *Hartmetall für den Praktiker* (Plansee Tizit GmbH, ed.), VDI Verlag, Düsseldorf, 1988.

[27] R. Storf, *Das Drehen* (Plansee Tizit GmbH, ed.), VDI Verlag, Düsseldorf, 1987.

[28] U. Deker, *Bild der Wissenschaft* **1986**, *7*, 86.

[29] T. J. Shaffner, *Semicond. Int.* **1989**, *2*, 98.

[30] P. Wilhartitz, H. M. Ortner, R. Krismer, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 3* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1989, p. 575.

[31] P. Wilhartitz, H. M. Ortner, R. Krismer, H. Krabichler, *Mikrochim. Acta [Wien]* **1990**, *II*, 259.

[32] R. Kiessling, *Non-Metallic Inclusions in Steel, Part V*, The Institute of Metals, London, 1989.

[33] R. Danzer, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 2* (H. Bildstein, H. M. Ordner, eds.), Tyrolia, Innsbruck, 1989, p. 183.

[34] H. M. Ortner, V. Sychra, *Colloquium Spectroscopicum Internationale, Vol. 2*, Institut für Spektrochemie und angewandte Spektroskopie, Dortmund, 1985, p. 346.

[35] H. M. Ortner, W. Birzer, B. Welz, G. Schlemmer, A. J. Curtius, W. Wegscheider, V. Sychra, *Fresenius' Z. Anal. Chem.* **1986**, *323*, 681.

[36] H. M. Ortner, P. Wilhartitz, J. Dolezal, R. Hlavac, P. Püschel, V. Sychra, *European Patent Application No. 89203293.9*, Metallwerk Plansee GmbH, Reutte, Austria.

[37] *Molybdenum*, Metallwerk Plansee GmbH, Reutte, Austria, 1989.

[38] G. Leichtfried, Metallwerk Plansee GmbH, Reutte, Austria (personal communication).

[39] *TZM, A High-Temperature Molybdenum Alloy*, Metallwerk Plansee GmbH, Reutte, Austria, 1986.

[40] E. Pink, *Int. J. Refractory and Hard Metals* **1986**, *5*, 192.

[41] R. Eck, *Metall* **1979**, *33*, 819.

[42] Y. Fukasawa, T. Matsumoto, S. Ogura, H. Koizumi, in: *Proceedings of the 11th International Plansee Seminar 1985, Vol. 1* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1985, p. 295.

[43] *HT-Molybdenum*, Metallwerk Plansee GmbH, Reutte, Austria, 1979.

[44] R. Eck, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 1* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1989, p. 1047.

[45] H. Rystad, W. Hoffelner, in: *Proceedings of the 11th International Plansee Seminar 1985, Vol. 2* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1985, p. 1.

[46] G. Leichtfried, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 1* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1989, p. 1023.

[47] M. Endo, K. Kimura, T. Kolagawa, S. Tanabe, H. Seto, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 1* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1989, p. 37.

[48] D. Härdtle, R. Schmidberger, in: *Proceedings of the 12th International Plansee Seminar 1989, Vol. 1* (H. Bildstein, H. M. Ortner, eds.), Tyrolia, Innsbruck, 1989, p. 53.

[49] P. Püschel, Z. Formanek, R. Hlavac, D. Kolikova, V. Sychra, *Anal. Chim. Acta* **1981**, *127*, 109.

[50] *Weta-82, Tungsten Tube Electrothermal Atomizer for Atomic Absorption Spectrometry*, Company Brochure of Laboratorni Pristoje, K. p., Prague, CSFR, 1982.

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