Performance Report 1999/2000

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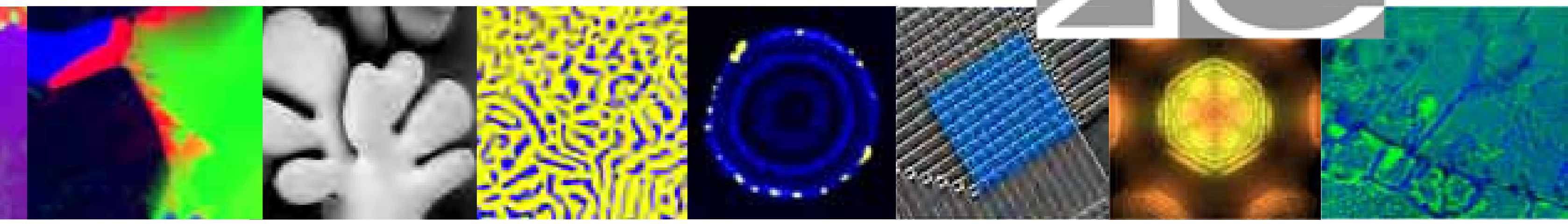

Performance Report 1999/2000

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Forschungsinstitut für Elektronenmikroskopie
Technische Universität Graz

Zentrum für Elektronenmikroskopie Graz

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Preface

This performance report contains an overview of accomplishments of the Research Institute for Electron Microscopy (FELMI) of the Graz University of Technology for the period 1999 to 2000. In addition it includes activities of the Center for Electron Microscopy Graz (ZFE Graz). The ZFE is operated by the "Verein zur Förderung der Elektronenmikroskopie und Feinstrukturforschung" and works in close liaison with the FELMI.

The reason to publish a performance report for the first time in institute history is twofold: First of all, we proudly celebrate 50 years of electron microscopy activities at the Graz University of Technology. It started in 1951 with the "Forschungsstelle" led by Fritz Grasenick, a central electron microscopy facility on the TU Graz campus that was possessing only one instrument. Over the decades it evolved into an exceptionally well-outfitted microscopy facility of European format.
Secondly, with the purchase and installation of the first analytical high-resolution field emission transmission electron microscope in Austria in December 2000, the FELMI-ZFE has made a huge leap forward, worthwhile to dedicate a section of this report to the present status and some future prospects of the department.
In the final chapter we have furthermore included a few abstracts, which shall highlight the broad range of our collaborations with other university institutes and companies over the last two years.

Ferdinand Hofer and Peter Golob

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1. 50 Years Electron Microscopy in Graz

Back in the year 1949, inspired by a suggestion of Professor B. Baule, the senate of the Technical University in Graz (formerly known as "Technische Hochschule") made a trend setting and far-reaching decision: An industrial donation over 100,000 Austrian Schillings, meant as an acknowledgment for organizing the first international congress on powder metallurgy at the TH Graz, was not evenly divided up between different at that time rather poorly equipped departments, but instead was supposed to provide the financial basis for the acquisition of an electron microscope. With large foresight people had sensed the possible impact of electron microscopy on natural and material sciences, thereby laying the foundation-stone for a state-of-the-art research unit, which –up till today- serves both the university and many industry partners.

In order to properly implement and represent this unit, in the year 1950 a committee was formed, consisting of Profs G. Jantsch, G. Hüttig, K.W.F. Kohlrausch and P. Klaudy. This committee unanimously agreed to establish a special research center for electron microscopy ("Forschungsstelle für Elektronenmikroskopie") with a so far unprecedented status. Unlike other conventional university institutes, the primary function of the center was supposed to be cooperative research rather than teaching, and furthermore, since electron microscopy was judged to be substantial for any research area, the committee refrained from a faculty allocation of the center.

From the very beginning on, one of the prime goals for the research institute of electron microscopy was to establish itself as a sympathetic listener to the various needs of electron microscopy in different research areas. Out of this understanding, the first head of the unit consequently should not come from another university department, but instead should qualify as somebody having expertise in electron microscopy plus a decent perception of the economic interests of the institute. An external advisory board was installed (including Prof. W. Glaser, Vienna) which helped finding such a suitable personality for this position – Dr. Fritz Grasenick. One was also aware that for an efficient operation, a highly qualified and well-trained staff would be needed and that employees should obtain possibilities for long-term positions.

With the help of the donation, the microscope model "Übermikroskop UEM100", engineered by Siemens & Halske Inc. in Berlin, was ordered at the "high price" of 500,000 Schillings. The instrument was finally delivered and installed in March 1951. It carries the inventory #1 of the research center.

The inauguration ceremony of the research center for electron microscopy took place on the 30th of June 1951 in the context of a symposium with the participation of numerous international capacities, like Ernst Ruska (the later Nobel price winner) Berlin, Bodo v. Borries Düsseldorf, Walter Glaser Vienna and Otto Wolf from Siemens Halske Berlin. The provincial governor of Styria, as well as the head of the TH Graz joined the symposium as well.

In its first years of existence extraordinary difficulties had to be overcome:
Despite the joint efforts from all faculties of the two Graz universities, there was hardly a possibility to raise further money for the research center. Only in 1961, a second electron microscope, funded by the Austrian Ministry for Science and Art, could be afforded. However, since the ministry to some extend supported the tremendous efforts in Graz to keep the research center alive, it very slowly started generating stuff positions. And although the Technische Hochschule made some rooms available, it became clear very quickly that in order to financially cover the necessary investments in equipment and maintenance, the research center had to generate additional income through industrial collaborations. Numerous successful projects for instance with foreign partners like Du Pont, Degussa and

the Int. Kautschukbüro, finally encouraged public institutions like the ministry for trade, the provincial government of Styria and the chamber of commerce also to subsidize the research center.

The rapidly increasing interest and the rising demand in electron microscopic investigations soon made it necessary to expand both in personnel and in equipment. For this purpose it was thought to be useful to combine and represent the interests and promotional efforts of all partners in a special foundation – the "Verein zur Förderung der Elektronenmikroskopie". First thoughts concerning such a foundation have been brought up by Dipl.-Ing. J. Fränzel, director of the Ebenseer Solvaywerke. Through his company, he greatly helped the foundation growing and provided financial and a lot of ideal support.

After careful consideration of all pros and cons and the impact of such a foundation for the universities in Graz, Professor Koren finally chaired the inaugural meeting on June 24th, 1959. Joseph Krainer, the provincial governor of Styria, was elected the first president of the "Verein zur Förderung der Elektronenmikroskopie". Important industrial and public institutions soon joined the "Verein": Böhler, Ebenseer Solvaywerke, Plansee, Semperit, Veitscher Magnesitwerke, the Chamber of Commerce to name just a few. Furthermore, the "Verein" also installed an advisory board consisting of members both from academia and industry. This board should represent the research unit in front of the faculties, sense new developments and implement necessary changes and infrastructures.

In order to underline the faculty and university independent character of the research center, it was renamed into "Forschungszentrum der Hochschulen in der Steiermark". In parallel, the foundation established the so-called "Zentrum für Elektronenmikroskopie (ZfE) Graz" with the status of a private industrial non-profit organization.
The close connection between the two institutions is documented by the fact that it was conducted by one director only, who primarily had to act as a mediator between scientific research and industrial needs.

One of the ZfE´s main efforts was to steadily advance the overall infrastructure of the microscopy site while carefully coordinating between all interested parties. A special success of these efforts was the financing of a new building via ERP credits. This credit allowed the closely cooperating research center and the ZfE to move into one building in 1965. The importance of the ZfE for the development of electron microscopy in the Graz area cannot be overemphasized. Most of today's infrastructure, including a large number of electron microscopes as well as the entire specimen preparation equipment has been financed through the ZfE solely. Up until 1983, funding for electron microscopes by the federal ministry of science was rather poor. Apart from the microscope bought in 1961, the governmental department had only financed one additional microscopy related piece of equipment. Successful cooperation between the two cooperating institutions therefore was - and still is- absolutely essential, and mutually beneficial.

In 1980, after the new university organization law UOG75 took place, the research center was given a different organizational structure and the status of a "special university facility for electron microscopy" called "Forschungsinstitut für Elektronenmikroskopie (FELMI)". At the same time, a senate was authorized to represent FELMIs interests at the ministry and university. These administrative changes facilitated the purchase of two new modern electron microscopes, financed by the responsible governmental department. After Dr. Herwig Horn became head of the FELMI-ZfE in 1982, the first analytical transmission electron microscope was bought in 1983 and only one year later an analytical scanning electron microscope followed.

After the director position was handed over to Professor Wolfgang Geymayer in the year 1989, an additional transmission electron microscope could be installed. However, all analytical accessories for this instrument have been charged to the ZfE foundation itself. This type of “mixed financing” was also applied to the purchase of another modern field emission scanning electron microscope in 1995, clear evidence for the efficient cooperation between the two units.

Slowly the Austrian universities were given more rights and responsibilities, a circumstance that made it possible to link the two units FELMI-ZfE contractually even more tightly with each other, to the benefit of both academia and industry. While in the early days the focus of research for the electron microscopy facility was mainly lying on the improvement of specimen preparation techniques and equipment, nowadays it has shifted more towards a comprehensive understanding of material properties using micro- and nanoanalytical characterization techniques. According to this trend, one of the latest investments was the acquisition of a high-end field emission transmission electron microscope with exceptional analytical additions. This instrument once more underlines the advantages of such a constellation and ensures international competitiveness of the FELMI-ZfE in the field of electron microscopy for the future.

1961:
Landesrat Prof. Hanns Koren (right) looks at the ÜM100, with Dr. Fritz Grasenick (2. from left) and Dr. Erich Jakopic (3. from left).

1967:
The Austrian Cancellor Dr. Josef Klaus (left) is looking at an electron microscopical preparation unit which is explained by Dr. Fritz Grasenick (right).

1978:
The Austrian Minister for Science and Research Dr. Herta Firnberg (2. from left) visits the institute; with Dr. Jakopic (1.from left), Dr. Fritz Grasenick (3.from left).

1982:
The Austrian Federal President Dr. Rudolf Kirchschläger (4. from left) and the provincial governor Dr. Josef Krainer (2. from left) meet the former heads of institute Dr. Herwig Horn (1. from left), Dr. Fritz Grasenick (5. from left) and Dr. Wolfgang Geymayer (6. from left).

50 Jahre Elektronenmikroskopie in Graz

Angeregt durch einen Vorschlag von Prof. B. Baule hat der Senat der damaligen Technischen Hochschule in Graz im Jahr 1949 eine weitreichende und zukunftsweisende Entscheidung getroffen: Eine Industriespende als Anerkennung für die Abhaltung des ersten Internationalen Kongresses über Pulvermetallurgie an der TH Graz in Höhe von 100.000,-- Schilling wurde nicht wie erwartet auf die damals ohnehin nur sehr dürftig ausgestatteten Institute aufgeteilt, sondern als Grundstein für die Anschaffung eines Elektronenmikroskops bereitgestellt. Mit großem Weitblick hat man schon zum damaligen Zeitpunkt die Bedeutung der Elektronenmikroskopie für die Entwicklung der Natur- und Materialwissenschaften erkannt und damit den Grundstein für eine Forschungseinrichtung gelegt, die bis zum heutigen Tag ihre Spitzenstellung gewahrt hat und nach wie vor sowohl den Universitäten als auch der Industrie zur Verfügung steht.

Zur Verwirklichung des Vorhabens wurde im Jahr 1950 durch einstimmigen Kollegiumsbeschluß die Forschungsstelle für Elektronenmikroskopie geschaffen sowie ein Ausschuß (Kuratorium) bestehend aus den Professoren G. Jantsch, G. Hüttig, K.W.F. Kohlrausch und P. Klaudy gebildet, der die weiteren Schritte vorbereiten und die Stelle nach außen hin vertreten sollte. Für diesen Status hat man sich entschieden, weil die Einrichtung im Unterschied zu herkömmlichen Hochschulinstituten weniger Lehraufgaben sondern vorwiegend solche der kooperativen Forschung erfüllen sollte. Da die Elektronenmikroskopie außerdem als wesentlich für die verschiedensten Fachrichtungen erachtet wurde, hat man von einer Fakultätszuordnung abgesehen.

Um eine gleichmäßige Berücksichtigung aller zu erwartenden Untersuchungswünsche zu gewährleisten sollte der zu bestellende Leiter einem anderen Hochschulinstitut weder als Leiter noch als Mitarbeiter angehören und außerdem neben Erfahrung auf dem Gebiet der Elektronenmikroskopie auch die Qualifikation zur Wahrnehmung der wirtschaftlichen Belange des Institutes aufweisen. Unter Einbindung externer facheinschlägiger Berater (u.a. Prof. W. Glaser, Wien) konnte für diese Position Dr. Fritz Grasenick gewonnen werden. Man war sich dessen auch bewußt, daß für einen effizienten Betrieb gut eingearbeitete hochqualifizierte und langfristig beschäftigte Mitarbeiter erforderlich sind.
Mit Hilfe der zur Verfügung stehenden Finanzierungsbasis wurde ein Übermikroskop ÜM100 der Fa. Siemens & Halske Berlin im Wert von 500.000,-- Schilling bestellt und mit dem für die damalige Zeit sehr hohen Betrag von 100.000,-- Schilling angezahlt. Geliefert und installiert wurde das Instrument im März 1951, es trägt die Inventarnummer 1 der Forschungsstelle.

Die feierliche Eröffnung der Forschungsstelle für Elektronenmikroskopie erfolgte am 30. Juni 1951 im Rahmen eines Festsymposiums durch Festansprachen des Landeshauptmannes der Steiermark und des Rektors der TH-Graz sowie unter Beteiligung und durch Vorträge internationaler Kapazitäten, wie Ernst Ruska (den späteren Nobelpreisträger), Berlin, Bodo v. Borries, Düsseldorf, Walter Glaser, Wien und Otto Wolf, Siemens Halske Berlin.

In den ersten Jahren waren außerordentliche Schwierigkeiten zu überwinden: Trotz des Zusammenwirkens aller Fakultäten beider Grazer Hochschulen bestand vorerst keine Möglichkeit, die Einrichtung durch Investitionen zu fördern, erst im Jahr 1961 konnte ein weiteres Elektronenmikroskop durch das Bundesministerium für Unterricht und Kunst finanziert werden. Da dieses aber den gemeinsamen Bestrebungen sehr positiv gegenüberstand, teilte es der Forschungsstelle allmählich Dienstposten zu. Wohl stellte die Technische Hochschule die Räume zur Verfügung, dennoch war es von Anbeginn an notwendig, die nötigen Investitionen und die hohen Betriebskosten durch Übernahme von industriellen Forschungsaufträgen und die daraus erzielten Einnahmen zumindest teilweise zu decken. Zahlreiche positiv abgeschlossene Arbeiten, unter anderem auch für namhafte ausländische Betriebe, wie Du Pont, Degussa, Int. Kautschukbüro usw., haben bewirkt, daß sich neben der Industrie auch öffentliche Stellen, wie das Ministerium für Handel und

Wiederaufbau, das Land Steiermark, die Kammer der gewerblichen Wirtschaft und die Arbeiterkammer, mit Subventionen beteiligt haben.

Das rasch zunehmende Interesse und die damit verbundene erhöhte Inanspruchnahme machte alsbald den Ausbau der Forschungsstelle in personeller und apparativer Hinsicht notwendig. Dafür war es sehr vorteilhaft, die Bemühungen aller fördernden Stellen zusammenzufassen, was die Gründung eines Fördervereines sinnvoll erscheinen ließ. Die ersten Vorschläge und organisatorische Überlegungen wurden durch Dipl.-Ing. J. Fränzel, den Direktor der Ebenseer Solvaywerke, eingebracht, der auch von Anbeginn an Forschungsaufträge und jährliche Zuschüsse erteilte.

Nach sorgfältiger Abwägung der Vorteile einer Vereinsgründung auch für die Hochschulen erfolgte am 24. Juni 1959 unter dem Vorsitz von Landesrat Prof. Koren die Gründungsversammlung des Vereines zur Förderung der Elektronenmikroskopie unter der Präsidentschaft von Landeshauptmann Josef Krainer. Diesem Verein traten in rascher Folge namhafte Industriebetriebe und öffentliche Institutionen, wie Böhler, Ebenseer Solvaywerke, Plansee, Semperit, Veitscher Magnesitwerke, Kammer der gewerblichen Wirtschaft u.a. bei. Weiters wurde ein Beirat gebildet, der die Darstellung der Dringlichkeiten und Ausbauwünsche der Forschungsstelle im Kollegium und in den Fakultäten übernehmen sollte. In diesem Beirat waren widmungsgemäß Kollegiumsmitglieder der Hochschulen sowie Persönlichkeiten aus staatlichen Stellen und aus der Wirtschaft vertreten. Dieses Gremium sollte auf die weitere Entwicklung steuernd Einfluß nehmen und auftretende Schwierigkeiten im Betrieb beseitigen.

Um den interfakultären und interuniversitären Charakter der Forschungsstelle zu unterstreichen, wurde sie in Forschungszentrum der Hochschulen in der Steiermark umbenannt. Demgegenüber wurde das vom Fördererverein gehaltene und abrechnungstechnisch und inventarmäßig vom Bundesteil getrennte Institut als Zentrum für Elektronenmikroskopie (ZFE) Graz bezeichnet. Durch die Personalunion des Leiters beider Institute wird die Verbindung von staatlicher und privatwirtschaftlicher Einrichtung dokumentiert und der Zielsetzung der ursprünglichen Forschungsstelle, als Mittler zwischen Forschung und Praxis zu wirken, in besonderem Maße entsprochen.

Der Verein zur Förderung der Elektronenmikroskopie stellte es sich zur Aufgabe, den Ausbau des Institutes unter Koordinierung der interessierten Stellen aus Wirtschaft und Staat voranzutreiben. Ein besonderer Erfolg dieser Bemühungen war die Beteiligung an einem durch ERP-Kredite finanzierten Neubau, welchen die beiden eng kooperierenden Institutionen, das Zentrum und das Forschungszentrum für Elektronenmikroskopie, im Jahr 1965 neben anderen Instituten beziehen konnte. Die eminente Bedeutung des Vereins für den Ausbau der Elektronenmikroskopie im Grazer Raum geht aus der Tatsache hervor, daß durch ihn neben dem Anteil am Neubau auch die gesamte Infrastruktur, eine große Zahl verschiedener Arten von Elektronenmikroskopen sowie alle Präparationseinrichtungen finanziert worden sind, während durch das Bundesministerium für Unterricht und Kunst bis zum Jahr 1983 außer dem bereits erwähnten Mikroskop aus dem Jahr 1961 nur ein weiteres Gerät im Jahr 1967 finanziert werden konnte. Das erfolgreiche Zusammenwirken der beiden Institute war und ist demnach auch ganz wesentlich auf die Aktivitäten des Vereins zur Förderung der Elektronenmikroskopie zurückzuführen.

Nach Inkrafttreten des UOG75 konnte das Forschungszentrum auf eine neue organisatorische Basis gestellt werden, indem man es im Jahr 1980 in eine „besondere Universitätseinrichtung“, das Forschungsinstitut für Elektronenmikroskopie (FELMI), überführte und die Vertretung gegenüber der Universität und dem Ministerium einer bevollmächtigten Senatskommission übertrug. Auf Grund dieser neuen administrativen Strukturen ist es gelungen, das zuständige Ministerium zu veranlassen, in kurzer Folge zwei moderne Elektronenmikroskope zu finanzieren, Nachdem die Leitung der beiden Institutionen im Jahr 1982 auf Dr. Herwig Horn übergegangen ist, wurde zunächst 1983 der

Ankauf eines Analytischen Transmissionselektronenmikroskops und im darauffolgenden Jahr der eines Analytischen Rasterelektronenmikroskops durch das Bundesministerium für Wissenschaft und Forschung ermöglicht.

Nach der Übernahme der Leitungsfunktion durch Prof. Wolfgang Geymayer im Jahr 1989 konnte 1990 ein weiteres Transmissionsgrundgerät aus Mitteln des Bundesministeriums für Wissenschaft und Forschung angeschafft werden, wobei der Verein allerdings für alle nötigen analytischen Zusatzeinrichtungen aufgekommen ist. Diese Art der Mischfinanzierung ist auch bei der Finanzierung eines modernen Feldemissions-Rasterelektronenmikroskops im Jahr 1995 durchgeführt worden, wodurch die enge Kooperation der beiden Einheiten noch verstärkt werden konnte.

Mit der Einführung der Teilrechtsfähigkeit für die Universitätseinrichtungen wurde es auch möglich, die Kooperation der beiden Institutsteile vertraglich zu untermauern und die beiden rechnerisch auch weiterhin getrennten Einheiten im Forschungsverbund FELMI-ZfE zusammenzuführen und zum Nutzen der Universitäten sowie von Industrie und Gewerbe zu betreiben. Während in den Anfangszeiten dem damaligen Stand der Technik entsprechend die Erprobung elektronenmikroskopischer Präparationsmethoden und die Entwicklung der hierfür erforderlichen Geräte die Schwerpunkte der wissenschaftlichen Tätigkeit bildeten, hat sich das Interesse seit der Einführung analytischer Techniken in der Elektronenmikroskopie zunehmend in die Richtung der umfassenden Probencharakterisierung in Mikro- und Nanobereichen verlagert. Diesem Trend Rechnung tragend betrifft der letzte, zur Zeit in Umsetzung befindliche große Investitionssprung die Anschaffung und Installation eines Analytischen Feldemissions-Transmissionselektronenmikroskops, das wiederum durch die gemeinsame Anstrengung von TU Graz und dem Verein zur Förderung der Elektronenmikroskopie finanziert werden konnte. Dieses Instrument wird den Grazer Forschungsverbund an den Leistungsstandard der internationalen Spitzeninstitutionen auf diesem Gebiet heranführen.

Philips CM20 TEM/STEM with twin lens, LaB_6 cathode, with a Gatan Imaging Filter and Noran HPGe EDX spectrometer (installed from 1989-1994)

2. The Laboratory: Present Situation and Future Prospects

2.1. Research Objectives

For both the development and application of advanced technology it is becoming increasingly important to characterize the structure of materials on the microscopic scale. Whether the interests are in diagnostic techniques for product development or applied materials research, understanding the microstructure and its relationship to the performance of the material is critical.

The FELMI of the TU Graz in cooperation with the ZFE Graz is one of the leading facilities in Europe for state-of-the-art atomic resolution microstructure and chemical analysis. With several types of microscopes, it offers a comprehensive array of advanced imaging and spectroscopy techniques for studying technologically relevant materials and associated problems.

The institute attempts to take advantage from the synergies that emerge from the various fields of research interests, from different, sophisticated experimental tools and from fundamental research and applications of these techniques performed in conjunction with companies.

Consequently, the FELMI-ZFE tries to improve existing microscopy preparation and characterization techniques and/or to develop new techniques especially in the field of materials science but on the other hand also applies these techniques to the characterization of all kinds of materials (problem solving!).

During the last two years there have been cooperations with about 60 university institutes and 100 companies (mainly from Styria but also from Europe and overseas). During this period 66 graduate and PhD students (mainly from the TU Graz) benefited from the support of the institute.

During the last decade several research groups have been established in the institute, each focussing on a specific aspect of microscopy or materials:

- Microanalysis using scanning electron microscopy and related techniques (P. Golob)
- Scanning electron microscopy (H. Waltinger)
- Transmission electron microscopy and specimen preparation (P. Warbichler)
- Analytical electron microscopy (F. Hofer)
- Microscopy of polymers and biological tissue (E. Ingolic)
- FTIR- and Raman microscopy (P. Wilhelm)
- Electrical measuring techniques (R. Eßl)
- Apparatus development (A. Aldrian)

In a meeting of the scientific and economical advisory board on May 5, 2000 this strategy has been recognized as worthwhile. Nevertheless certain profound changes in the scientific environment have caused a reorganization and shift of our activities:

- Focus on nanostructured materials
- Shift to fundamental research (quantitative simulation of experiments)
- Introduction of new characterization methods

2.2. Research Tools and New Developments (and Applications)

The research is based on sophisticated equipment operated by specialized groups. The goal is to develop group activities in the framework of existing or new collaborations thereby making sure other institutes can benefit. This is because the cost of much equipment is too high for the institute alone and secondly by the fact that research in more extended groupings will favour the exchange of knowledge, scientific results and improve the publicity of our work.

Since the FELMI-ZFE is a central facility, a significant portion of electron microscopes of the Graz University of Technology are concentrated in the institute. It is our aim to improve the instrumentation but also to further educate our scientists and operators in order to provide state-of-the-art investigations both for university institutes and companies.

Our laboratory includes one high-resolution electron microscope, two analytical transmission electron microscopes, several scanning electron microscopes as well as FTIR- and Raman microscopy. Associated techniques include energy-dispersive x-ray analysis (EDX), wave length dispersive x-ray analysis, elemental mapping, electron energy-loss spectrometry, energy-filtering microscopy, low-dose imaging, electron diffraction and many other special techniques.

In the last year one outstanding event for our institute was the delivery of the first analytical high-resolution electron microscope in Austria, which is equipped with a field emission gun (December 2000), thereby essentially improving the resolution of many methods, such as in HREM, EELS, EFTEM, STEM. This was an enormous effort, because we firstly had to establish a completely new facility in the cellar of the building in order to meet the extremely high requirements for vibrations and electromagnetic fields which are necessary for high resolution work. This was managed by Ing. A. Aldrian and his group. Secondly, we have to mention the financial effort of more than 18 Mio ATS, which was split up between TU Graz and the "Verein zur Förderung der Elektronenmikroskopie" with support from the "Forschungsförderungsfonds der Gewerblichen Wirtschaft" in Vienna.

This new instrument will be used for characterizing materials at atomic resolution. It will help to meet the challenges of new classes of materials e.g. nanostructured materials, nanoparticles and semiconducting materials and devices.

2.3. Most significant scientific results

Hereafter are summarized a few significant results obtained during the last period. Most of them have already been published in major scientific journals.

- Essential improvements in quantitative EELS and EFTEM elemental mapping by introducing new techniques such EFTEM spectrum imaging.
- Development of a novel imaging technique for polymers in a high resolution scanning electron microscope.
- Automatic analysis of submicron environmental particles was brought onto a quantitative level.
- Characterization of lung tissue of the Tyrolean Iceman Ötzi provides important information on the living conditions and environmental situation 5300 years ago.
- Successful characterization of many newly developed materials, e.g. steels with nanosized particles, nanostructured coatings, nanoparticles.

2.4. The life of the laboratory

During that period, the situation of the institute has not been idyllic, but was very difficult due to the enormous efforts to improve the instrumentation and to maintain the staff. Nevertheless, the particular situation of the institute has allowed us to overcome many of the difficulties. Indeed, thanks to the broad diversity of contracts and partnerships, we could even increase the number of PhD students and maintain the number of employees at a similar level as before.

- <u>Staff</u>
  Change of staff during the last two years has been considerable when compared with the years before. Due to several reasons we expect this situation to continue in the future.

- Hofrat tit.ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Wolfgang Geymayer was awarded the “Große Goldene Ehrenzeichen am Band” of the TU Graz on December 13, 1999.
- The head of the institute Hofrat tit.ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Wolfgang Geymayer retired on December 31, 1999. Dr. Geymayer has been a member of the institute since 1962 and he has been head of the institute since January 1, 1989.
- Oberrat Dipl.-Ing. Dr.techn. Rupert Eßl retired on December 1, 2000; Dr. Eßl was heading the working group for electrical measuring techniques.
- Ing. Gerlinde Grubbauer retired on May 1, 2000; she was working in the ultramicrotomy group since 1970.
- Ferdinand Hofer is the head of the institute since January 1, 2000.
- Dr. Gerald Kothleitner came back on August 1, 1999 from a 2 ½ year employment as researcher with Gatan R&D, Pleasanton, USA.
- Dr. Werner Grogger got a granting of a Max Kade Scholarship for performing research work at the National Center for Electron Microscopy at the LBNL Berkeley, USA (from September 1, 1999 to February 28, 2001).
- Caroline Fleischhacker (Chemical engineer) has been employed since September 1, 2000 in a project of the FELMI.
- Four new PhD students during the last two years
- Daniela Rauchenwald & Ferdinand Hofer were one of the five winners of the contest “Philips 50 years in Microscopy – Anniversary Image Contest” in 1999.

- Most significant equipment bought in 1999-2000:

  Due to the cooperation of the FELMI-ZFE equipment has been bought together, e.g.
  - Electron backscattered diffraction equipment for crystallographical investigations in the scanning electron microscope (FFF-project of the ZFE).
  - Low angle ion milling apparatus (PIPS of Gatan) for TEM specimen preparation (ZFE supported by FWF-project of the FELMI).
  - Analytical high-resolution transmission electron microscope: TECNAI F20 with a FEG, HR-STEM with HAADF detector, an Imaging Filter and an energy dispersive x-ray detector (1/3 from TU Graz, 2/3 from “Verein” supported by FFF, Vienna).

- Acceptance in the scientific community
  - F. Hofer is member of the editorial board of MICRON (International microscopy journal) and board member of the Austrian Society for Electron Microscopy (ASEM).
  - F. Hofer is “Speaker” of the Working Group “EFTEM & EELS” within the German Electron Microscopy Society (DGE), from 1999-2001.
  - Organisation of a working group meeting of the German Electron Microscopy Society (DGE) at the TU Graz, “EELS-EFTEM”, from September 18.-20., 2000 with 80 participants (mostly from abroad).
  - Collaboration with research groups from the Styrian Universities in the Special Research Programme “Electroactive Materials” started with May 1999.
  - Cooperation with the Materials Center Leoben and with the planned Polymer Competence Center in Leoben.
  - Cooperation with several European institutes within COST523 „Nanostructured materials“ from Sevilla to Helsinki.
  - The institute successfully participated in the presentation of the TU Graz at the “Hannover Industriemesse” during March 2000.
  - The number of invited talks given by members of the institute abroad increased considerably and the activities range from America over Europe to Australia and even Japan.
  - F. Hofer was invited to visit the National Center for Electron Microscopy at the LBNL in Berkeley (USA) February 1999.

- ZFE Graz is a member of the Austrian Cooperative Research (ACR) with several scientific cooperations with other ACR institutes.

2.5. Plans for the future

A major point of focus is to exploit existing instrumentation and to introduce new leading edge instrumentation. Here we will focus on the following developments:

- High performance SEM (Low vacuum SEM with field emission gun) which can be used as a kind of micro-manipulation laboratory and for investigation of "wet" samples (important for biochemistry and biotechnology).
- In order to obtain chemical bonding information at near atomic resolution, we are working on a project to extend the high resolution microscope Tecnai F20 ST with a monochromator and a high resolution spectrometer for HREELS.
- Focus ion beam apparatus for electron microscopical specimen preparation mainly for semiconducting devices and coatings on materials.
- Light microscope for automatic image analysis of large specimen areas with improved depth of field.
- Replacement of out-dated equipment which is still under usage for routine work e.g. old EDX-spectrometer or computer facilities.

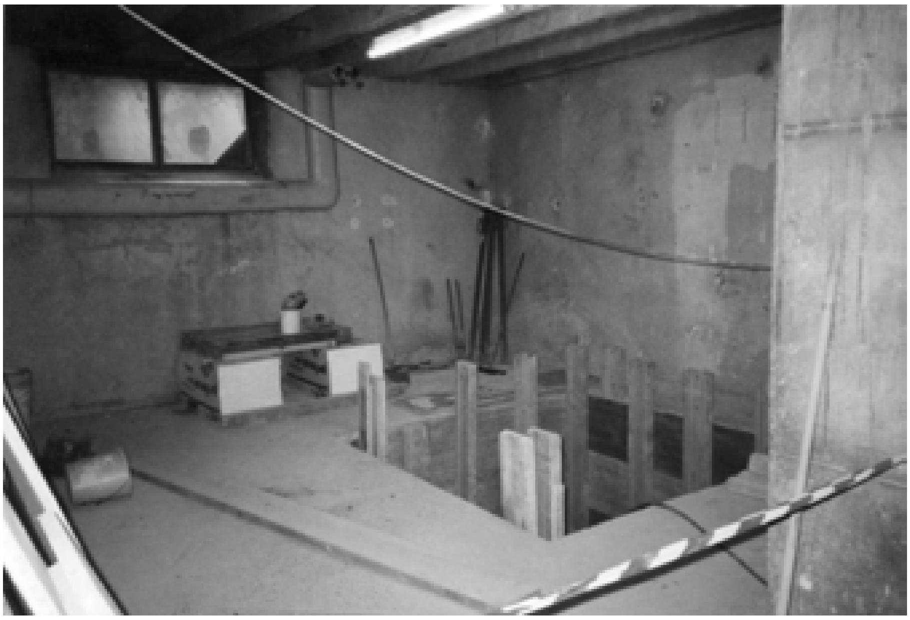
Furthermore, we hope to increase scientific exchange through cooperation with well known research institutes throughout the world. For example, we currently prepare a TMR proposal together with Dr. Asuncion Fernandez (Sevilla, Spain).

2.6. Acknowledgements

The experimental work in a scientific institute in the field of high resolution microscopy not only needs full motivation of all coworkers, but also significant financial support. Without the help of many institutions it would not be possible to provide the instrumentation, the cooperations and the results presented in this performance report. We are especially grateful to the officials of our university, the Rectors Dr. Irolt KILLMANN, O.Univ.-Prof. Dr. Hartmut KAHLERT, O.Univ.Prof.Dr. Erich HÖDL, the Vice-Rectors Hofrat Dr. Johann THEURL and O.Univ.-Prof. Dr. Hans SÜNKEL and the central administration of the university.

Financial support of our work was mainly granted by many subsidizing organisations. These are in particular the „Forschungsförderungsfonds der Gewerblichen Wirtschaft" (FFF), the Forschungsförderungsfonds der wissenschaftlichen Forschung (FWF), Austrian Cooperative Research (ACR), the Federal Ministry of Economics in Vienna and our industry cooperation partners and institutions at home and abroad.

Last but not least we must particularly thank Prof. DI Helmut LIST, Komm.Rat DI Ulrich SANTNER and Komm.Rat DI Helmut KATZENBERGER, who spend much of their valuable time supporting our work in the "Verein zur Förderung der Elektronenmikroskopie".



July 2000: Preparation of the installation of the Tecnai F20:
Construction work in the cellar of the building Steyrergasse 17

December 2000:
The Tecnai F20 already installed in the institute (in the room shown above)

Das Institut: Gegenwärtige Situation und künftige Entwicklung

2.1. Forschungsziele

Sowohl für die Entwicklung als auch für die Anwendung moderner Technologien wird es zunehmend bedeutsam, die Struktur der Materialien in mikroskopischen Bereichen zu charakterisieren. Die Interessensgebiete reichen von Diagnosen im Bereich der Produktentwicklung bis zur angewandten Materialforschung, wo die Kenntnis der Mikrostruktur und ihr Zusammenhang mit technologischen Eigenschaften von grundlegender Bedeutung ist.

Das FELMI der TU Graz in Kooperation mit dem ZFE Graz des Vereines ist eine der führenden Einrichtungen Mitteleuropas im Hinblick auf die modernsten Verfahren der Mikrostrukturuntersuchung mit bis zu atomarer Auflösung sowie der Nanobereichsanalyse von Werkstoffen. Mit einer Auswahl verschiedener Mikroskoptypen bieten wir einen umfassenden Bereich fortschrittlicher Verfahren zur Abbildung und Spektroskopie für technologische Problemlösungen.

Die wissenschaftliche Ausrichtung des Institutes zieht Vorteile aus den Synergien zwischen den verschiedenen Forschungsrichtungen, zwischen verschiedenen sich ergänzenden, anspruchsvollen experimentellen Einrichtungen sowie zwischen Grundlagenforschung und Anwendung elektronenmikroskopischer Verfahren für Industrieforschung. Dementsprechend versuchen wir einerseits die bestehenden mikroskopischen Präparations- und Charakterisierungstechniken besonders im Bereich der Materialwissenschaften zu verbessern, andererseits wenden wir diese Techniken zur Charakterisierung aller Arten von Werkstoffen, Festkörpern und technischen Produkten an.

Während der letzten zwei Jahre ist mit über 60 Universitätsinstituten und 100 Industriebetrieben kooperiert worden, wobei sich diese Aktivitäten vorwiegend auf die Steiermark, einige aber auch Europa und Übersee erstreckten. In diesem Zeitraum wurden außerdem 66 Diplomarbeiten und Dissertationen (hauptsächlich Studenten der TU-Graz) in bezug auf elektronenmikroskopische Untersuchungen betreut.

Im Laufe des letzten Jahrzehnts haben sich Forschungsbereiche entwickelt, von denen sich jeder auf einen bestimmten Aspekt der Mikroskopie an Materialien spezialisiert hat:

- Mikroanalytik am Rasterelektronenmikroskop und ergänzende Verfahren (P. Golob)
- Rasterelektronenmikroskopie (H. Waltinger)
- Transmissionselektronenmikroskopie und Probenpräparation (P. Warbichler)
- Analytische Elektronenmikroskopie (F. Hofer)
- Mikroskopie von Polymeren und biologischen Geweben (E. Ingolic)
- FTIR- und Raman Mikrospektroskopie (P. Wilhelm)
- Elektrische Meßtechnik (R. Essl)
- Geräteentwicklung (A. Aldrian)

Die bisherigen Zielsetzungen des Institutes wurden anlässlich des Treffens seines Wissenschafts- und Wirtschaftsbeirates am 5. Mai 2000 als nach wie vor richtungsweisend beurteilt und sollten als Hauptkriterien für die Festlegung der Entwicklungsrichtungen beibehalten werden. Dennoch haben uns tiefgreifende Änderungen im wissenschaftlichen Umfeld bewogen, gewisse Adaptierungen unserer Schwerpunkte vorzuschlagen und durchzuführen:

- Fokussierung auf nanostrukturierte Materialien
- Verstärkte Anwendung theoretischer Verfahren (quantitative Simulation von Experimenten)
- Einführung neuer Charakterisierungsmethoden

2.2. Instrumente und neue Entwicklungen (sowie Anwendungen)

Unsere Forschungstätigkeit verwendet sehr anspruchsvolle Einrichtungen, die durch spezialisierte Arbeitsgruppen betrieben werden. Es ist unser Bestreben die Aktivitäten dieser Arbeitsgruppen im Rahmen bereits existierender oder neuer Kooperationen zu verstärken und die Zugänglichkeit für andere Institute sicherzustellen, da einerseits die Kosten derartiger Geräte für einzelne Institute zu hoch wären, und andererseits das Arbeiten in ausgedehnteren Gruppierungen den wissenschaftlichen Austausch begünstigt und die Verbreitung unserer Ergebnisse verbessert.

Nachdem wir eine zentrale Einrichtung darstellen, ist ein Großteil der Elektronenmikroskope der Technischen Universität in unserem Institut konzentriert. Es muß daher unser Ziel sein unsere Instrumentierung ständig weiter zu verbessern sowie den Wissensstand unseres wissenschaftlichen Personals und der Bedienungsmannschaft voranzutreiben, um höchstwertige Untersuchungen sowohl für Universitätsinstitute als auch für die Industrie gewährleisten zu können.

Unser Institut umfaßte bisher zwei analytische Transmissionselektronenmikroskope, mehrere Rasterelektronenmikroskope, ein FTIR- und ein Raman-Mikroskop-Spektrometer. Die ergänzenden Verfahren erstrecken sich auf Energie- und Wellenlängendispersive Röntgenspektrometrie, Elektronenenergieverlustanalyse, energiegefilterte und elementspezifische sowie low-dose Abbildungen, Elektronenbeugung und andere spezielle Techniken.

Das für unser Institut herausragende Ereignis des letzten Jahres war die Lieferung des ersten analytischen Hochauflösungsmikroskops mit Feldemissionskathode in Österreich (Dezember 2000), wodurch das Auflösungsvermögen einer Reihe wichtiger Charakterisierungsverfahren, wie HREM, EELS, EFTEM, STEM entscheidend verbessert werden konnte. Dieses neue Instrument mußte, um die strengen Anforderungen im Hinblick auf mechanische Vibrationen und elektromagnetische Störfelder erfüllen zu können, im Keller des Institutsgebäudes installiert werden. Die hiefür erforderlichen großen technischen Vorleistungen wurden durch Ing. A. Aldrian und seine Gruppe erbracht. Es sollen aber auch die enormen finanziellen Aufwendungen von über 18 Mio. ATS hervorgehoben werden, die gemeinsam durch die TU Graz und den Verein zur Förderung der Elektronenmikroskopie mit Unterstützung durch den Forschungsförderungsfonds der gewerblichen Wirtschaft geleistet worden sind. Dieses neue Instrument wird für die Charakterisierung von Materialien bei atomarer Auflösung eingesetzt werden. Es soll helfen die Herausforderungen durch neue Klassen von Werkstoffen, z.B. nanostrukturierte Materialien, Nanoteilchen sowie Halbleitermaterialien und –bauelemente, zu meistern.

2.3. Die wichtigsten wissenschaftlichen Ergebnisse

Im folgenden werden einige wichtige Ergebnisse zusammengefaßt, die während der Berichtsperiode erarbeitet worden sind. Die meisten von ihnen wurden bereits in namhaften internationalen wissenschaftlichen Zeitschriften publiziert.

- Wesentliche Verbesserungen in der quantitativen EELS und bei EFTEM Elementverteilungsaufnahmen durch Einführung neuer Techniken wie EFTEM Spektrum Imaging.
- Entwicklung eines neuen Abbildungsverfahrens für Polymere in einem Hochauflösungsrasterelektronenmikroskop.
- Anhebung der automatischen Analyse von Umweltpartikeln in Submikrondimensionen auf ein quantitatives Niveau.
- Die Charakterisierung des Lungengewebes des Tiroler Eismannes „Ötzi“ lieferte wichtige Aufschlüsse über die Lebensgewohnheiten und die Umweltsituation vor 5300 Jahren.
- Erfolgreiche Charakterisierung von vielen in Entwicklung befindlichen Werkstoffen, z.B. von Stählen mit nanometergroßen Ausscheidungen, von nanostrukturierte Beschichtungen und Nanoteilchen.

2.4. Ereignisse und Aktivitäten im Zeitraum 1999-2000

Während des Berichtszeitraumes war die allgemeine Situation im Institut keineswegs idyllisch, sondern vielmehr geprägt von den enormen Anstrengungen, die Instrumentierung zu verbessern und den Personalstand zu halten. Dennoch ist es aufgrund der speziellen Institutsstruktur gelungen, viele dieser Schwierigkeiten zu überwinden. Dank der breiten Streuung der Projekte und Partnerschaften konnten wir sogar die Zahl der Dissertanten erhöhen und den Mitarbeiterstab auf ähnlichem Niveau wie bisher halten.

! Personal:

Der Wechsel im Personal war während der letzten beiden Jahre verglichen mit den Jahren zuvor beträchtlich, und es ist aus verschiedenen Gründen zu erwarten, das sich dies auch in Zukunft fortsetzen wird.

- Hofrat tit.ao.Univ.-Prof Dipl.-Ing. Dr.techn. Wolfgang Geymayer wurde am 21. Dezember 1999 mit dem Großen Goldenen Ehrenzeichen am Band der TU Graz ausgezeichnet.
- Der Leiter des Institutes, Hofrat tit.ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Wolfgang Geymayer trat am 31. Dezember 1999 in den Ruhestand. Er war Angehöriger des Institutes seit 1962 und wurde mit dem 1. Jänner 1989 zum Leiter ernannt.
- Oberrrat Dipl.-Ing. Dr.techn. Rupert Eßl trat am 1. Dezember 2000 in den Ruhestand. Dr Eßl leitete die Arbeitsgruppe für Elektrische Meßtechnik.
- Ing. Gerlinde Grubbauer ging am 1. Mai 2000 in Pension; sie war seit 1970 in der Arbeitsgruppe Ultramikrotomie beschäftigt.
- Ao.Univ.-Prof. Dipl.-Ing. Dr.techn. Ferdinand Hofer wurde mit 1. Jänner 2000 zum Institutsleiter ernannt.
- Gerald Kothleitner kam am 1. August 1999 von einem 2 ½ jährigen Forschungsaufenthalt als Mitarbeiter der Firma Gatan R&D, Pleasanton, USA zurück.
- Werner Grogger erhielt ein Max Kade Stipendium für einen Forschungsaufenthalt vom 1.September 1999 bis 28. Februar 2001 am National Center for Electron Microscopy am LBNL Berkeley, USA.
- Caroline Fleischhacker ist seit 1. September 2000 im Rahmen eines Projektes als Chemotechnikerin am Institut beschäftigt.
- Daniela Rauchenwald & F. Hofer waren unter den 5 Gewinnern des von Philips ausgeschriebenen Wettbewerbes “Philips 50 Years in Microscopy – Anniversary Image Contest” im Herbst 1999.
- Vier neue Dissertanten während der letzten beiden Jahre.

! Die wichtigsten im Zeitraum 1999-2000 erworbenen Geräte:

Im Rahmen der Kooperation zwischen FELMI und ZFE konnten wesentliche Investitionen gemeinsam durchgeführt werden, z.B.

- Rückstreu-Elektronen-Beugung für kristallographische Untersuchungen am Rasterelektronenmikroskop (FFF-Projekt am ZFE).
- Flachwinkel Ionendünnungs-Apparatur (PIPS von Gatan) für die TEM-Probenpräparation (ZFE unterstützt durch ein FWF-Projekt des FELMI).
- Analytisches Hochauflösungs-Transmissionselektronenmikroskop: TECNAI F20 mit FEG, HR-STEM mit HAADF-Detektor, Imaging Filter und Energiedispersivem Röntgenspektrometer (1/3 von der TU Graz, 2/3 vom Verein zur Förderung der Elektronenmikroskopie mit Unterstützung durch den Forschungsförderungsfonds der Gewerblichen Wirtschaft, Wien).

! Einbindung in die wissenschaftliche Gemeinschaft:

- F.Hofer ist Mitglied des Herausgeberrates von MICRON (Internationale Mikroskopie-Zeitschrift) und Vorstandsmitglied der Österreichischen Gesellschaft für Elektronenmikroskopie (ASEM).

- F.Hofer ist von 1999 bis 2001 Sprecher der Arbeitsgruppe „EFTEM&EELS“ innerhalb der Deutschen Gesellschaft für Elektronenmikroskopie (DGE).
- Organisation des Arbeitskreistreffens „EELS-EFTEM“ der Deutschen Gesellschaft für Elektronenmikroskopie (DGE) vom 18.-20. September 2000 an der TU Graz mit 80, vorwiegend ausländischen, Teilnehmern.
- Zusammenarbeit mit Forschungsgruppen der Steirischen Universitäten im Spezial-Forschungsbereich „Elektroaktive Stoffe“ seit seinem Start im Mai 1999.
- Kooperation mit dem Material Center Leoben und dem in Planung befindlichen Polymer Kompetenzzentrum in Leoben.
- Kooperation mit mehreren Europäischen Instituten von Sevilla bis Helsinki im Rahmen des Programmes COST523 „Nanostructured materials“.
- Erfolgreiche Teilnahme des Institutes an der Präsentation der TU Graz an der Hannover Industriemesse im Mai 2000.
- Beträchtliche Zunahme der Zahl der eingeladenen Vorträge von Institutsmitgliedern im Ausland, wobei die Aktivitäten von Amerika über Europa bis Australien und Japan reichen.
- F. Hofer war im Februar 1999 für einen Forschungsaufenthalt zu Gast im National Center for Electron Microscopy am LBNL in Berlely, USA.
- Das ZFE ist Mitglied der Austrian Cooperative Research (ACR) und betreibt wissenschaftliche Zusammenarbeit mit mehreren anderen ACR Instituten.

2.5. Pläne für die Zukunft

Die Verwertung und Ausdehnung der Potentiale der nunmehr bestehenden Instrumentierung sowie neue zukunftsweisende Verfahren aufzubauen ist für das Institut von größter Bedeutung. Erweiterungsinvestitionen sollten sich vor allem auf folgende Entwicklungen fokussieren:

- Hochleistungs-Rasterelektronenmikroskop (Nieder-Vakuum Gerät mit Feldemissions-Kathode), das als eine Art von Mikro-Manipulations-Labor verwendet werden kann, sowie zur Untersuchung feuchter Proben.(Biochemie und Biotechnologie).
- Um Informationen über die Art der chemische Bindung mit nahezu atomarer Auflösung zu gewinnen, wird an einem Projekt gearbeitet, mit dem Ziel das Hochauflösungsmikroskop TECNAI F20 ST mit einem Monochromator und einem Hochauflösungs-Spektrometer für HREELS aufzurüsten.
- Focus Ion Beam System für die elektronenmikroskopische Probenpräparation vorwiegend für Halbleiterbaulelemente und Beschichtungen von Werkstücken
- Lichtmikroskop für die automatische Bildanalyse von ausgedehnten Probenbereichen unter erweiterter Schärfentiefe.
- Ersatz von veralteten Geräten, die noch für Routinearbeiten im Einsatz stehen, wie z.B. altes EDX-Spektrometer oder spezielle Computerkomponenten.

Weiters bemühen wir uns über unsere Kooperation mit namhaften Forschungsinstituten aus aller Welt den Austausch von Wissenschaftern zu verstärken. Gegenwärtig wird z.B. ein TMR-Ansuchen gemeinsam mit Dr. Asuncion Fernandez (Sevilla, Spanien) vorbereitet.

2.6. Dank

Das experimentelle Arbeiten auf dem Gebiet der Hochauflösungselektronenmikroskopie in einem Forschungsinstitut wie dem unseren setzt über die volle Motivation aller Mitarbeiter auch beträchtliche finanzielle Unterstützung voraus. Ohne die Hilfe vieler Institutionen wäre es nicht möglich gewesen, die Instrumentierung, die Kooperationen und die Resultate, wie sie in diesem Leistungsbericht geschildert werden, zu erreichen. Besonderen Dank schulden wir daher den Repräsentanten unserer Universität, den Rektoren Dr. Irolt Killmann, O.Univ.-

Prof. Dr. Hartmut Kahlert, O.Univ.-Prof, Dr. Erich Hödl, den Vizerektoren Hofrat Dr. Johann Theurl und O.Univ.-Prof. Dr. Hans Sünkel sowie der zentralen Universitätsverwaltung.

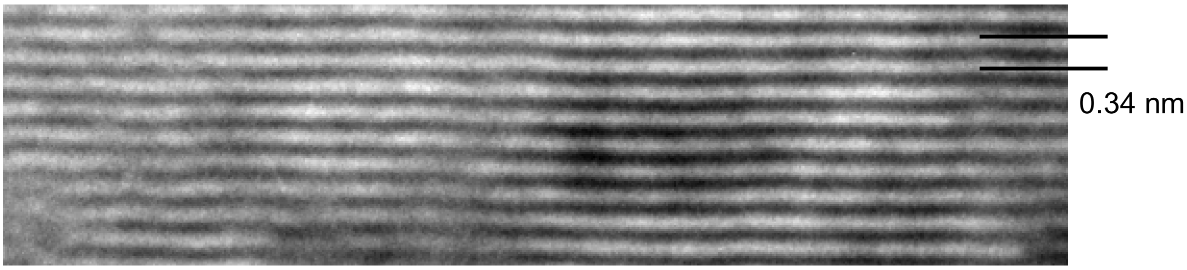
Finanzielle Unterstützung unserer Arbeit wurde in der Hauptsache durch fördernde Organisationen gewährt, vor allem durch den Forschungsförderungsfonds der gewerblichen Wirtschaft (FFF), den Forschungsförderungsfonds der wissenschaftlichen Forschung (FWF), über die Austrian Cooperative Research (ACR) das Bundesministerium für Wirtschaftliche Angelegenheiten, durch unsere Kooperationspartner aus der Industrie sowie aus dem Universitätsbereich hierzulande und im Ausland.

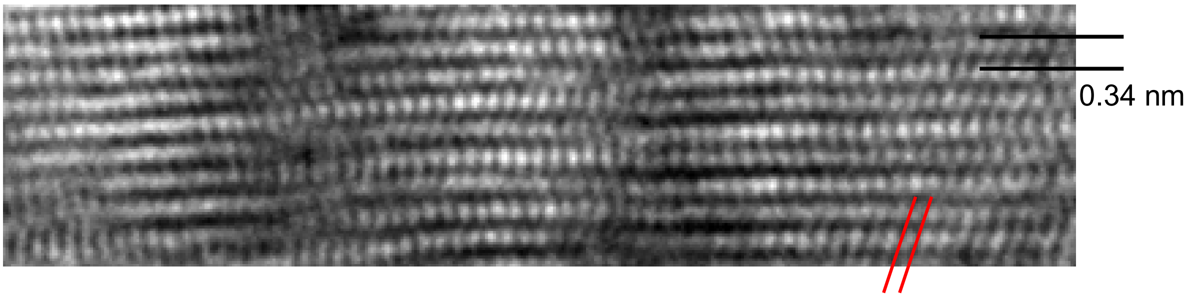
Abschließend, aber nicht zuletzt, danken wir ausdrücklich Prof. Dipl.-Ing. Helmut List, Komm.Rat. Dipl.-Ing. Ulrich Santner und Komm.Rat DDipl.-Ing. Helmut Katzenberger, die zur Unterstützung unserer Arbeit viel von ihrer wertvollen Zeit für ihre Tätigkeit im Verein zur Förderung der Elektronenmikroskopie aufgewendet haben.

Improvement of resolution with the new Tecnai F20

The high resolution TEM image of a graphite crystal viewed along [0001] is compared with an image recorded with the CM20.

recorded with CM20, 200kV, LaB$_6$, twin lens





recorded with Tecnai F20, 200kV, FEG, supertwin lens

3. Verein zur Förderung der Elektronenmikroskopie und Feinstrukturforschung

The industrial associates organisation was established in 1959 to support the institute and to facilitate greater interaction between industrial and academic scientists. On the one hand the "Verein" supported the institute in terms of improvement of instrumentation thus enabling state-of-the-art instrumentation (at least partly) which was always very important because of the limited resources of the university. On the other hand it allowed to maintain a high skilled and well trained permanent staff in the Center for Electron Microscopy Graz (ZFE Graz). The ZFE Graz is member of the "Austrian Cooperative Research" (ACR) organisation and the "Autocluster Styria".

The program of the ZFE Graz is designed to provide industry with useful results from established and emerging new microscopy techniques and to keep the in-house specialists in industry in touch with the latest developments in the field.

Policies and procedures of the "Verein" and the ZFE Graz are established by a steering committee consisting of academic and industrial scientists. Since 1995 the "Verein" is headed by Professor Dipl.-Ing. Helmut LIST (AVL Graz) and presently the "Verein" has 28 members mainly from Austria.

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Präsident / President: Prof. Dipl.-Ing. Dr-Ing.h.c. Helmut LIST
1. Stellvertreter des Präsidenten: Komm. Rat Dipl.-Ing. Ulrich SANTNER
2. Stellvertreter des Präsidenten: Komm. Rat DDipl.-Ing. Helmut KATZENBERGER

Vorstand / Managing Committee:
Vorsitzender / Head: Komm. Rat Dipl.-Ing. Ulrich SANTNER
Finanzreferent / Financial referee: DDr. Wilfried SCHÖNAUER
Vertreter der TU Graz /
Representative of TU Graz: O. Univ.-Prof. Dr. Hartmut KAHLERT
Leiter des / Head of ZFE Graz: Ao. Univ.-Prof. Dipl.-Ing. Dr. Ferdinand HOFER

Rechnungsprüfer / Controller:
1. Rechnungsprüfer: Dr. Hermann PUCHER
2. Rechnungsprüfer: Mag. Erhard LAUSEGGER

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Univ.-Prof. Dr. Hartmuth KAHLERT, TU Graz
Univ.-Prof. Dr. Klaus LEDERER, Montanuniversität Leoben
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Wirtschaftlicher Beirat / Economic advisory Board

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Min. Rat Dr. K. PERSY, Bundesministerium für Bildung, Wissenschaft u. Kultur, Wien
Dipl.-Ing. Christian RAINER, Omya, Gummern
Vizerektor Dipl.-Ing. Dr. Johann THEURL, TU Graz

Members of the “Verein zur Förderung der Elektronenmikroskopie”

AMS International, Unterpremstätten
AT&S, Leoben **
AVL LIST GmbH, Graz
BC Components GmbH, Klagenfurt
BÖHLER Edelstahl GmbH, Kapfenberg *
Borealis GmbH, Linz
Brigl & Bergmeister GmbH, Niklasdorf *
EPCOS OHG, Deutschlandsberg
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MAG Maschinen & Apparatebau AG, Graz
Montanuniversität Leoben
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TÜV Österreich, Wien
Voith Paper Service GmbH, Wimpassing
Wirtschaftskammer Steiermark, Graz

* member since 2000, ** member with 2001

4. Institute Representatives and Staff / Personalstand

Head of Department
HOFER Ferdinand, Dipl.-Ing. Dr.techn., ao.Univ.-Prof.
(since January 1, 2000)
GOLOB Peter, Dipl.-Ing.Dr.techn., Ass.-Prof.

Scientific Staff
Aldrian Adolf, Ing.
Brunegger Albert, Ing.
Essl Rupert, Dipl.Ing. Dr.techn. (retired Nov 2000)
Geymayer Wolfgang, Dipl.Ing. Dr.techn. (retired Dec 99)
Grogger Werner, (n/a) Dipl.Ing. Dr.techn.
Ingolic Elisabeth, Dr.phil.
Kothleitner Gerald, Dipl.Ing. Dr.techn.
Papst Ilse, Dipl.Ing. Dr.mont.
Pölt Peter, Dipl.Ing. Dr.techn.
Rom Irmgard, Dipl.Ing. Dr.techn.**
Schröttner, Hartmuth Ing.*
Waltinger Hanns
Warbichler Peter, Dipl.Ing. Dr.techn.
Wilhelm Peter, Dr.phil.
Zedlacher, Harald Dipl.Ing.

PhD students
Gupper Andreas, Dipl.Ing. *
Mitsche Stefan, Dipl.Ing.**
Mitterbauer Christoph, Dipl.Ing.*
Schmied Mario, Dipl.Ing.**

General Staff
Bahr Peter, EM-Operator
Birnstingl Gerhard, Mechanic
Brunegger Margit, Chem.lab-assistant *
Czapek Wolfgang, Mechanic *
Dienstleder Martina, Chem.lab-assistant *
Elis Christof, EM-Operator
Fauland Evelyn, Mech.apprentice
Fleischhacker, Caroline Chem.tech.-assistant **
Freund Angela, Cleaner
Goger Sabine, Secretariat *
Grubbauer Gerlinde, Ing. * (retired May 2000)
Gusmagg Anneliese, Secretariat *
Kranzlbinder Elke, Cleaner
Markovic Helmut, Image Processing
Oberbichler Martin, Mech.apprentice
Paller Manuel, Chem.lab-apprentice
Rauchenwald Daniela, Image Processing *
Streussnig Fatima, Secretariat *
Windisch Gerhard, Design, PC- & LAN-Admin

* ZFE staff, ** supported by projects and „Teilrechtsfähigkeit"

Guests
ZAKRISSON Jenny, Chalmers University of Technology, Sweden
WEYRICH Thomas, Dr., Technische Hochschule Darmstadt, BRD
HENS Steven, University of Antwerpen, Belgium
FERNANDEZ-RAMOS Christina, University of Sevilla, Spain
ZIES Gernot, MPA Stuttgart, BRD

Back row from left:
H.Schröttner, G.Kothleitner, H.Zedlacher, H.Windisch, S.Mitsche, C.Fleischhacker, M.Paller, W.Grogger, M.Dienstleder, M.Brunegger, P.Golob, H.Waltinger, C.Mitterbauer, A.Gusmagg, M.Schmied, C.Elis, P.Warbichler, W.Czapek, G.Birnstingl, P.Bahr, P.Pölt, P.Wilhelm, D.Rauchenwald, I.Papst

Front row from left:
H.Markovic, R.Eßl, A.Brunegger, G.Windisch, F.Hofer, E.Ingolic, S.Goger, F.Streussnig, A. Aldrian, A.Gupper

5. Laboratory Facilities and Highlights of Equipment / Laboreinrichtungen und wichtigste Instrumente

Scanning Electron Microscopes

- Analytical high resolution SEM: LEO Gemini DSM986
  0.1-30 kV, field emission gun, with EDX detector Noran Voyager 3105A, with TSM EBSD detector, micro hardness tester (Anton Paar) and cryogenic specimen transfer system (developed at FELMI-ZFE)
- Analytical SEM: Philips SEM505
  1-30kV, LaB_6 cathode, EDX detector DX4 (EDAX) with ultrathin window and Microspec WDX system 2A with multilayer crystals
- Scanning electron microscope: Leitz AMR 1600
  1-30kV, W-cathode
- Scanning electron microscope: Cambridge Instruments Mark IIA
  30kV, W-cathode, with Tracor EDX-system
- Specimen stages for cryo-investigations, micro x-ray fluorescence and x-ray microscopy (developed at FELMI-ZFE)

Transmission Electron Microscopes (TEM)

- Analytical high resolution TEM: Philips TECNAI F20
  200kV, field emission gun, supertwin objective lens, STEM (0.2 nm probe) with HAADF detector, with EDX Si(Li) light element detector (EDAX) and Gatan Imaging Filter 2000 with 1kx1k CCD camera
- Analytical TEM: Philips CM20
  200kV, LaB_6 cathode, twin lens, STEM with SE detector and Gatan BF/DF detector, EDX detector (HPGe, Noran) and Gatan Imaging Filter
- Analytical TEM: Philips EM420
  120 kV, LaB_6 cathode, twin lens, STEM with BF/DF, SE and BSE detectors and EDX Si(Li) detector with Be window (EDAX), low dose unit
- Specimen holders: Philips double tilt holder, Philips cryo-transfer and cooling holder Gatan double tilt cooling holder for analytical work, low background holders, rotation and heating holders

Further Instrumentation

- FT-infrared microscope: Spectratech Advanced Analytical Microscope attached to Bomem MB series spectrometer; sample compression cell with diamond windows, ATR objective (ZnSe and Ge crystals), Sadtler spectral libraries and search software.
- Raman microscope: Renishaw 2000
  Including LEICA research microscope, with dual laser system: diode laser (782 nm, 85 mW) & HeNe laser (633 nm, 17 mW), spectrometer with holographic notch filters, CCD detector, motorized xyz stage for mapping and confocal experiments, electrochemical cell, hot-cold stage, Raman imaging.
- Light microscope: Zeiss Axioplan for observation with transmitted and reflected light with brightfield, darkfield, polarization,interference contrast(DIC),phase contrast and a Polaroid DMC Digital Microscope Camera
- Stereo light microscope Leica M Z 6 for sample-preparation
- Light microscope METAVAR (Reichert)

Electron microscopical preparation equipment

- Diamond Saw (Well)
- Diamond Saw (Buehler)
- Minimet Polisher (Buehler)
- Ultrasonic disc cutter (Gatan)
- Dimple Grinder (Gatan)
- Tripod Polisher (Southbay Technology)
- Electrolytic thinning device (Struers Tenupol)
- Low angle ion milling apparatus (developed at FELMI-ZFE)
- Ion milling and polishing system PIPS with digital zoom camera (Gatan)
- Sawing microtome (Leitz)
- Milling cutter (Reichert-Jung)
- Ultramicrotome: OmU3 (Reichert-Leica)
- Ultramicrotome: Ultracut UCT with EM FCS for low-temperature sectioning (Leica)
- Microtome Supercut 2050 for light microscopy thin sections
- Ultramicrotome Ultracut E (Reichert-Leica)
- Clean air facility DLF (Wörden)
- Plasma Cleaner (ZFE development)
- Etching and Sputtering Coater GEA005 (ZFE development)
- Cryo-preparation system EPA 101 with quadrupol mass spectrometer QMG311 (ZFE development)
- Evaporation and sputtering apparatus (ZFE development)
- Preparation system EPA101 (ZFE development)
- Electron beam evaporators (Leybold, Balzers)
- Experimental electron microscopical preparation system based on EPA101 (ZFE development)

- Computer network with 45 computers (PC, Mac, Unix)
- High quality printers for photographs

High
resolution
SEM:

LEO
Gemini
DSM986

6. Academic Education / Lehrveranstaltungen

provided by the FELMI staff at the TU Graz

No.	Sem.	Title	Type	Lecturer
511.075	WS	Measuring Errors	2 V	R. Essl
511.078	SS	Electrical Experiments	2 V	R. Essl
511.106	WS	Introduction in Measuring Techniques	1 V	R. Essl
513.038	WS	Electron Microscopy in Solid State Physics I	2 V	P. Golob
513.039	SS	Electron Microscopy in Solid State Physics II	2 V	P. Golob
535.065	WS	Analytical Electron Microscopy	2 V	F. Hofer
535.066	SS	Materials Characterization using Electron Microscopy	2 P	F. Hofer, P. Golob
535.067	WS	Special Aspects of Analytical Electron Microscopy	3 Se	F. Hofer
535.068	SS	Special Aspects of Analytical Electron Microscopy	3 Se	F. Hofer
303.018	WS	Electron Microscopy in Materials Science	2 V	G. Kothleitner
513.012	WS	Applied Physics Laboratory Course	5 P	I. Papst, W. Grogger
46 03 60*	WS	Physics Laboratory Course	6 P	I. Papst

* in cooperation with the Institut für Physik, Montanuniversität Leoben

7. Diploma Theses and Doctoral Theses / Diplomarbeiten und Dissertationen

were performed in cooperation with the „Institute of Physical and Theoretical Chemistry” of the TU Graz:

Finished diploma thesis:

MITTERBAUER Christoph (April 2000): „Analytische Elektronenmikroskopie zur Identifikation von Ablagerungen im Lungengewebe des Tiroler Eismannes“

Doctoral theses in progress:

GUPPER Andreas, Dipl.-Ing.: “Beiträge zur Charakterisierung von Polymeren”
MITSCHE Stefan, Dipl.-Ing.: „Chemische und kristallographische Charakterisierung von Mikroteilchen und dünnen Schichten im SEM“
MITTERBAUER Christoph, Dipl.-Ing.: „Charakterisierung von nanostrukturierten Materialien mittels Elektronenenergieverlustspektroskopie“
SCHMIED Mario, Dipl.-Ing.: „Charakterisierung von Mikroteilchen mittels analytischer Rasterelektronenmikroskopie”

8. Main Research Areas of the work groups / Forschungsaktivitäten der Arbeitsgruppen

The institute's main research activities are devoted to the study of the microstructure of all kinds of solids, materials and biological samples; e.g. alloys, steels, metals, ceramics, composites, minerals, polymers, nanoparticles, clusters, biological tissue. Additionally, members of the institute are actively involved in furthering the development of the methods serving these research areas. In 1999 and 2000 research funds were allocated by the FFF, ACR, the FWF within the Special Research "Electroactive materials" and COST 523.

Microanalysis using scanning electron microscopy

Scanning electron microscopy enables a nearly complete characterization of a bulk specimen: surface topography, (also quantitative, including surface roughness by use of stereo images); chemical composition (EDXS, WDXS); and the crystallographical microstructure (EBSP).

The use of a motorized stage enables also the unattended analysis of both the geometrical and chemical parameters of thousands of individual particles down to a size of around 100 nm. This is used in one of the main research topics, the analysis of aerosols and fly ash particles in biomass heating plants. Another application is the determination of the size distribution of the modifier particles in modified polypropylene.

Low voltage scanning electron microscopy (E_0 7 keV) offers both high spatial resolution and a greatly reduced X-ray generation depth. But the necessity to use the L-lines of the elements of the first transition series for the X-ray analysis entails a lot of problems. Investigations, whether a sound quantitative analysis with these lines is possible from purely fundamental physical principles, independent of the device used, forms another part of the research priorities of the SEM – group.

A new field of research, which has just started, is the determination of the crystallographic microstructure in SEM. It enables mappings of the crystallographic orientation of the angles of crystallites in a polycrystalline material, the determination of misorientation angles and of texture, and in combination with EDXS also phase analysis.

Nanoanalysis using analytical transmission electron microscopy

The mechanical, chemical or electrical properties of different materials are not only determined by the crystal structure of the perfect material, but also by their defect structure.. For example, the mechanical properties of steels depend on the type, size and distribution of precipitates, the strength of ceramics is monitored by the presence of impurity phases and the quality of semiconducting devices depends on the control of chemical and structural defects. A major research objective of the group is to correlate these physical properties to the microstructure of materials. Transmission electron microscopy (TEM) allows to obtain structural information of most solid state materials (including polymers and biological tissue) down to an atomic scale. Due to its almost continuous magnification range between 20x and 1 000 000x defects can be easily identified and studied. These investigations are supported or supplemented by analytical techniques such as electron energy-loss spectrometry (EELS), energy-filtering TEM (EFTEM) and energy-dispersive x-ray spectrometry (EDXS) which allow to analyse the elemental and chemical composition of thin samples down to a nanometer scale.

Research within the group is concentrated on improving techniques for recording EELS- or EFTEM data at high spatial resolution such as elemental mapping with EFTEM, EFTEM spectrum imaging and EELS linescans. In a second step we focus on the development or improvement of new or existing data reduction methods, e.g. quantitative analysis of EELS spectra and/or EFTEM elemental maps, interpretation and simulation of near edge fine structures (ELNES) and extended energy-loss fine structures (EXELFS) for revealing chemical bonding information from nanometer sized specimen regions.

Furthermore, we try to increase the understanding of the interaction of high energy electrons with matter which is prerequisite for quantitative analysis using EELS and EFTEM or for understanding the ultimate limits for the characterization of chemistry at near atomic scale.

Raman- and FTIR microspectroscopy

Results arising from complimentary techniques always enhance the confidence into a given information or interpretation. So one of the main goals of the Raman- and FTIR spectroscopy group is to compliment electron microscopical results with data from vibrational spectroscopy, i.e. information on the molecular structure. Especially when dealing with inorganic oxides Raman spectroscopy is a very versatile tool. On the other hand Infrared Spectroscopy is the method of choice for the identification of organic substances.

Independent scientific research within in the group is concentrated on the studies of polymers using micro Raman spectroscopy. Orientation and crystallinity of polypropylene, one of the most important synthetic materials, are of a very high interest. A lot of work is also done in order to reveal the morphological behaviour of polymer blends, and the newest research area is concerned with the description of the thermal degradation of poly (vinyl chloride).

Specimen preparation and apparatus development

The institute has a long and well known tradition in the development of electron microscopical preparation equipment. Due to these efforts we have a high standard for the preparation of which is prerequisite for the successful application of electron microscopy in materials science. The efforts devoted in the sample preparation field are clear benefits for electron microscopy work!

During the last years we concentrated on the construction of auxiliary tools, such as a specimen cryo transfer system for the LEO scanning electron microscope. In projects underway we try to improve the preparation of TEM specimens and of specimen holders both for SEMs and TEMs.

Raman microscope: Renishaw 2000 With a LEICA research microscope and a dual laser system: diode laser (782 nm) & HeNe laser (633 nm)

9. Projects at the FELMI-ZFE / FELMI-ZFE Projekte

- “Characterization of polymers using Raman microscopy”, ACR-Impulsproject for ZfE Graz, September 1, 1998 – March 31, 1999.

- “Improved preparation of metal(oxide)-polymer composites by means of cryo-ultramicrotomy for investigations in the analytical transmission electron microscope” supported by the Federal Ministry for Science and Research (BMWV), Vienna, July 1, 1998 – June 30, 1999.

- "Electron microscopical characterization of electroactive, nanostructured materials" Project F00923 within the Special Research Program “Electroactive Materials” and COST523 “Nanostructured materials”
  supported by FWF, Vienna, May 1, 1999 – April 30, 2002.

- “Improvement of nanoanalytical characterization techniques for the study of inner boundaries in materials“
  supported by FFF, Vienna, January 1, 2000 – June 30, 2001.

- “Improvement of the infrastructure of the ZFE Graz”
  supported by Federal Ministry of Economics, Vienna, until December 1999.

- „Study of polymer orientation with Raman microscopy“
  supported by FFF, Vienna, September 1, 2000 - August 31, 2002.

- „Behaviour of ash forming elements in biomass firing plants“
  supported by FWF-project P13527-TEC (in cooperation with Univ.Doz. Dr. J. Obernberger, Institut für Verfahrenstechnik, TU Graz), January 1, 2000 – December 31, 2000.

- „Aerosols in biomass firing - characteristics, development and influence“
  supported by „Bund-Bundesländer Kooperation“ (in cooperation with Univ.Doz.Dr.J. Obernberger, Institut für Verfahrenstechnik, TU Graz) June 30, 1999 – July 1, 2001.

- “Orientation imaging microscopy and phase analysis of materials“
  supported by FFF, Vienna, November 1, 2000 – October 31, 2001.

- „Surface treatment of inorganic fillers for the modification of polymers“
  supported by Federal Ministry for Science, Research and Transport (BMWV), Vienna in cooperation with Univ.Prof. Dr. Klaus Lederer, MU Leoben, January 1, 2000 – December 31, 2001.

10. Presentations at the Institute / Vorträge am Institut

24.3.1999: Prof. Dr. Bernd **KOLBESEN** (Inst. f. Anorgan. u. Analyt.Chemie, Universität Frankfurt, BRD): "Chemie, Präparation und Charakterisierung von Oberflächen und dünnen Schichten: Beispiele aus der Mikroelektronik-Technologie"

26.4.1999: Prof. Dr. Harald **ROSE** (Institut für Angewandte Physik, Technische Universität Darmstadt, BRD) "Zukünftige Entwicklungen in der hochauflösenden Elektronenmikroskopie: Korrektur von Elektronenlinsen, Utopie oder Realität?"

27.9.1999: Prof. Dr. V. **RADMILOVIC** (National Center for Electron Microscopy, Lawrence Berkeley Laboratory, Berkeley, USA) „Application of Quantitative HREM in Perfect Crystal and Interface Structure Determination“

16.9.1999: Dr. Stefan **SCHERER** (Institut für Maschinelles Sehen und Darstellen, TU Graz) "Das Rasterelektronenmikroskop als 3 D Meßgerät"

24.1.2000: Dr. Philipp **KOHLER-REDLICH** (Max-Planck-Institut f. Metallforschung, Stuttgart, BRD) „Synthese und Charakterisierung von reinen und modifizierten Kohlenstoff-Nanoröhrchen“

1. 2. 2000: Dr.Thorsten **KRAFT** (Institut für Mineralogie, Petrologie u. Geochemie, Universität Tübingen, BRD): „Hydrothermaler Kohlenstoff: Darstellung, Beschichtung, Verhalten & Analytik“

2.2.2000: Dr. Mark **RAINFORTH** (Department of Engineering Materials, University of Sheffield, U.K.) „Electron Microscopical Investigations of Steels“

15.6.2000: Prof. Dr. Renu **SHARMA** (Arizona State University, Center for Solid State Science, Tempe, USA) „In Situ Studies of Gas-Solid Reaction by Electron Energy-Loss Spectroscopy“

18.-19.9.2000 Tutorials at the Working Group Meeting “EELS-EFTEM” of the DGE
Prof. Dr. Helmut **KOHL** (Universität Münster, BRD)
Prof. Dr.Joachim **MAYER** (RWTH Aachen, BRD)
Prof. Dr. Harald **ROSE** (TU Darmstadt, BRD)
Prof. Dr. Peter **SCHATTSCHNEIDER** (TU Wien, Austria)
Dr. Richard **LEAPMAN** (NIH, Bethesda, USA)

19.10.2000: Prof. Dr. Alan **CRAVEN** (Department of Physics, University of Glasgow, U.K.) „Electron Energy Loss Near Edge Structure and the Study of Materials“

9.11.2000: Prof. Dr. Pavol **SAJGALIK** (Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia) “Silicon Nitride/Carbide Based Nanocomposites for High Temperature Applications”

9.11.2000: Prof. Dr. Ralf **RIEDEL** (Fachgebiet Disperse Feststoffe, Fachbereich Materialwissenschaften, Technische Universität Darmstadt, Germany) "Neue Hochdruckphasen auf der Basis von Siliciumnitrid**“**

28.11.2000: Fr. Cristina **FERNANDEZ-RAMOS** (Organisation ICMSE, Instituto Cien.Mat. Sevilla, Spain) „CN_x thin films prepared by magnetron sputtering“

11. Publications of members of the institute
Publikationen von Institutsmitarbeitern

1999

P. Sajgalik, K. Rajan, P. Warbichler, F. Hofer, J. Dusza
Silicon Nitride Based Nano- and Micro-Composites with Enhanced Mechanical Properties, Key Engineering Materials Vols. 159-160 (1999) 405-410

B. Mlekusch, E.A. Lehner, W. Geymayer
Fibre Orientation in short-fibre-reinforced thermoplastics; I. Contrast enhancement for image analysis, Composites Science and Technology 59 (1999) 543-545

P. Warbichler, I. Papst, F. Hofer
Mikrocharakterisierung und Nanobereichsanalytik des Schnellarbeitsstahles S 6-5-2-5, in Sonderbände der Praktischen Metallographie Bd.30,1999, 181-187 (Hg. G. Petzow)

I. Papst, P. Warbichler, F. Hofer, G. Pöckl
Analytische Transmissionselektronenmikroskopie am Beispiel des Schnellarbeitsstahles S 6-5-2-5, Werkstoffwoche 1998, Band VI; Symp.8: Metalle, Symp.14: Simulation Metalle; R.Kopp et al. (Hg.), WILEY-VCH 1999, 419-424

J. Zackrisson, W. Grogger, F. Hofer, H.-O. Andren
A comparison between EELS and APFIM for quantitative microanalysis of carbonitride grains in cermets, Ultramicroscopy 79 (1999) 273-281

P. Golob
Rasterelektronenmikroskopie und Elektronenstrahlmikroanalyse, in St. Hasse, Guß- und Gefügefehler, S13-19, Schiele und Schön, Berlin 1999

K.M. Krishnan, E. Girt, E.C. Nelson, G. Thomas, F. Hofer
Microstructure of Fe-Nd-B Alloys Taylored to Approach Theoretical Coercivity Limits, Microscopy and Microanalysis 5 (Suppl. 2), Proceedings of the Microscopy Society of America 1999, 26-27

P. Wilhelm
Fast, Easy Analysis of Polymer Failures with Confocal Raman Microscopy, Renishaw Spectroscopy Innovations, Issue 4, June 99, 1-2

P. Hofer, H. Cerjak, P. Warbichler
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P. Warbichler, I. Papst, F. Hofer, G. Pöckl
Mikrocharakterisierung und Nanobereichsanalytik des Schnellarbeitsstahles S 6-5-2-5, Prakt. Metallogr. 36 (1999) 621-630

A.V. Krajnikov, H.M. Ortner, S. Weinbruch, W. Grogger, P. Warbichler, F. Hofer, V.M. Yurchenko
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F. Hofer, W. Grogger, P. Warbichler, I. Papst
Quantitative Energy-Filtering Transmission Electron Microscopy,
Book of Abstracts EMAS 99, Konstanz (BRD), (1999) 165-18

C. Mitterer, P.H. Mayrhuber, M. Beschliesser, P. Losbichler, P. Warbichler, F. Hofer, P.N. Gibson, W. Gissler, H. Hruby, J. Musil, J. Vlcek
Microstructure and properties of nanocomposite Ti-B-N and Ti-B-C coatings,
Surface and Coatings Technology 120-121 (1999) 405-411

W. Grogger, F. Hofer, P. Warbichler, O. Leitner
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F. Hofer, W. Grogger, G. Kothleitner, P. Warbichler
Quantitative compositional imaging with energy-filtering TEM, Inst. Phys. Conf. Ser. No. 161, Electron Microscopy and Analysis Group Conf. EMAG99, Sheffield, IOP Publ. Ltd (1999) 169-174

M. Winter, H. Buqa, P. Golob, F. Hofer, J.O. Besenhard et al.
The carbon anode/electrolyte interface in lithium ion cells, ITE Battery Letters 1 (1999) 129-139

P. Pölt
Low Voltage EDXS and First Row transition Elements,
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M. Wachtler, I. Papst, F. Hofer, M. Winter, J.O. Besenhard
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I. Papst, P. Warbichler, F. Hofer, B. Schaffernak, E. Letofsky
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I. Papst, I. Rom, F. Hofer, M. Wachtler, J.O. Besenhard, M. Winter
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P.A. Barbic, L. Binder, S. Voss, F. Hofer, W. Grogger
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M.A. Pabst, F. Hofer
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P. Pölt, X-ray spectrometry in SEM and elements of the first transition series,
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J.A. Hunt, G. Kothleitner, R. Harmon
Comparison of STEM-EELS Spectrum Imaging vs. EFTEM Spectrum Imaging,

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J.H. Obenholzner, C. Siebe, H. Delgado, P. Golob
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Mitt. Naturwiss. Ver. Steiermark 129 (1999) 71-80

K. Kimoto, G. Kothleitner, J. Hunt, H. Tanaka, S. Isakozawa
EELS Performance of the HD-2000 Dedicated STEM, Optik, Suppl.8,vol.110 (1999) 9

M.A. Pabst, G. Pfeiler, E. Schöninkle, I. Papst, P. Wilhelm, K. Crailsheim, A. Hammer
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P. Pölt, M. Schmied, T. Brunner
Automated Analysis of Submicron Particles in SEM?, Proc.12th European Congress on Electron Microscopy, EUREM 2000, Brünn, I283-I284

M. Schmied, P. Pölt, J. Dahl
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G. Kothleitner, H.A. Brink
Factors affecting the performance of EELS energy-filters, Proc. 12th European Congress on Electron Microscopy, EUREM 2000, Brünn, I343-I344

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“Analytical TEM with Energy-filtered Electrons”, EMAS’99, Konstanz, BRD, May 5, 1999.

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„Verfahren zur Darstellung der Morphologie von Polymeren“, Bundesanstalt für Materialprüfung, Berlin, BRD, June 17, 1999.

P. Wilhelm
„Kunststoffcharakterisierung mit schwingungsspektroskopischen Methoden wie z.B. RAMAN- und FTIR-Mikrospektroskopie“, Montanuniversität Leoben, June 17, 1999.

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“Quantitative Compositional Imaging with Energy-filtering TEM”, JEELS ’99, Autrans, Grenoble, France, October 18, 1999.

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“Electron Spectroscopic Imaging with the GIF”, 1. Europ. Post-column Imaging Filter User Meeting, Complutense Universitat, Madrid, Spain, January 25, 2000.

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14. Abstracts of scientific main results 1999-2000
Kurzbeschreibungen wichtiger Ergebnisse 1999-2000

With the next pages we try to give an impression of the very many activities that have characterized our research during the last two years. Some contributions have been included in revised form from conference proceedings, others have been extracted from already published papers in scientific journals.

Automated Analysis of Submicron Particles in SEM ?

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Summary: Automated particle analysis of submicron particles by EDXS is possible in SEM. The main limiting parameters are specimen drift and X-ray yield, whereas analytical resolution is sufficient independent of the primary electron energy.

1. Introduction

Automated analysis of particles by SEM / EDX, especially environmental particles collected on filters, has already become commonplace[1,2], albeit generally with particle diameters greater 1 µm. But the analysis of submicron particles, both of their shape and their chemical composition, is important for the the investigation of aerosol and fly ash formation in power plants. Automated analysis in a computer controlled SEM with a motorized stage enables the unattended analysis of hundreds or even thousands of particles.

2. Results and Discussion

Contrary to phase analysis in bulk materials, for X-ray analysis of particles dispersed on filters resolution is approximately independent of the primary electron energy. The smaller the particles, the smaller the beam broadening inside the particles. The greater part of the interaction volume is inside the filter and does not contribute to the characteristic X-ray peaks of the particle. But the distance of a particle to its nearest neighbours has to be great enough, so that they are not hit by scattered electrons. Electron backscattering from carbon filters is fortunately nearly negligible. Low energies are favourable both to get an acceptable X-ray yield and a low penetration depth in case of agglomerated particles of different chemical composition. Fig. 1 demonstrates, that even particles with a diameter of around 40 nm can be successfully analyzed (point 1), although this may depend on particle density and composition. At analysis point 2, around 80 nm distant from point 1, only traces of lead were found. The ratio of Pb to Cl corresponds very well with that of $PbCl_2$. Thus the minimum size of particles suitable for analysis is mainly determined by their X-ray yield.

Fig. 1 also highlights the two other limiting effects for automated particle analysis: specimen drift and radiation damage. The cut-like shape of the damage at point 1 is caused by specimen drift during the analysis, with zero drift it would be of circular shape. Fig. 2 demonstrates, that the amount of the drift is approximately 10 nm/min, which resembles values measured by Vladár[3]. Thus for analysis times of 10 - 20 seconds for a single particle and a minimum particle diameter of 100 nm a maximum of around 20 particles per field can be analyzed by automated particle analysis. Then either drift correction has to be performed or the stage has to move to the next field. The drift was measured for typical conditions used for particle analysis, but proved to be independent of the type of specimen. Also stage movements did not change its value substantially. This fact and the higher drift rates immediately after the turning on of the SEM point to instabilities of the lens currents as the main source for the drift.

High probe currents are necessary to get an acceptable X-ray yield. This entails a high energy input into the particle. Especially environmental particles are often prone to radiation damage, and thus to a possible change in the specimen composition. Even for particles with a good heat conductivity, heat conduction may be obstructed by poor contact between particles and substrate and a poor heat conductivity of the substrate itself. Thus radiation damage can have a different impact on particles and bulk material of the same composition and structure.

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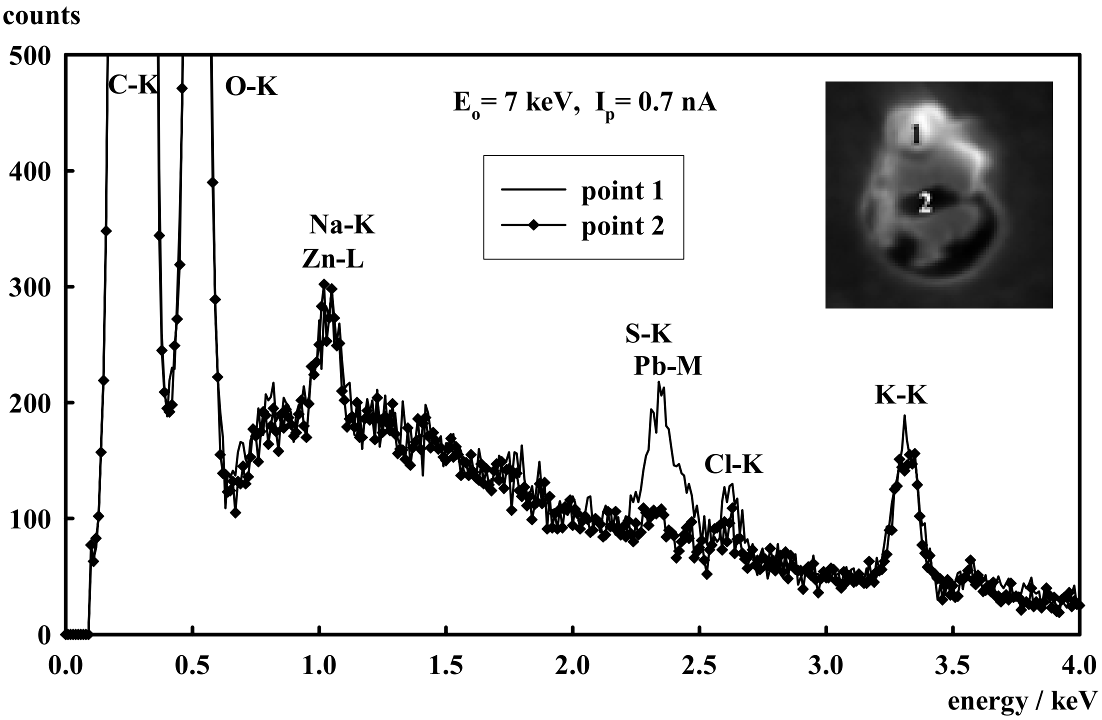

Fig. 1: EDX-Spectra recorded by spot analysis at the two points marked on the particle in the inset (biomass fly ash, picture width: 0.26 µm, image recorded after X-ray analysis).

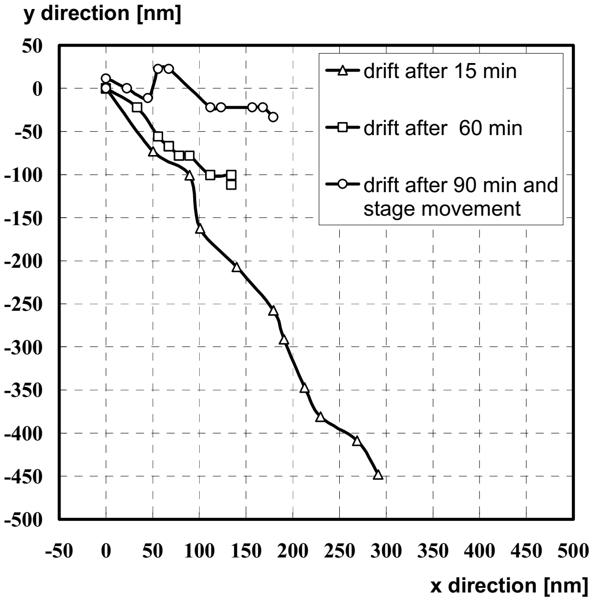

Fig. 2: Specimen drift in 30 minutes

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Standards for Analysis of Submicron Particles by SEM / EDXS

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Summary: Standards for Submicron Particle X-ray analysis have been created from various substances. The accuracy of the quantitative results is often stronger affected by specimen damage than by shortcomings of the quantification procedures with regard to particle size and shape.

1. Introduction

Conventional quantification procedures for EDXS in SEM have been generally developed for polished bulk specimens or flat films. Special correction programs for particle analysis demand an analytical expression for the particle shape and may be of little use for particles with very irregular shapes[1]. Additionally, radiation damage can affect particles and bulk specimens in a different way. Therefore it is necessary, that standard particles resemble the unknown particles both in composition and structure.

2. Results and Discussion

Certified particle standards are rather rare and cover mainly particles with diameters greater 1 µm. Conventional quantitative procedures seem to work well for glass spheres, as long as they contain no alkaline elements[2]. But unfortunately Na and K are often main elements of environmental particles, e.g. biomass fly ash. It is well known, that glasses and also feldspars containing these elements are susceptible to compositional changes by electron bombardment. But these damages may depend strongly on electron energy, probe current and especially particle size. Because of poor heat conduction between particles and substrate small particles could be heated up to very high temperatures even if the material itself has a good thermal conductivity.

Standards have been prepared by grinding glasses, minerals and pure chemicals (K_2SO_4, $PbSO_4$, $CaSO_4$, ...) in a ball mill, dispersing the particles in alcohol and subsequently filtering them through a Nuclepore® filter. The smallest particles had mean diameters d_m of around 0.2 µm. Fig. 1 demonstrates for example clearly the dependence of concentration changes caused by specimen damage both on the particle size d_m of glass particles and the electron energy E_0. Whereas particles with d_m = 10 µm show a dependence which is similar to that of bulk material, those with d_m = 0.5 µm show a strong deviation from it for higher E_0.

A similar effect is observable for K_2SO_4 (Figs. 2, 3). With increasing irradiation time the ratio of the K-K_a / S- K_a peak heights is changing. The relative height of the S- K_a peak decreases (Fig. 2). The smaller the particle, the quicker the decrease. In Fig. 3 a deviation of the measured K- and S-concentrations from the nominal ones is observed for small particles. But it is mainly caused by specimen damage[3,4] and not by shortcomings of the correction procedure. Actually there was little difference, whether PROZA correction was used or only k-ratios were calculated. The reasons for this may be the small energy difference between the absorption edges of the S- and K- K_a lines and the already rather small ZAF - corrections necessary at E_0 = 7 keV. But if one would not be aware of the extent of the specimen damage, one might interpret the deficit of S as presence of a carbonate in case of particles of an unknown composition.

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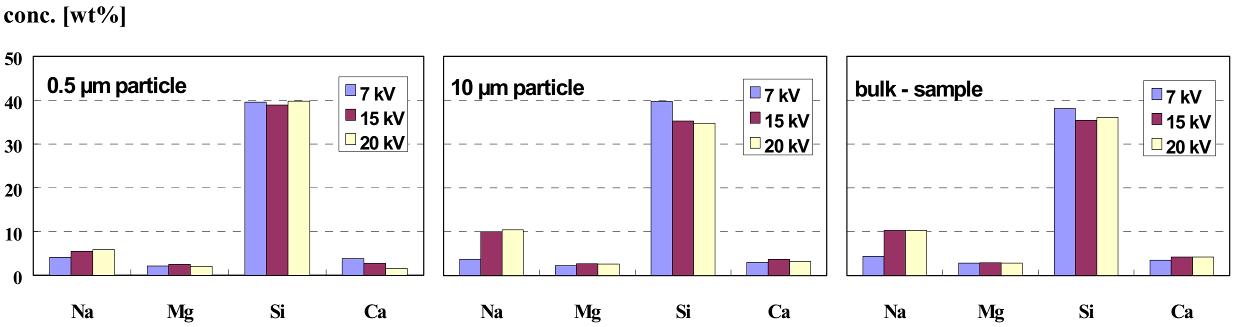

Fig. 1: EDX analysis of glass, both bulk specimen and particles (spot-mode), main elements only, oxygen by stoichiometry

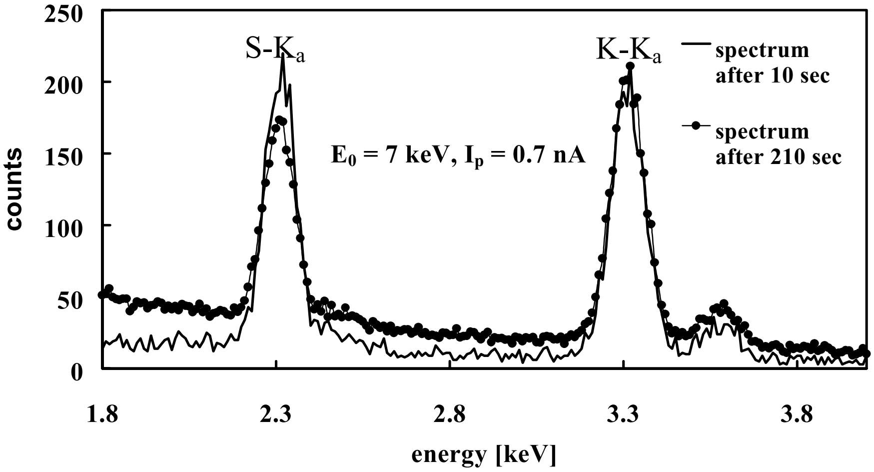

Fig. 2: Specimen demage: change of element intensities of K_2SO_4 particle (substrate: Nuclepore filter) in dependence on aquisition time (spot-mode, particle diameter: 700 nm)

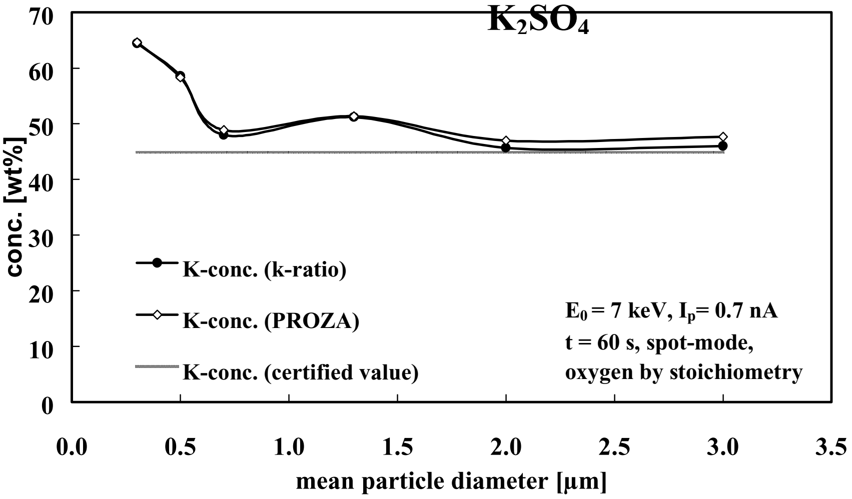

Fig. 3: Dependence of measured element conc. of K_2SO_4 on particle size, no correction for carbon coating (~ 20 nm)

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Solid Aerosols from the Plume of Popocatepetl Volcano, Mexico

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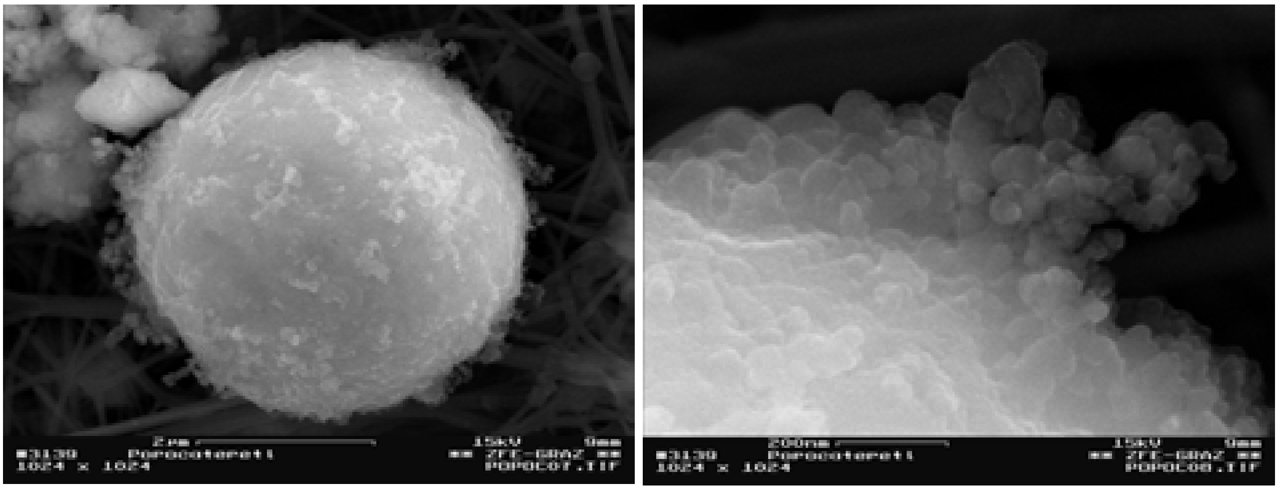
The high resolution FESEM can contribute to many problems under discussion in the fields of environmental research, earth sciences and especially to volcanology. Small particles in the environment (soil, water and air) are becoming a target for environmental planners and industry. Years ago all environmental standards had been defined by bulk geochemical analysis. For many questions, there is an urgent need to investigate what kind of particles contribute to the bulk chemical results (Laskin et a., 2000; Qian et al., 1993).

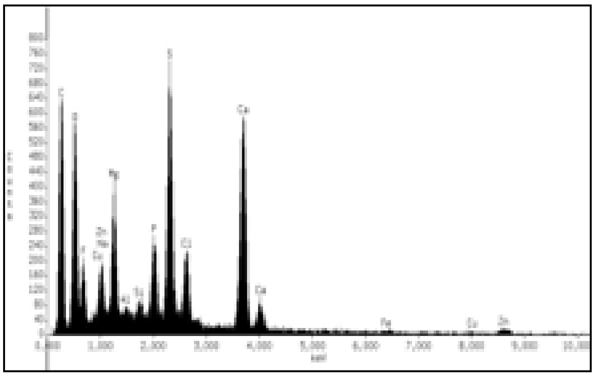
A cooperation with the Universidad Nacional Autonoma de Mexico (UNAM), the Naturhistorisches Museum (NHM)/Mineralogie and the FELMI-ZFE at the Technische Universität Graz was established to analyze fine particles and aerosols from the plume of Popocatepetl volcano, Mexico. Popocatepetl means smoking mountain in Nahuatl, the Aztec language. Popocatepetl is again in a state of activity since 1994. The activity ranges from increased fumarolic degassing, phreatic eruptions (?) to intra-crater dome growth and dome explosions, subsequently producing small pyroclastic flows. A documenation is available through the Bulletin of the Global Volcanism Network published by the Smithsonian Institution (USA).

Popocatepetl volcano is a stratovolcano, situated on continental crust on top of a subduction zone. The edifice is mantled with intermediate to dacitic lavas and pyroclastic rocks of the younger history of the volcano (Siebe et al. 1996). Lime-, dolostones and evaporites from the base of the volcano are metamorphosed by magmatic processes and can contribute to the volcanic gas budget SO_2, CO_2, HCl and HF and their reaction products (Obenholzner et al. 1998). Popocatepetl is for these reasons a laboratory volcano, which can be monitored and analyzed by state-of-the-art techniques at his (Popocatepetl is male according to local mythology) active phase.

During the early stages of the recent activity (1996) Dr. Hugo Delgado (UNAM) was able to measure volcanic gases by air-borne correlation spectrometry. This campaign was accompanied by a cascade impactor equipment to collect aerosols at the periphery of the plume. The teflon filter had been recovered and analyzed for gas condensates at the Los Alamos National Laboratory, USA and was also sent to the NHM/Mineralogie for SEM analysis and to the FELMI-ZFE Graz for FESEM analysis. Wet chemical analysis could barely detect gas condensates or rare elements, standard SEM could analyze several particels mineralogically, but was unable to document small particle aggregates and aerosols being the product of complex condensation processes. The very high resolution FESEM at the FELMI-ZFE Graz could document and partially analyze small solid aerosols (smaller 1-10µm in diameter).
This analytical work documents morphology and chemical composition of aerosols (fig. 1a & 1b, fig. 2a & 2b) and small fragments of volcanic ash.



Figures 1a and 1b (close-up) are examples of a solid aerosol from the analyzed filter. A Ca-P–O microsphere (apatite?) with traces of Fe, Cu, Zn, Si and Al formed probably during a condensation process and by passing through the plume a fluid condensed on top of the sphere. After evaporation of the fluid, dissolved matter crystallized as a scattered, complex Mg-(Na?)-S-Cl mineral.



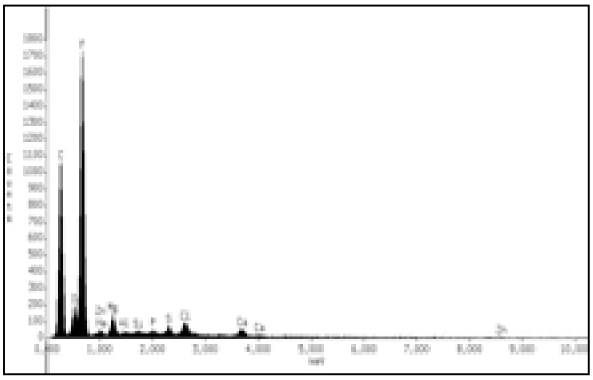


Fig. 2a EDS of fig. 1a.

Fig. 2b : EDS of close-up fig. 1b.

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Solid/Liquid Extraction of Metal Oxides with Carboxylic Acids

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Environmental legislation will lead to an increased demand of technological routes in separating heavy metals like zinc, lead or cadmium from solid bulk residues. State of the art technology is pyrometallurgical separation of the mentioned class of heavy metals by the so called Waelz process. As a matter of fact the Waelz process can not cover detoxification of solid residues with low heavy metal load of less than 15 wt% [1].
Solid/liquid extraction of metal oxides is a supplement to several pyrometallurgical processes. Due to the caustic properties of metal oxides, separation of these oxides from the solid carrier can be based on extraction with neutralisation. Application of both inorganic acids as well as carboxylic acids will result in an efficient separation of metal oxides from the carrier [2, 3]. Opposite to inorganic metal salts formed during the extraction process, metal carboxylates have limited thermal stability and therefore offer the technological route of solvent recovery by thermal degradation of the extract phase.
Solid/liquid extraction of zinc, lead and cadmium from EAF-dust with aqueous acetic acid has therefore been investigated. Acetic acid corresponds with the necessity of high rate and yield of extraction and several routes of processing the separated metal ions.

Basically extraction of lead oxide is possible quantitatively. Extraction of zinc depends on the nature of the solid bulk material. Zincite (ZnO) can be separated quantitatively too while Franklinite ($ZnFe_2O_4$) shows poor extraction properties what could be verified by means of X-ray diffraction [4] (fig.1). Morphology of the EAF-dust before and after the leaching step was determined by scanning electron microscopy, so the mean particle diameter of the filter dust and its porosity could be estimated (figs.2 and 3). To describe the extraction kinetics of zinc the best results were achieved by using the algorithm of a combined (1st / 1st) - order rate law.
The yield of extraction is based on the mass balance of the neutralisation process. It can be kept at the maximum value of solubility, independent of the feed concentration in the solid bulk phase. Mutual interaction between several heavy metal ions is limited due to similar basicity of the oxides. Interaction with the solvent shows different properties for several species. The solubility of zinc acetate decreases with increasing acid concentration while opposite the solubility of lead increases.
The rate of extraction is controlled by the chemical reaction of the oxidic substance with acetic acid. Temperature dependency is not very significant.

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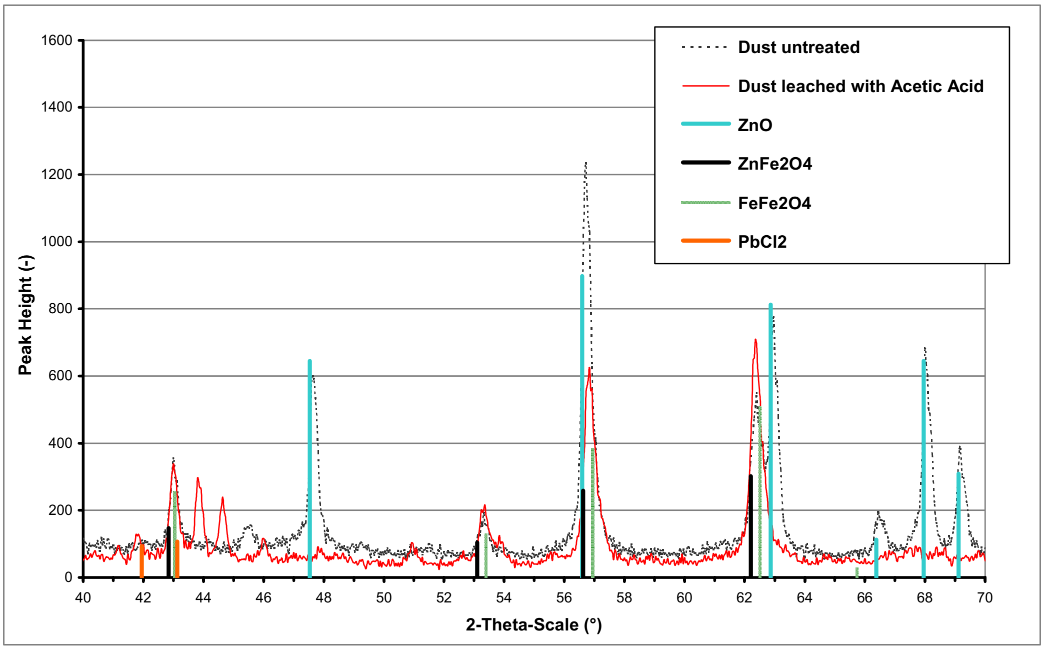

Figure 1: X-ray diffraction of untreated EAF-dust and the dust sample after leaching with acetic acid

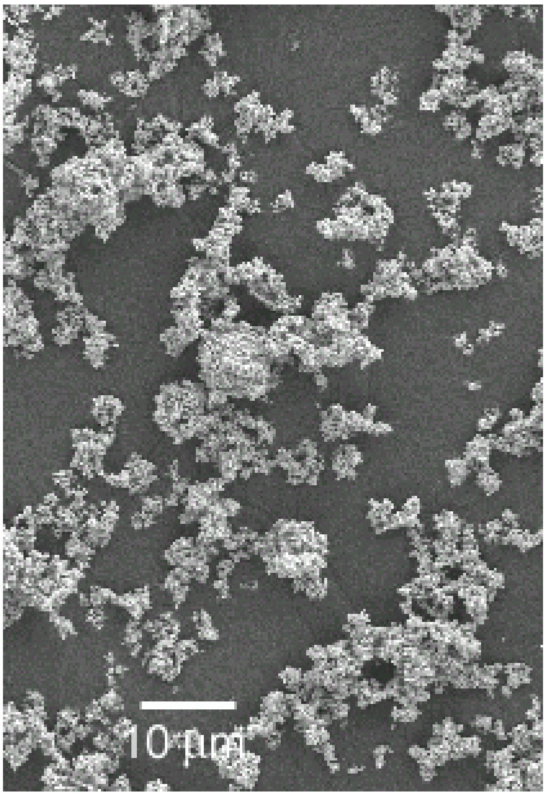

Figure 2: Scanning electron microscope image of a sample of untreated EAF-dust

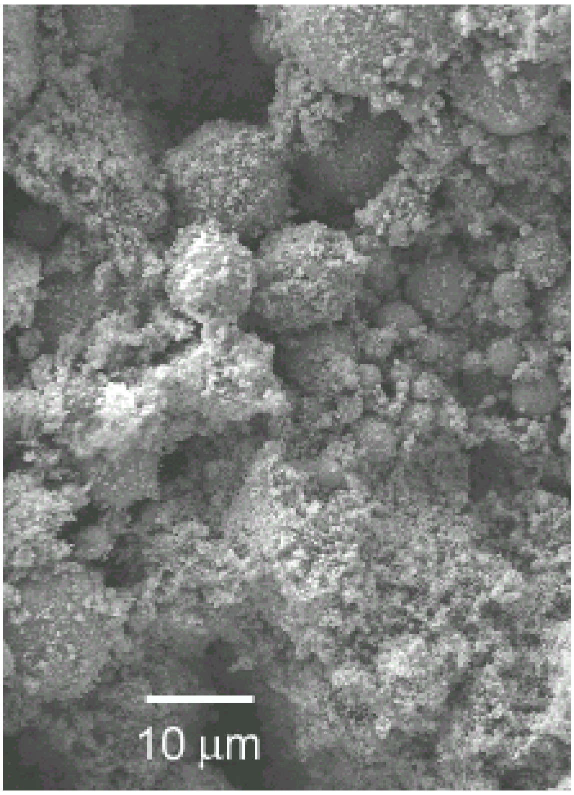

Figure 3: Scanning electron microscope image of dust sample (EAF-dust) after leaching with water

AFM and TEM Investigations of Indium Tin Oxide Thin Films

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Both transmission electron microscopy (TEM) and atomic force microscopy (AFM) are powerful tools to study the structure of materials down to the nanometer level.

Specifically we applied these two techniques to characterize an indium tin oxide (ITO) thin film on a glass substrate. ITO films feature high luminous transmittance, good electrical conductivity, excellent substrate adherence as well as hardness and chemical inertness. The samples in our investigations have been used as transparent electrodes in light emitting devices (LED) [1].

To study the surface roughness, two particular types of ITO layers have been investigated. Sample number 1 (Fig.1) was cleaned with toluene, isopropyl alcohol and acetone only, whereas sample number 2 (Fig.2) was treated with chromium-sulfuric-acid in a final step, in order to improve adhesion of the organic active layer of the LED.

For TEM, two samples have been cross-sectioned. The preparation included standard procedures like cutting, embedding into a cylinder, slicing, polishing and finally Ar^+ ion milling. The milling angles were less than 6°, and the ion beam voltage was set to 3kV to reach an end-thickness of approximately 50 nm [2]. All subsequent TEM investigations have been performed on a Philips CM 20/LaB_6 at 200kV.

For AFM the samples could be used without additional preparation and the measurements have been realized with a Digital Instruments Dimension 3100 in the TappingMode™.

Fig.1a and 2a shows the TEM bright-field images of the two differently treated ITO thin films. It is possible to see the column shaped crystals of the ITO layer (130-140nm thick). The analysis of the two displayed TEM images results in comparable surface roughness of less than 15 nm.

Fig.1b and 2b shows AFM images of the ITO surfaces of the two samples. The brightness given by the scale bar on the side indicates the surface roughness. A section analysis (Fig.1c and 2c) was performed with Nanoscope IIIa® software from Digital Instruments along the white lines in Fig.1b and 2b. Again, we find a comparable surface roughness of max. 15 nm. This corresponds well with the TEM measurements.

The results show that both types of measurements yield comparable roughness values. Both techniques are equally well suited for this kind of analysis and the TEM cross-sections samples provide additional information about the internal structure of the layers. TEM, therefore, is a promising method to investigate also more complex samples like e.g. multilayer organic LED’s.

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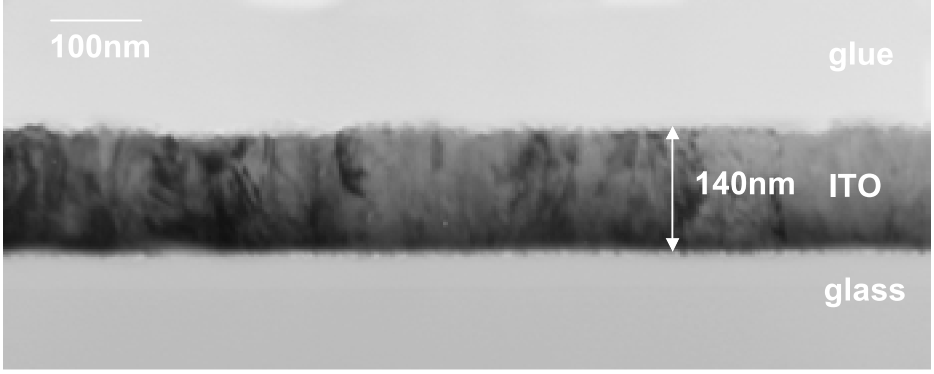

Fig.1a TEM bright-field image of an unetched ITO layer

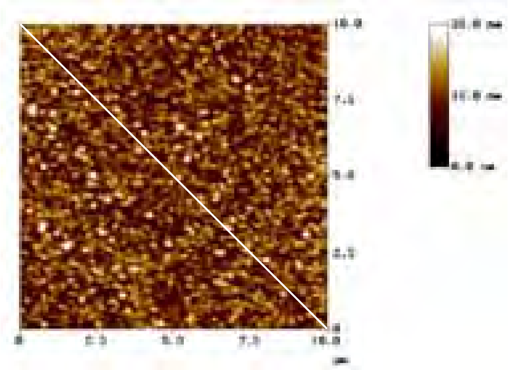

Fig.1b AFM image of an unetched ITO layer

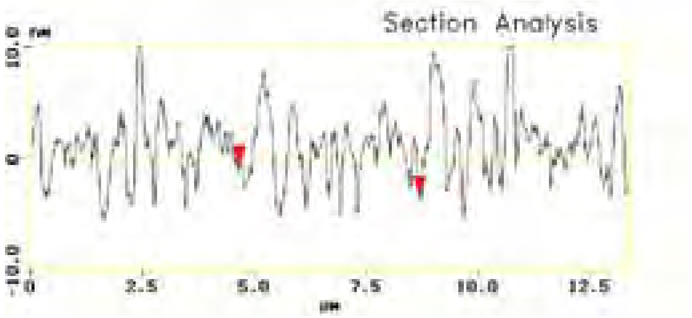

Fig.1c Section analysis along the white line, indicated in Fig.1b

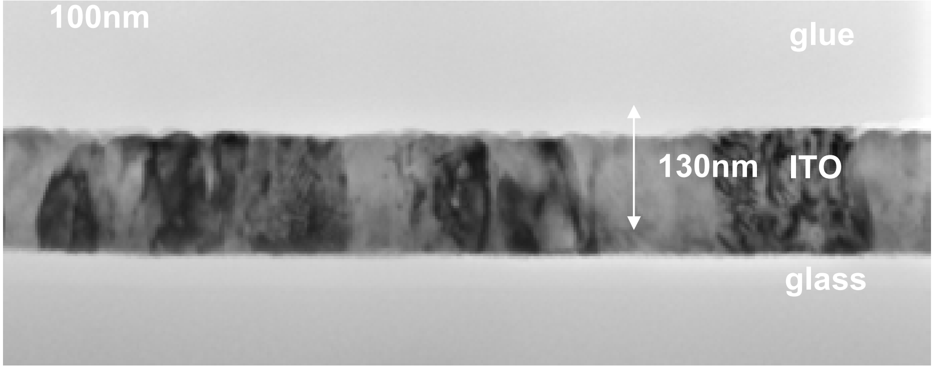

Fig.2a TEM bright-field of an etched ITO layer
(treatment with Chromium-Sulfuric-Acid to improve adhesion)

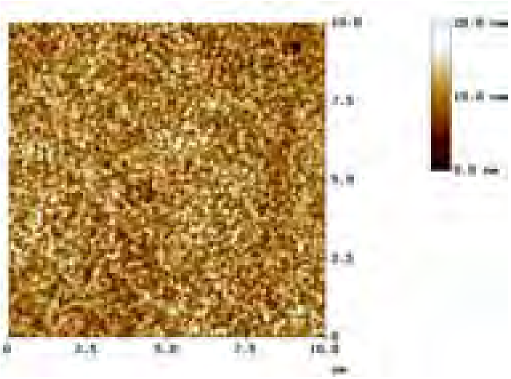

Fig.2b AFM image of an etched ITO layer

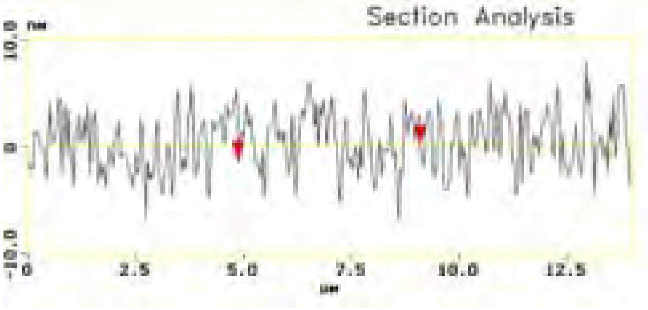

Fig.2c Section analysis along the white line, indicated in Fig.2b

Graphites with Modified Surface Morphology for Improved Anodes in Lithium Ion Cells

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Due to their high energy density and cell voltage, lithium ion cells play a major role in the rechargeable battery market, in particular for powering mobile electronic applications such as cellular phones and portable computers. Usually, lithium insertion compounds, e.g., transition metal oxides such as $LiCoO_2$ for the cathode and graphitic carbon for the anode are the electrode materials of choice through a combination of electrochemical, economic and environmental reasons [1].

The high cell voltage of up to 4.5 V, however, corresponds to operation conditions which are beyond the thermodynamic stability window of the battery electrolyte. At the anode strong electrolyte decomposition and anode corrosion has to be anticipated, which leads to irreversible loss of charge (so called irreversible capacity) and of electroactive material and electrolyte. As these reactions deteriorate cell performance, anode and electrolyte components have to be combined that induce the electrolyte reduction products to form a film at the anode/electrolyte interface, which minimizes the extent of decomposition reactions, but still allows for the desired anode performance.

One route to the reduction of the decomposition reactions and to the formation of a more effective film is to chemically treat the surface of the graphite prior to electrode construction. We employ a gas-treatment process, which involves a "pre-cleaning" step in inert Ar atmosphere at elevated temperatures, before, the carbon surfaces are exposed to (reactive) gaseous partners, e.g., O_2, CO_2, etc. at a certain temperature and for a certain time. As a result from the treatment procedure, "new" carbon surfaces with different surface chemistry [2] and morphology [2-4] are formed, which also show different anode performance with comparison to the untreated graphite. The morphology changes have been imaged by high resolution scanning electron microscopy (LEO DSM982 Gemini with field emission gun) and are shown in Fig 1.

Best electrochemical results in terms of reduced irreversible capacities have been obtained with graphites with roughened ("nano-rough") prismatic surface morphologies, which are obtained after a short-term (15 min) treatment with O_2.

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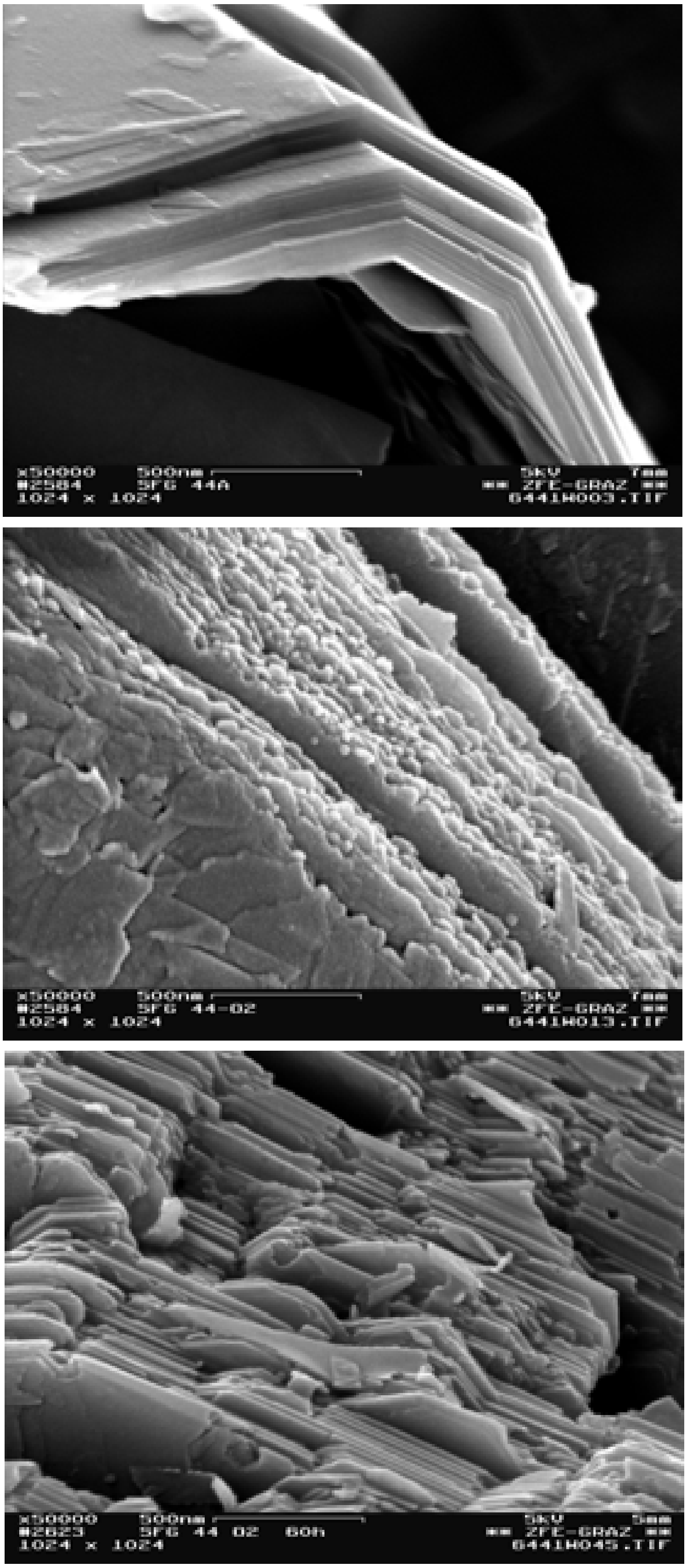

Fig.1 SEM images of TIMREX® SFG 44 synthetic graphites (supplier: TIMCAL group, Bodio, Switzerland), a. untreated, b. after “cleaning” in Ar at 1000 °C and subsequent O_2 gas treatment at 420 °C for 15 min, and c. after “cleaning” in Ar at 1000 °C and subsequent O_2 gas treatment at 420 °C for 60 h.

Characterization of Modified Polypropylene by Scanning Electron Microscopy

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Characterizing the morphology of modified multiphasic polymer systems, in the present work of four different grades of heterophasic EP copolymers with different amounts and compositions of EPR modifier, is normally a complicated and tedious task. Nevertheless, knowledge about the volume fraction and particle size distribution of the elastomer phase is important for the specific development of high impact systems. Direct production in the reactor enables only indirect control of these two quantities.

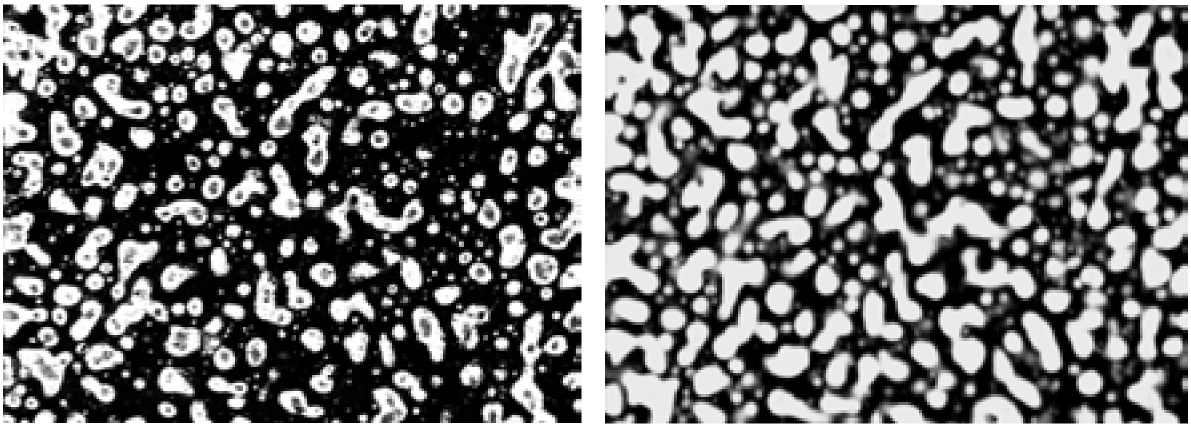
Computer controlled Scanning Electron Microscopy in combination with image processing allows an automated measurement of both all the necessary particle parameters (size distribution, shape, orientation, ...) and the elastomer content of the material. Since bulk materials are used for the investigation, additionally three dimensional information about the structure of the material can be gained by simply varying the electron energy, without the necessity to resort to multiple slices (see Fig. 1). This information is especially important in case of particles with extremely irregular shapes, as obtained for example by strong agglomeration of the modifier particles. The mathematical routines used for calculation of the particle size distributions from the measured profile size distributions cannot be applied in such cases.

In Fig. 2 the results of the size distribution measurements for the four materials, both before and after thermal relaxation, scaled to the same area, are presented. Thus, for the material 07 the initially finer particle structure compared to the materials CSC and DSC has disappeared after the thermic relaxation. Only the material 09 preserved a substantial amount of the fine modifier particles. Comparison of the size distributions in Fig. 2 demonstrates a drastic reduction in particle number per unit volume for the materials 07 and 09 after thermic relaxation. Thus extremely strong agglomeration occurred (see Fig. 1). Additionally, for the specimen 09 the pronounced orientation vanished after the thermic relaxation (see Fig. 3). This may also be due to agglomeration.

Thermic relaxation did not change the size distribution for the materials CSC and DSC substantially.

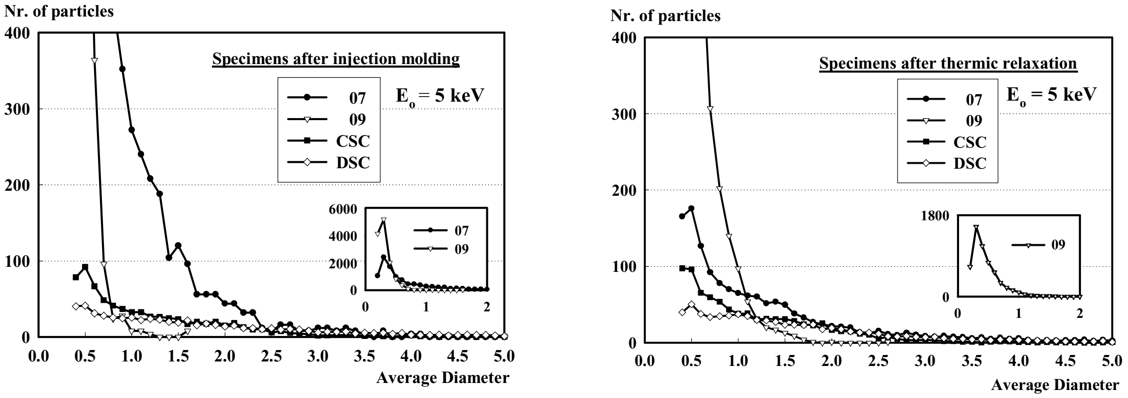
Reference:

P. Poelt, E. Ingolic, M. Gahleitner, K. Bernreitner, W. Geymayer: J. Appl. Polym. Sci. 78, 2000, 1152 - 1161



5 keV **15 keV**

Fig.1 : Dependence of particle shapes and sizes for material 07 on the electron energy used in SEM (BSE detector, picture width: 39 µm).



Figl. 2: Particle size distributions for four different materials before and after thermal relaxation, scaled to the same surface area.

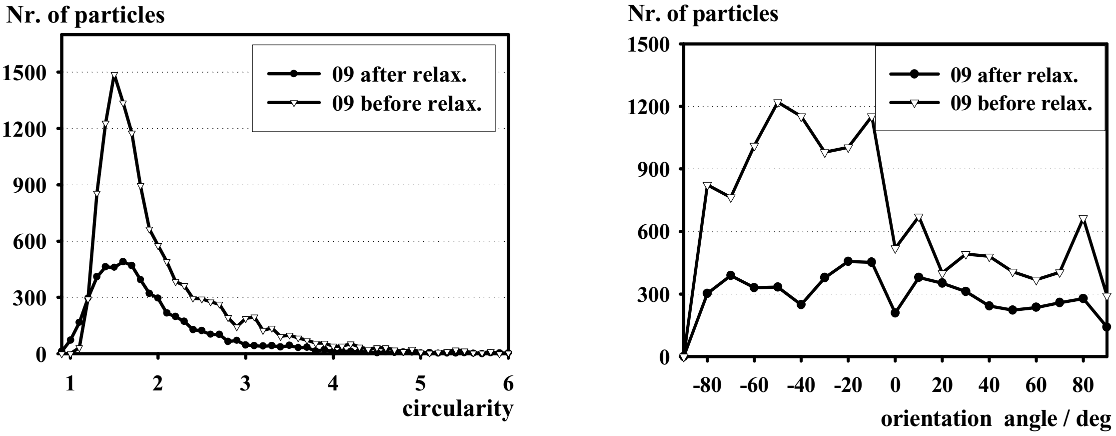


Fig. 3: Comparison of (left) circularity (C = perimeter²/(4∗π∗area) and (right) orientation (angle between positive X-axis and maximum particle projection) for material 09 before and after thermal relaxation.

Raman Spectroscopy Used for Investigations on Polypropylene

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Among the huge variety of available polymers and polymer blends polypropylene holds an outraging position comparable to only a few other synthetic materials. As widespread as applications like flower wrapping foils, coffee cups or shock absorbers in cars are the individual processing conditions to reach the desired mechanical and optical properties for these products. The main difference between them is confined to the morphology, i.e. crystallinity and orientation of macromolecules.

In addition to the classical techniques for the characterisation of these properties we want to introduce vibrational spectroscopy, namely micro Raman spectroscopy, as a non destructive method for investigations of polymers. Figure 1 shows our Raman equipment.

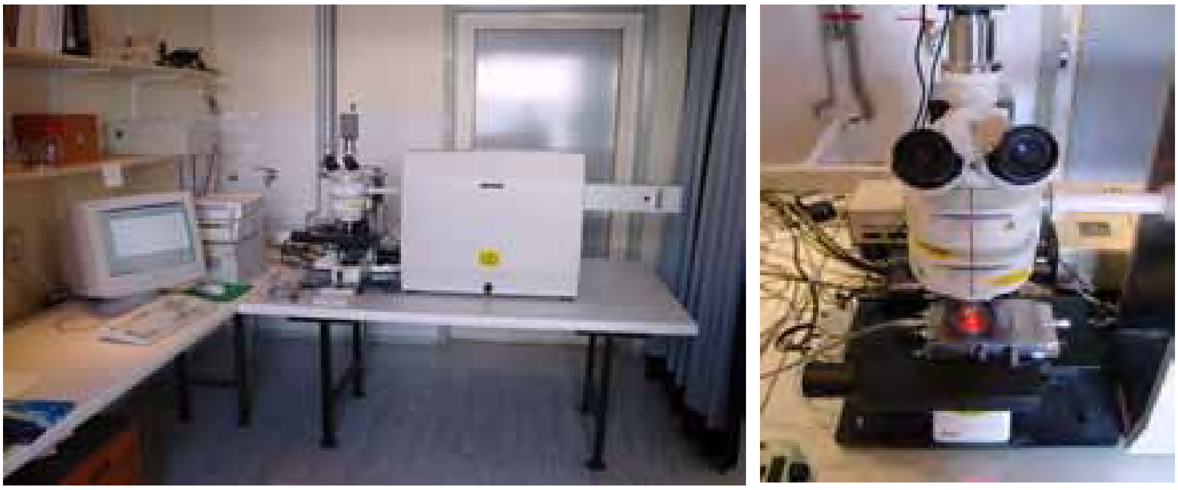

Fig. 1: Raman equipment at the institut (left). Microscope with hot/cold stage (right)

A Raman signal depends on several parameters. Incident radiation intensity, wavelength of the exciting laser line, instrumentational set-up and of course from sample specific parameters. The last one is described by the so called polarisability tensor. A 3x3 matrix which lists up the space components for the polarisability of the system. More common although is the description in terms of

$\frac{1}{\sqrt{\alpha_i}}$ α_i ... polarisability for the direction i

and the resulting polarisation ellipsoid. If and only if this ellipsoid changes size, shape or orientation during a vibration, we obtain a Raman signal according to theory. Now it becomes obvious, that the orientation of the polymer chain relative to the incident laser line plays an important role as the polarisability is not the same in all directions. The effect of orientation in respect to laser polarisation is demonstrated in figure 2, where the spectra of a PP fibre in different orientations to the incident radiation are compared.

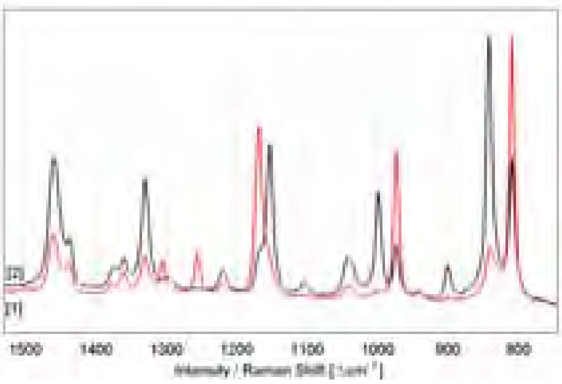

Fig. 2: Raman spectra of a PP fibre [1] parallel and [2] perpendicular to laser polarisation

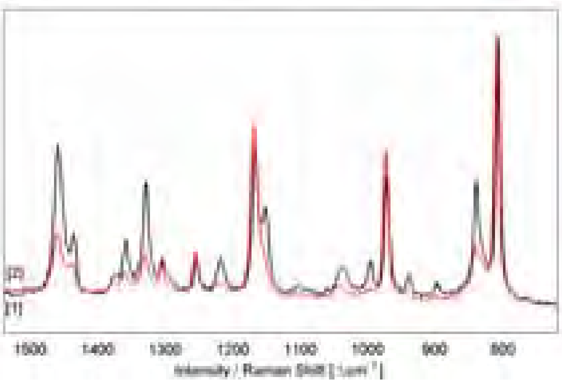

Fig. 3: Raman spectra of [1] injection moulded work piece [2] a PP fibre. Both with flow/spinning direction parallel to laser polarisation

Finally the degree of orientation and crystallinity is shown is figure 3. As expected the orientation on the surface of an injection moulded work piece is much lower then that of a high temperature spun fibre.

The final goal of our work is the establishment of Raman spectroscopy as a new powerful tool in polymer characterisation. The combination of non-destructiveness and a quantitative characterisation of the morphology would yield in a good combination. The cross-linking of Raman spectroscopy and mechanical properties would then be the next step on the way to a new tool for materials characterisation.

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Co-operations:

All this work would not be possible without partners from universities and companies. The Borealis GesmbH is supporting us in many ways, financially together with the “Fonds zur Förderung der Wissenschaft” in form of a FFF-Project, with commercial PP samples of different types and with a lot of knowledge about polypropylene production, applications and general behaviour. The working group of Prof. Eder at the university Linz provides shear induced samples, the necessary theory about crystallisation and light microscopic pictures for the important morphological studies. Prof. Zipper from the Institute of chemistry at the university of Graz performs WAXS measurements of PP-samples which are used as reference materials, when calibration of degrees of orientation and crystal structures are of interest. Dr. Gregor-Svetec from the Textile institute at the university of Ljubljana, Slovenia, kindly provided us a set of different PP-fibres for investigations on highly oriented PP-materials and Prof. Piccarolo from the university of Palermo made measurements of polypropylene without orientation but with different degree of crystallinity possible to us.

Quantitative Energy-Filtering Transmission Electron Microscopy

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[2] Gatan Research & Development, Pleasanton CA, USA

Equipping a transmission electron microscope with an energy-filter offers extraordinary advantages for the characterization of both materials science and biological samples. Besides improvements for TEM imaging and electron diffraction like better contrast and resolution, elemental mapping using inner-shell ionisations has become the main application of EFTEM [1]. Elemental maps with resolution down to about 1 nm and elemental sensitivities down to a single monolayer have been reported [2].

Using a Philips CM20 equipped with a Gatan Imaging Filter (GIF) for our experimental work, we acquired elemental maps with the three window method ($A.E^{-r}$ background extrapolation from two pre-edge windows) and jump ratio images (division of post-edge image by a pre-edge image).

One important application of EFTEM is the detection of secondary phases in materials, e.g. precipitates and grain boundary phases. Figure 1a shows the TEM-image of a 10% Cr steel with the secondary phases mostly invisible. The secondary phases can be best visualized by recording a jump ratio map of the matrix element (=Fe) under rocking beam illumination (fig.1b), where all secondary phases with Fe-concentration lower than the matrix appear as dark regions. The diffraction effects are completely eliminated thus enabling unequivocal visualization of all secondary phases regardless of their orientation [3]. Recently, even precipitates down to a diameter of 2 to 3 nm could be detected in a microalloyed steel [4].

EFTEM elemental maps can be quantified by dividing by a low-loss image and by the partial ionisation cross-section thus yielding concentration maps in terms of atoms per unit area [1]. However, problems arise with crystalline materials, because the intensities in the elemental maps are strongly influenced by diffraction contrast and thickness variations. These effects can be only partially accounted for by normalization by specimen thickness which yields elemental concentrations in atoms per unit volume. According to EELS quantification artefacts can be cancelled out by calculating elemental ratios. Therefore, we quantify elemental maps by calculating "atomic ratio maps" using net elemental maps and the corresponding partial ionisation cross-sections (k-factors) [5]: $N_A/N_B = I_A/I_B \,.\, \sigma_B/\sigma_A$. This method yields concentration maps with the advantage that diffraction and thickness effects are minimized like demonstrated in the application example (fig.2a-c). A Ba-Nd-titanate ceramics consists of three phases; $Nd_2Ti_2O_7$, Nd-Ba-Ti-oxide and an amorphous Ba-rich phase which can be clearly visualized in the Ba/Nd atomic ratio map due to their different Ba/Nd ratios [6].

EFTEM cannot only be used to detect the presence of elements, but also to reveal the presence of different bonding states using the energy-loss near edge structure [7]. Fig.3 shows a TEM-image of a diamond layer which was grown by on a hard metal by chemical vapour deposition (CVD). The distribution of "diamond-like" carbon is imaged in fig.3b by utilizing the π^*-peak of the C-K edge.

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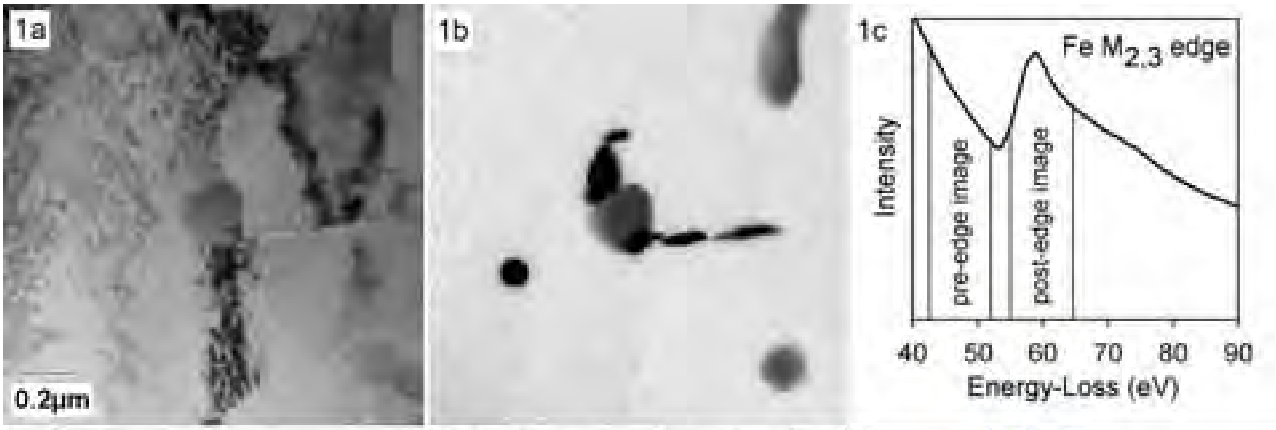

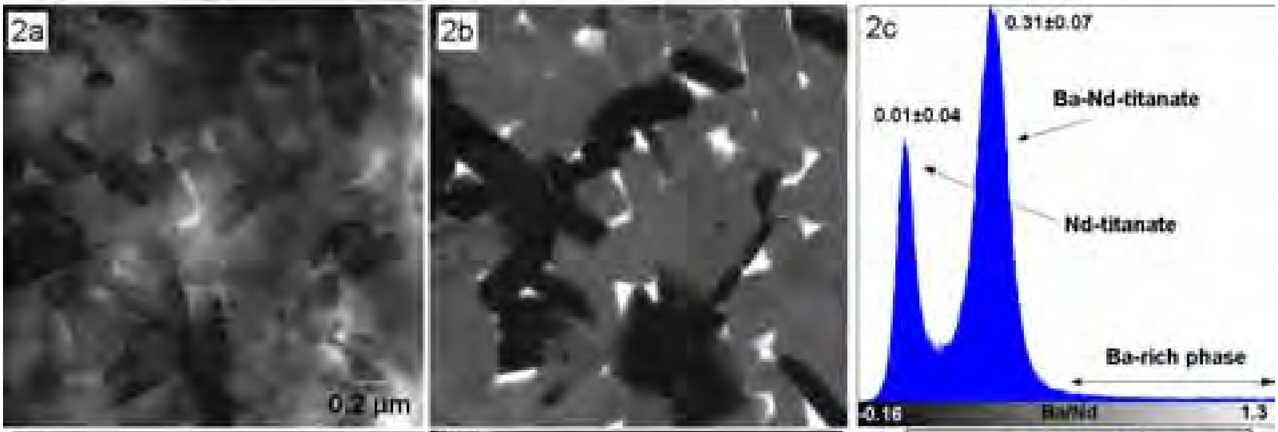

Fig.1a. TEM image of a steel sample; b. distribution of secondary phases with the Fe-M_{23} jump ratio image recorded under rocking beam illumination; c. Fe-M_{23} edge.

Fig.2. Quantitative elemental mapping of a Ba-Nd-titanate ceramics; a. TEM-image; b. atomic ratio map calculated from Ba- and Nd-M_{45} elemental maps; c. histogram of image 2b.

Fig.3. ELNES-mapping of diamond-like carbon in a diamond layer on hard metal; a. TEM-image; b. C-K map recorded with the π*-peak; c. C-K edges of diamond-like carbon and diamond.

Spectroscopy and Imaging with Energy-filtering TEMs: Parameters that Matter

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Spectroscopy and imaging techniques based on electron energy-losses (EELS), which are accessible through energy-filtering transmission electron microscopes (EFTEMs), have proven to be important tools in both materials and life science investigations. [1]

The two most widely used techniques on commercially available EFTEMs are elastic imaging and elemental mapping. Elastic imaging enhances image resolution and contrast by extracting the zero-loss signal and eliminating the inelastic background, whereas elemental mapping, which involves signals coming from element-specific inner-shell ionization edges, is employed to form two dimensional elemental distribution images. In both cases relatively large energy windows of a range of 10 to 30eV are typically used to form energy-filtered images with usually low to moderately high magnifications.[2-4]

There is however much more information available in an EELS spectrum, which is contained in the detailed fine structure within 0-20eV of a core excitation edge (ELNES) or in the very low energy-loss up to 5eV. This fine structure for instance relates to oxidation states, interatomic bonding and electronic structure of a sample. EELS experiments trying to record this detailed finestructure with an energy resolution at the fractional eV level or attempts to use very narrow spectral features to form a map displaying the electronic properties of a sample, challenge current EFTEM systems.
Ideally this type of application would require a high current, high brightness illumination system with low inherent energy spread (or a monochromator), electronically interconnected to an ultra stable, high energy resolution-, high performance, aberrations corrected spectrometer that in addition features a small and very precisely tunable energy selecting slit.[5,6]

Practical performance of an EFTEM microscope hence is depending on the application and operation mode and can therefore not be described by a single number. Instead performance criteria have to be related to the particular type of experiment and can be affected by numerous parameters.
In imaging mode, system parameters like the filter's detector pixel size, its aberrations (which relate to its transmissivity), the size of spectrometer entrance apertures, as well as the objective lens' chromatic and spherical aberrations etc. will determine optimal experimental magnifications and define the maximum objective aperture size for a required spatial- and energy resolution. [7,8]
As depicted in figure 1, it can be easily seen that both filter aberrations (transmissivity) and objective lens aberrations will limit the acceptance angles for a certain magnification due to their respective effect on energy and spatial resolution.

In spectroscopy – as carried out in the STEM mode - probe size, spectrometer aberrations, spectrometer entrance aperture sizes and stability will define the minimum camera lengths and the detection efficiency for a certain energy resolution. In practice however the most limiting factors for practical high resolution EELS work are the fluctuations in the TEM acceleration voltage as well as spectrometer energy instabilities rather than the filter's transmissivity.

The paper will discuss the impact of the different variables on the experimental conditions for energy filtering TEM and EELS experiments. An attempt will be made to explain and illustrate the interdependencies by means of practical examples and graphs.

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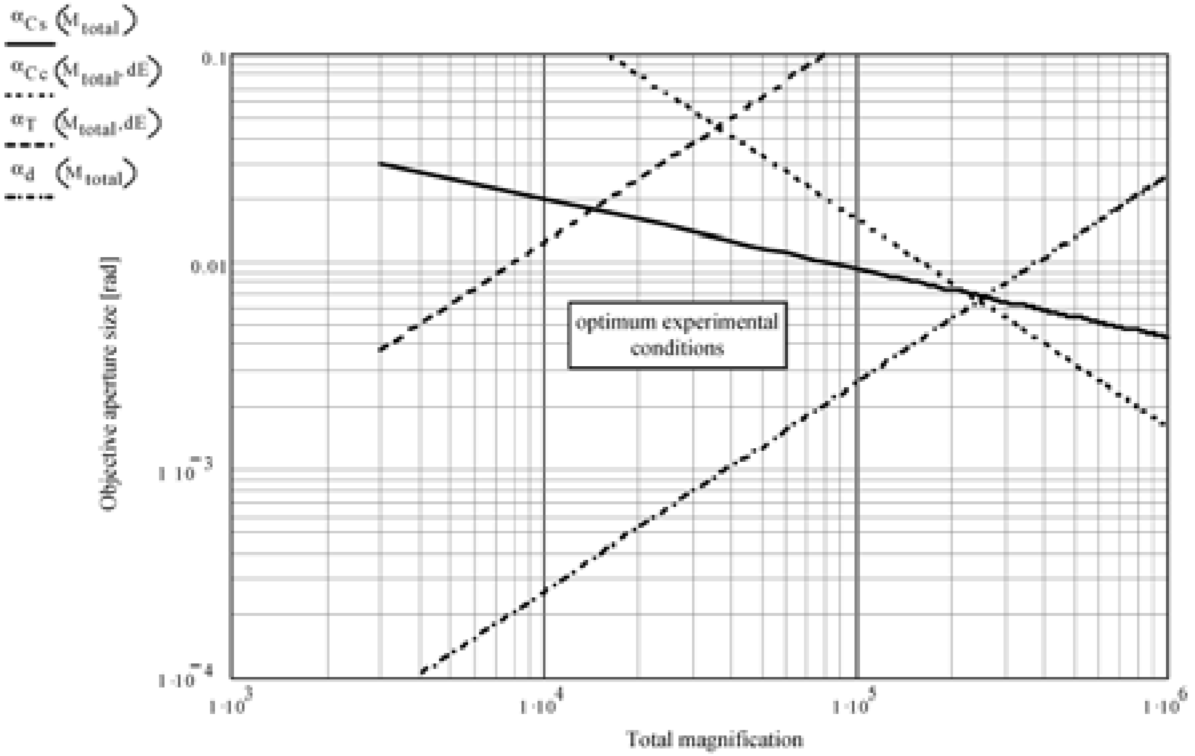

FIG 1. System parameters like the chromatic aberration, spherical aberration, transmissivity and diffraction limit define an optimal magnification and objective aperture range for energy filtering TEM. The plot has been calculated for $C_S=C_C=1.2$ mm and an energy window of dE=5 eV for 200kV.

Analytical TEM Characterization of SiGe Semiconductor Devices

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As one of the first semiconductor companies, Austria Mikrosysteme International is using the BICMOS process based on silicon germanium technology for commercial products. The combination of two materials (silicon and germanium) with different band gaps is the basis for hetero bipolar transistors (HBT). Varying the germanium content in the silicon substrate in a well defined way will directly change the band gap and furthermore tune the electrical properties for the intended application of the semiconductor device (e.g. high frequency applications). To systematically investigate these phenomena, detailed knowledge of the layer structure is essential. The morphology and the chemical composition of the layers and their interfaces are of paramount importance, as they directly influence and determine the transistor parameters (i.e. electrical properties). During the last years, transmission electron microscopy (TEM) has turned into an important technique for evaluating critical process steps in "deep submicron" (0.35 µm) processes. As in the development of a SiGe transistor the morphology as well as the chemical composition change on a nanometer scale, analytical TEM (AEM) is a perfect investigation tool, because of its high spatial resolution (down to less than 0.2 nm) and the high analytical resolution (down to less than 1 nm).[1,2]

For optimizing HBT devices, the local concentration of germanium is essential. As the investigations of SiGe transistors show, the combination of different analytical methods in an AEM allow for an excellent characterization of these and similar systems. In this work we investigated the emitter of a HBT and used energy-filtering TEM (EFTEM) images in combination with scatter diagrams to fully characterize this particular region of the device.
TEM preparation was performed using standard preparation techniques including dimpling and final low-angle ion milling. All experiments were carried out on Philips CM20/STEM operated with a LaB_6 cathode at 200 kV and equipped with a Gatan Imaging Filter.

Figure 1a shows a TEM bright field image of the region around the emitter of an HBT. In the top left corner of the images the Al and the insulating TiN layer (dark) can be seen. Diffraction contrast allows a further differentiation between the oxide and the pure silicon. However, no elemental information is obtained in the bright field image, which makes it impossible to clearly distinguish between the different phases. Therefore, elemental maps of Si, Ge, O, N, Al and Ti were acquired from which the maps of O, Si and Ge are shown in figs.1b-d. From these maps an overview about the chemical situation and the different phases in this sample can be obtained. However, in order to understand the elemental composition of the specimen in detail, it is necessary to know the correlation of the elemental distributions (spatial relationship), since there are many different elements involved. Using many two-dimensional scatter diagrams (for further information about scatter diagrams see [3] and references therein) of various element combinations a real phase map was created (fig. 2). This image clearly shows all different chemical phases near the emitter of a HBT with a spatial resolution around 1 nm.

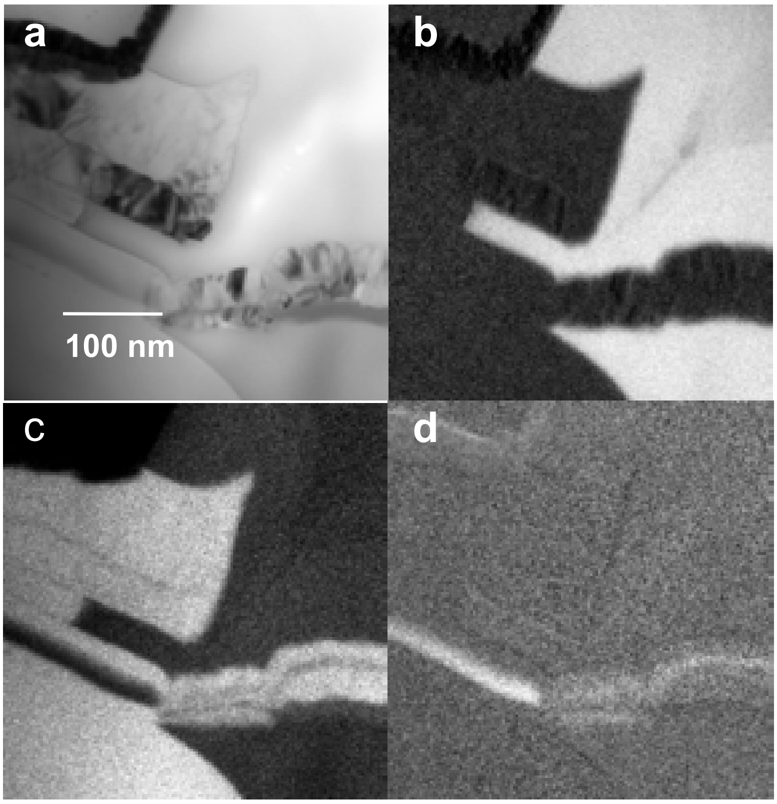

Figure 1: EFTEM investigation of a SiGe transistor: a. TEM bright field image, b. O-K elemental map, c. Si-K jump ratio image, d. Ge-L jump ratio image.

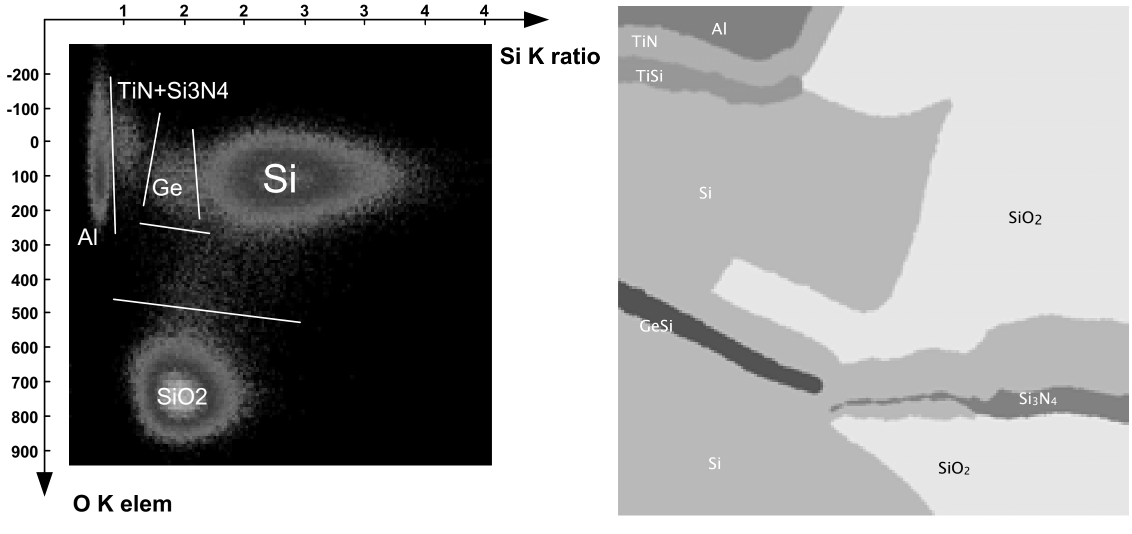

Figure 2: Phase image (right) of the specimen area shown in fig. 1 calculated from two-dimensional scatter diagrams (Si/O scatter diagram shown as an example on left).

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EFTEM-Investigations on High Speed Steels

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Tool steels are iron-based alloys used for manufacturing tools, dies and moulds that shape, form and cut other materials. The application requires hard materials with a high resistance against fracture. Hardening of tool steels is based on a martensitic phase transformation. An adequate ductility and toughness is achieved by subsequent multiple tempering. Highly alloyed tool steels are usually tempered at 500 to 570°C which is significantly higher than for plain carbon steels. During tempering several structural changes take place, in particular the precipitation of fine nanometer-sized alloy carbides (secondary hardening carbides). The secondary hardening carbides precipitate as small disks or needles in defined orientations within the martensitic matrix.

Depending on the composition of the steel the alloy carbides leading to the peak hardness have been identified as carbides of the types MC or M_2C in various volume fractions. Higher tempering temperatures lead to the precipitation of more stable carbides like M_6C or $M_{23}C_6$. The secondary hardening carbides are most relevant for some important properties of highly alloyed tool steels, e.g. hardness, hot hardness and thermal stability.

The extreme fineness of the secondary hardening carbides makes their characterization very difficult. However, energy-filtering transmission electron microscopy (EFTEM) proved to be a powerful tool for analysing microstructures containing nanometer-sized precipitates. In the present study EFTEM was applied to study the precipitation of secondary hardening carbides in tool steels. The investigations were carried out on the high speed steel HS2-10-1-8. The chemical composition of the material investigated is 1.1C-3.9Cr-1.4W-9.2Mo-1.2V-8Co (wt%).

The EFTEM investigations were performed with a Philips CM20/STEM, equipped with a Gatan Imaging Filter. The samples for electron microscopical investigations were austenitised at 1180°C for 10 min, quenched in oil and subsequently triple tempered at various temperatures for 2 hours and thinned to electron transparency by using ion milling.

Fig.1 shows the microstructure of the high speed tool steel HS2-10-1-8 hardened from an austenitising temperature of 1180°C followed by a triple tempering for 2h at 590°C, which is about 70°C above the tempering temperature for achieving peak hardness. In the TEM bright field image (Fig.1a) the carbides can hardly be separated from the matrix, but by recording a jump ratio map of the main constituent of the matrix i.e. iron very small secondary phases can be visualized (Fig.1b-e). These precipitates appear dark in the Fe $M_{2,3}$ jump ratio map (Fig.1b) and bright in case of Cr $L_{2,3}$, V $L_{2,3}$ and C K jump ratio images, which show that these precipitates are V-and Cr-rich carbides.

However, the early stages of precipitation and even structures at peak hardness exhibit very small precipitates which are extremely difficult to detect, whereas excellent results can be obtained by studying the over aged condition. Figs.2a to 2c show a series of Fe $M_{2,3}$ jump ratio images of the steel HS2-10-1-8 after triple tempering at temperatures of 530, 590 and 680°C, respectively. The micrographs indicate that especially the lower tempering temperatures lead to extremely fine carbides, which cannot be resolved satisfactorily (fig.2a). For higher tempering temperatures and longer times the particles become clearly separated from each other, (fig.2c), but there are some indications that their crystal structure changes too. Images with different specimen orientations reveal the cylindrical shape of the carbides after tempering at 680°C (fig.2c).

From this work the conclusion can be drawn that EFTEM is a powerful method for observing the development of the size of the secondary hardening carbides.

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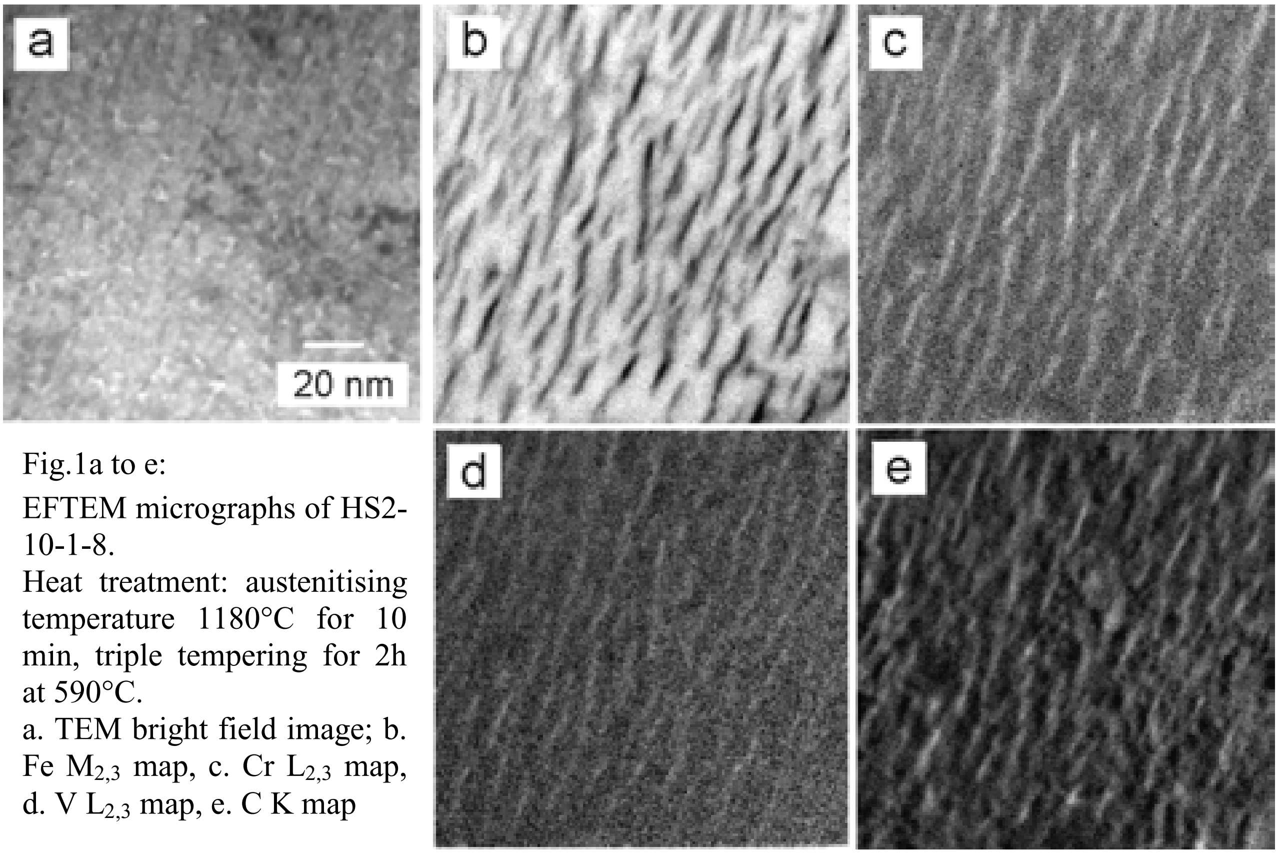

Fig.1a to e:
EFTEM micrographs of HS2-10-1-8.
Heat treatment: austenitising temperature 1180°C for 10 min, triple tempering for 2h at 590°C.
a. TEM bright field image; b. Fe $M_{2,3}$ map, c. Cr $L_{2,3}$ map, d. V $L_{2,3}$ map, e. C K map

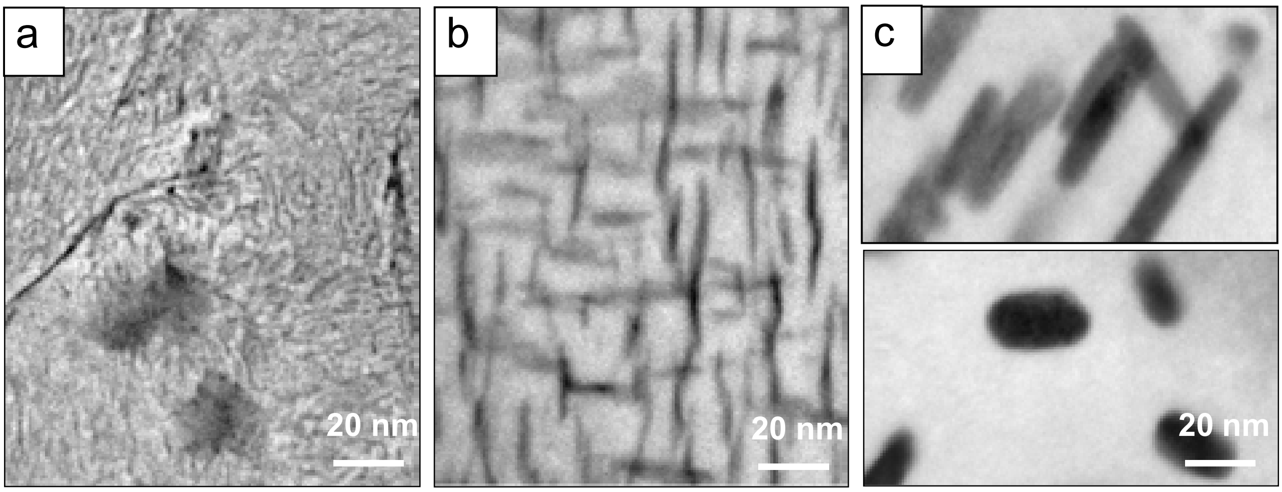

Fig.2a-c EFTEM micrographs of HS2-10-1-8; Fe $M_{2,3}$ jump ratio maps. Heat treatment: austenitising temperature 1180°C for 10 min, triple tempering for 2h at a. 530°C, b. 590°C, c. 680°C

Micro-Characterisation and Orientation-Relationship of two Carbide-Phases of S 6-5-2-5- High Speed Steel

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Summary: Precipitates in the high speed steel S 6-5-2-5 were investigated by energy filtering transmission electron microscopy (EFTEM) and electron energy-loss spectroscopy (EELS). The crystal structure of two carbide phases and the orientation of their crystal lattices were determined with the help of convergent beam electron diffraction (CBED).

1. Introduction

High speed steels are used for the manufacture of high speed rotating cutting tools (e.g. drills and milling) because of their excellent resistance to wear. Their high temperature strength is mainly caused by the high portion of primary carbides, which are formed during their solidification and which are changed in shape, size and orientation during hot working. In earlier investigations [1] it was demonstrated that a vanadium rich MX-phase exists at the edge of the primary M_2C-carbides. To give clear conclusions regarding the growth of carbides in such steels the crystallographic structures of the two carbide phases and the orientation-relationship of their crystal lattices had to be determined.

2. Results and Discussion

With the help of energy filtering TEM (EFTEM) all precipitates within a given volume of specimen may be analysed both morphologically and analytically, regardless of their particular orientation within the matrix [2]. In the bright field image (fig. 1a) the precipitates are only partially visible as they are masked by diffraction contours. In order to reveal all secondary phases in a selected area of interest, a Fe-$M_{2,3}$ jump ratio image was recorded under rocking beam illumination (fig. 1b). In this image all compositional heterogeneities with an iron concentration lower than the matrix are visualized as dark regions [2,3]. The bright areas in the V-$L_{2,3}$ jump ratio images (fig. 1c) indicate a vanadium rich phase at the edge of the large precipitate in the middle of the image. The EFTEM results have been confirmed by recording EEL-spectra from each precipitate phase (fig. 1d).

CBED patterns of both phases confirm, that the large precipitate is the hexagonal primary M_2C-carbide and the vanadium rich phase is a face centered cubic vanadium-carbide. Considering the lattice parameters [4] the orientation relationship of the two lattices can be described by a rotation axis [2.4 –10 9] and a rotation angle 57.1°. The two coordinate systems become congruent by rotating one crystal coordinate system around the mentioned axis by 57.1. Thus the formation of the vanadium rich phase could be explained as follows: During the formation of the M_2C-carbides, the vanadium enrichment taking place at the solidification front continuously increases. Finally, the presence of a random stacking fault could cause the originally hexagonal lattice of the M_2C-carbide to continue to grow on the face centered cubic lattice of the vanadium richer VC-precipitate. The stacking sequence changes abruptly from ABAB in the hexagonal lattice to ABCAB in the face centered cubic lattice.

We gratefully thank M. Albler and A. Brunegger for the preparation of TEM specimens.

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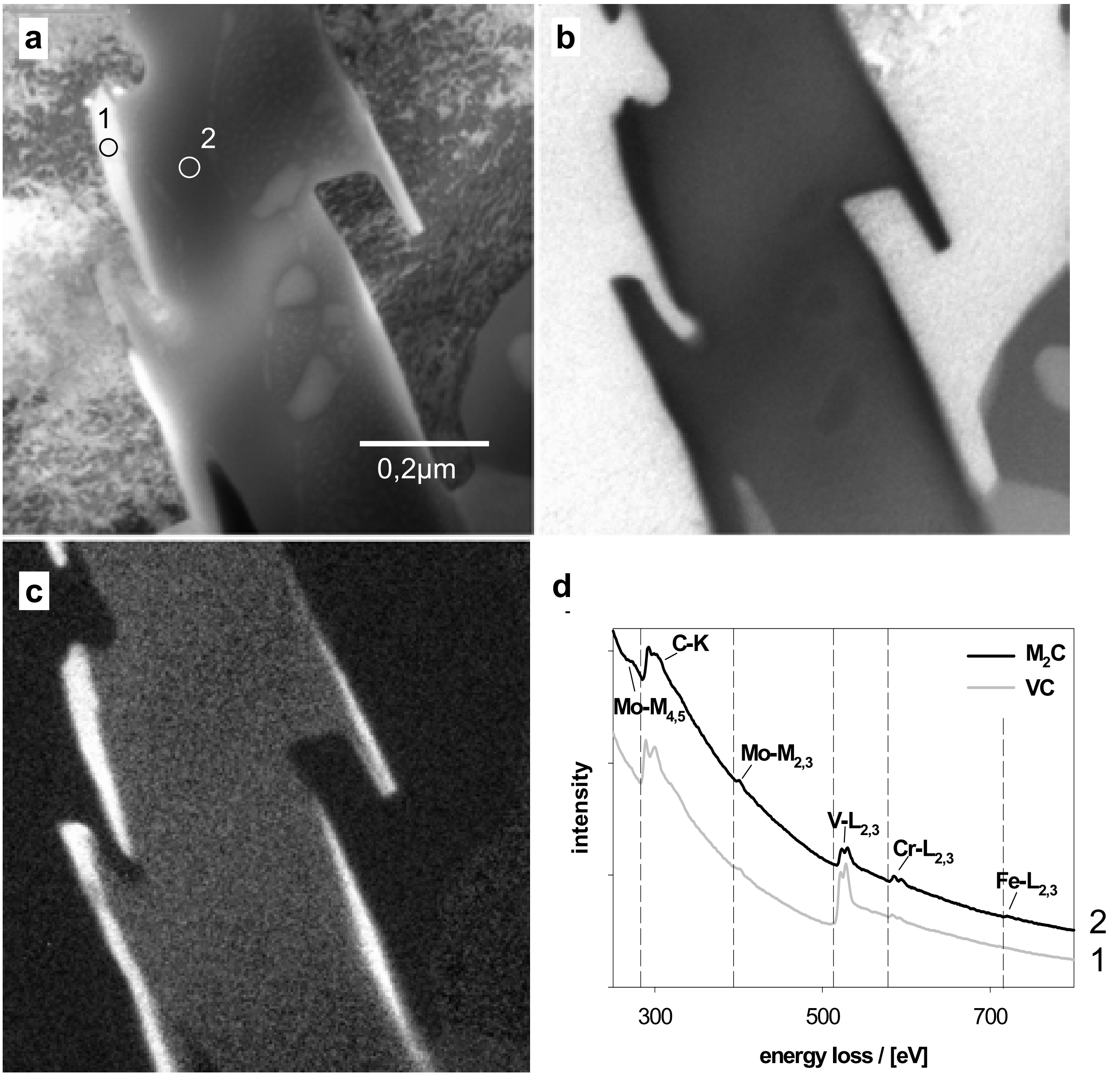

Figure 1a. TEM-bright field image of a primary carbide in the high speed steel; b. Fe-$M_{2,3}$ jump ratio image; c. V-$L_{2,3}$ jump ratio image; d. EEL-spectra of the vanadium rich MX-phase and the primary M_2C-carbide.

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Characterization of Modified z-Phase in 10% Cr-Steels with EFTEM, EELS and Electron Diffraction

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Essential for investigation of the microstructural evolution of long term creep tested advanced 10% Cr-steels and their resulting change of properties is the exact knowledge of the microstructure. Energy-filtering transmission electron microscopy (EFTEM) is a powerful tool to visualize precipitates which cannot be easily detected by simple TEM [1,2]. Previously, EFTEM investigations have been shown a new type of precipitate [3]. It's chemical composition (Cr, V, Nb, N) obtained from EELS- and EDX- analyses is - apart from the presence of vanadium - similar to that of the well known z-phase in Cr-Ni steels. That's why it is called „modified z-phase" [4]. For thermodynamic modelling the chemical composition and lattice parameters of all precipitates are essential. Therefore is was also necessary to verify the tetragonal lattice parameters of this vanadium-rich phase by electron diffraction.

For TEM sample preparation two different techniques were applied. In a first approach the 3 mm discs were mechanically grinded and dimpled and finally argon milled under low angle. To overcome the magnetic properties of the ferritic matrix which influences the electron beam during sample-tilting a second approach was used. The matrix was dissolved in a mixture of 1 part HNO_3 and 3 parts HCl. The remaining precipitates were mounted on holey carbon grids following standard TEM preparation procedures.

The investigation was performed with a Philips CM20 TEM/STEM (LaB_6 cathode, 200kV) equipped with a Gatan imaging filter (GIF) and an EDX detector (HPGe, Noran).

In order to locate the vanadium rich precipitates within the matrix it is necessary to record EFTEM jump ratio images under rocking beam illumination (in order to reduce the unwanted diffraction contrast) [2]. While the precipitates are almost invisible in the conventional TEM bright field image (fig.1a), the Fe $M_{2,3}$ jump ratio image reveals all secondary phases with an iron concentration lower than the steel matrix. By recording Cr, V and N jump ratio images, it is possible to visualize a Cr-V-Nb-N phase. The quantification of the EELS-spectrum of this phase (fig.2f) reveals the chemical composition of the precipitate to be examined: 33at% V, 31at% Cr, 33at% N and 3at% Nb. Several SAED- and microdiffraction-patterns of different precipitates were interpreted by using tetragonal lattice parameters of modified z-phase (Fig.2). With these results it could be confirmed that the vanadium rich phase is in fact the modified z-phase.

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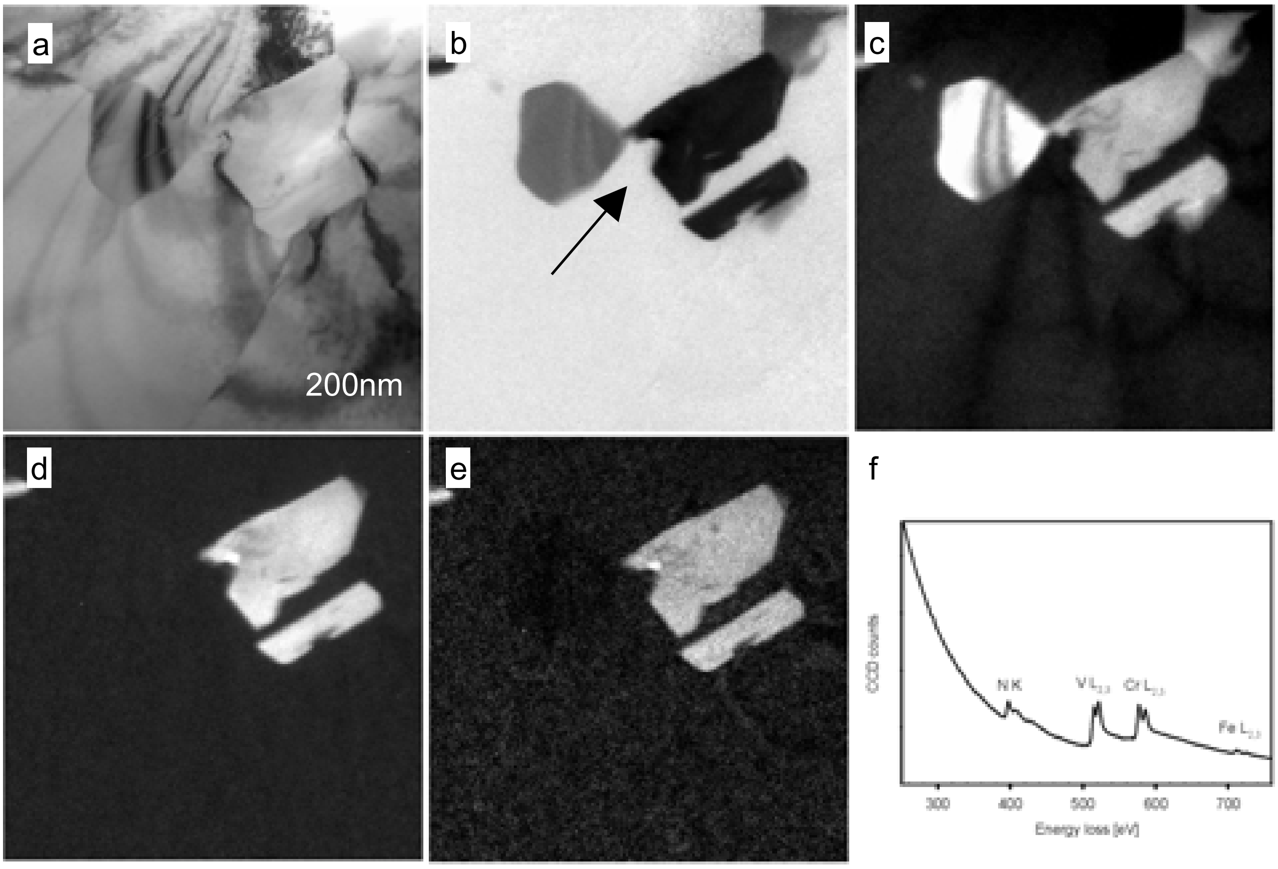

Fig.1a. TEM bright field image, b. Fe $M_{2,3}$ jump ratio image, c. Cr $L_{2,3}$ jump ratio image, d. V $L_{2,3}$ jump ratio image, e. N K elemental map, f. EELS-spectrum of the z-phase particle arrowed in b.; (sample prepared by ion-milling).

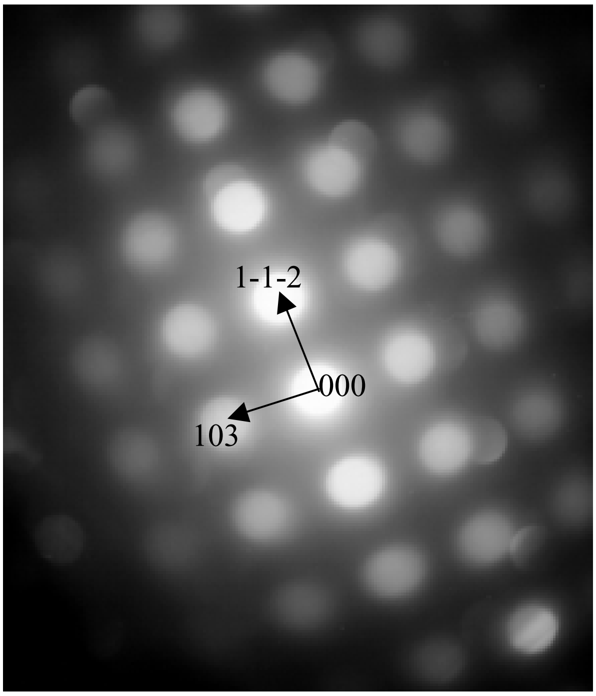

Fig.2:
Microdiffraction pattern of z-phase in [3 5 -1] orientation.

Electron Energy-Loss Near Edge Structure (ELNES) on the Nitrogen K-Edge in Vanadium Nitrides

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In the phase diagram of vanadium – nitrogen two binary phases have been reported: Firstly, vanadium mononitride VN which exhibits a rock salt structure and exists over a range of stoichiometry having the general form VN_x, where x is usually 1. Secondly vanadium subnitride V_2N exhibits a hexagonal ε-Fe_2N type structure with a space group P3-1m.

Due to the technological importance of VN and other similar transition metal nitrides and carbides there is considerable interest in their characterization on a nanometre scale using analytical electron microscopy. In this respect electron energy-loss near edge structures (ELNES) are particularly interesting, because they can be used as "fingerprints" for rapid identification of chemical compounds (Hofer, 1988).

Detailed studies of ELNES of transition metal carbides and nitrides with the rock-salt structure have been published by Fink (Pflüger et al., 1982, 1985; Fink, 1989) and by Craven (Craven, 1995, Craven & Garvie, 1995, MacKenzie et al., 1997), but all these investigations have been performed with special instrumentation (high resolution EELS, cold field emission source). On the other hand many examples have been reported, where useful ELNES information can be measured by using more conventional instrumentation, such as TEM's with LaB_6 sources or Schottky emitters (Hofer & Golob, 1987). Here we show a new example, where a conventional TEM-EELS system with an energy resolution of about 1.5 eV can be successfully used to distinguish between similar compounds.

By rapid thermal processing of vanadium layers in pure nitrogen at high temperatures the two known vanadium nitrides VN and V_2N could be prepared (Fig.1)(Galesic & Kolbesen, 1999). The phases have been checked by energy-filtering TEM, electron diffraction and quantitative EELS-analysis. The N K-edges of the vanadium nitrides have been modelled using a band structure approach within the formalism of density functional theory (DFT); the full potential linearised augmented plane wave (FLAPW) code, WIEN97, of Blaha (1999) was employed.

The ELNES observed on the nitrogen K-edge (fig.2) of VN agrees well with those in previous investigations which have been acquired with better energy resolution and there is close correspondence to the calculated N K-edge. The ELNES of the N K-edge of VN is quite similar to the isostructural trasnsition metal nitrides and carbides and is a kind of fingerprint thus supporting the identification of these compounds (Hofer, 1988).

The ELNES of the hexagonal V_2N phase exhibits a completely different ELNES; instead of the two sharp peaks found in the N K-edge of VN, there is only one sharp peak and a broad shoulder which are accurately predicted in the calculated N K-edge.

Since the ELNES of V_2N and VN differs considerably even at the energy resolution of 1.5 eV, these fine structures can be used to serve as a means for distinguishing between the two compounds. Similar ELNES fingerprints can be expected for other isostructural binary compounds, e.g. TiN-Ti_2N or CrN-Cr_2N.

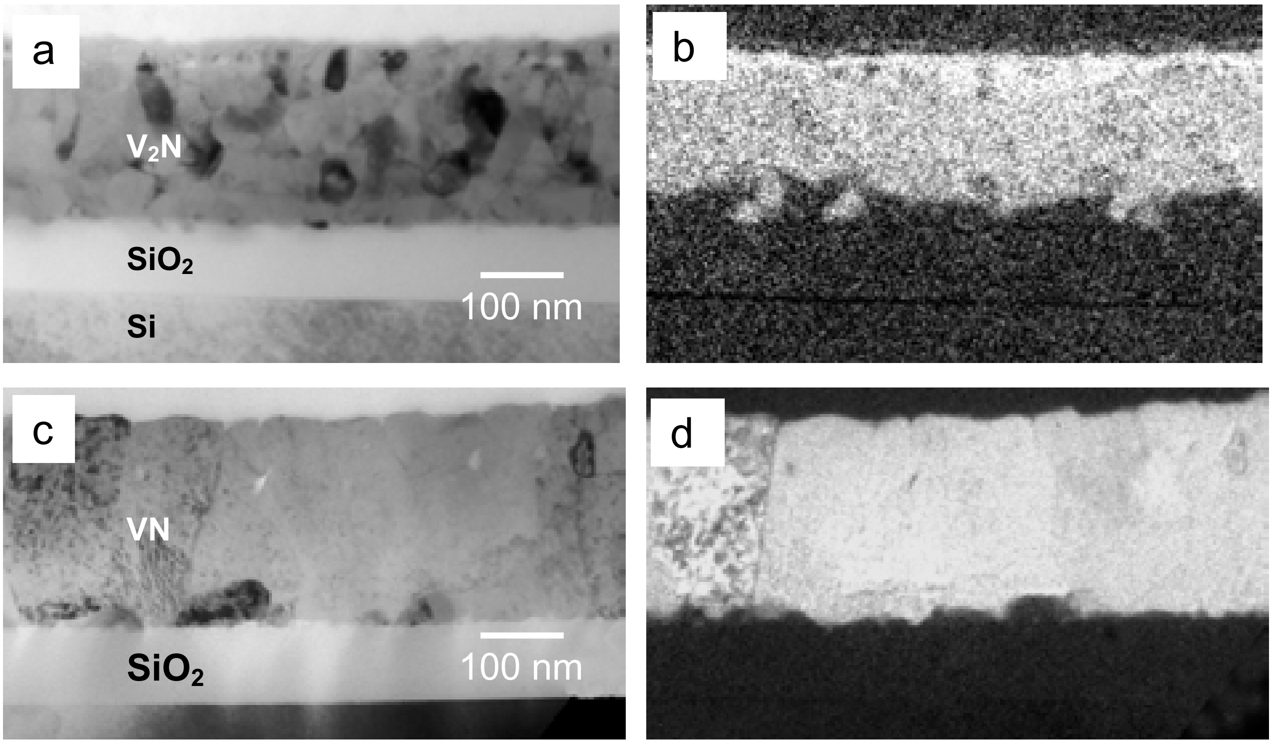

Figure 1: TEM images of cross-sections through RTP-vanadium nitride layers and nitrogen maps recorded with the N K edge; a. TEM image of a layer processed at 900°C; b. nitrogen map (900°C); c. TEM image of a layer processed at 1100°C; d. nitrogen layer (1100°C) with the marked analysis regions.

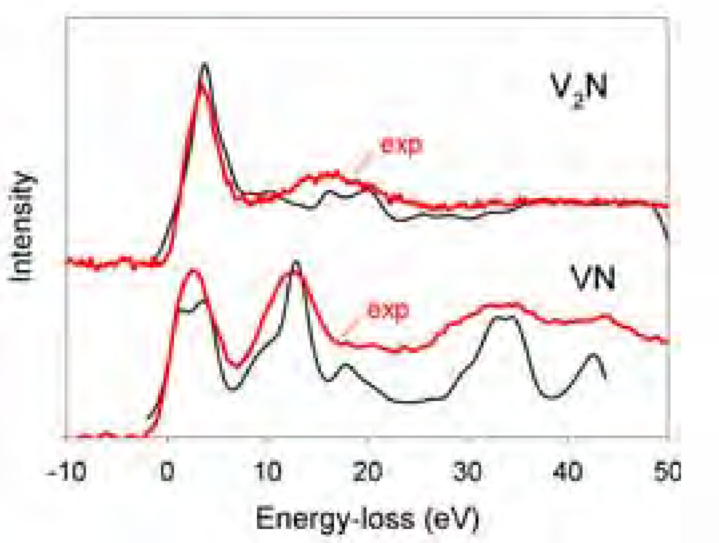

Figure 2: Nitrogen K-edge of VN (1100°C) and V_2N (900°C) compared with the band structure calculations.

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EFTEM-EELS Characterization of VC and Cr_3C_2 Doped Cemented Carbides

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Cemented carbides and cermets are materials commonly used in wear parts and cutting tool application. One way of gaining a better understanding of their behaviour is to study their complex microstructures and relate them to the fabrication process parameters and the mechanical properties. This has been done previously using above all scanning electron microscopy (SEM) with x-ray spectrometry. However, this method has its limitations in quantitative microanalysis, as it lacks the resolution needed for the fine-scale microstructure of these materials. As the hard material industry moves towards the fabrication of super- and ultrafine WC/Co grades with an average grain size ranging from 0.2 to 0.5 µm and with vanadium carbide or chromium carbides as grain growth inhibitors, their structure-property optimisation needs high resolution microanalysis, such as atom probe field ion microscopy (APFIM) (1) and analytical transmission electron microscopy (AEM) (2,3).

Micro-grained cemented carbides are interesting for their high hardness and high transverse rupture strength. For production of these alloys, it is necessary to retard the grain growth of WC during sintering of ultra fine WC powders by adding small amounts of vanadium carbide used either alone or in combination with other carbides, e.g. Cr_3C_2 (4).

The starting materials for this study were WC powders with an average grain size of 0.5 µm doped with vanadium carbides and cemented carbides sintered at 1350°C from micro-grained WC-Co hard metals which have been doped with vanadium and chromium carbides. The TEM samples were prepared using the standard procedures, such as cutting, dimpling and finally low-angle ion milling. The investigation was performed with a Philips CM20/STEM operated at 200 kV with a LaB_6 cathode and equipped with a Gatan Imaging Filter.

The TEM images (fig.1) exhibit typical microstructures of two different WC-Co hard metals: a non-doped conventional alloy (fig.1a) and a VC doped alloy (fig1b), respectively. In both cases the main phases WC and Co can be easily recognized; tungsten carbides appear as crystals and the Co binder fills the small gaps between the crystals. There is a clear difference in the morphology of WC/Co interfaces between the two alloys, i.e. WC/Co interfaces look like straight and smooth in the non-doped alloy. However, if the hard metal is doped with VC the microstructure changes significantly (fig.1b): The surfaces of WC at the WC/Co interfaces of the VC-doped alloys are finely facetted and consist mainly of two kinds of crystal planes, (1010) and (0001). Steps appear in the WC/Co interface along <1120> directions of WC. Since conventional TEM images do not allow to locate the doping elements, EFTEM elemental mapping has to be employed. By recording V $L_{2,3}$ jump ratio images we could detect vanadium enrichments at the facets of a facetted WC crystal and thin vanadium rich layers along several WC/Co interfaces indicating a vanadium segregation of a thickness of 1-3 nm.

The EFTEM investigations confirm previous results (4), where the formation of the WC skeleton in the alloy was said to be impeded by the presence of VC on the surface of the WC crystals. During the liquid stage sintering phase the VC layer hinders the atom exchange between the liquid phase and WC and therefore reduces the rate of WC grain growth.

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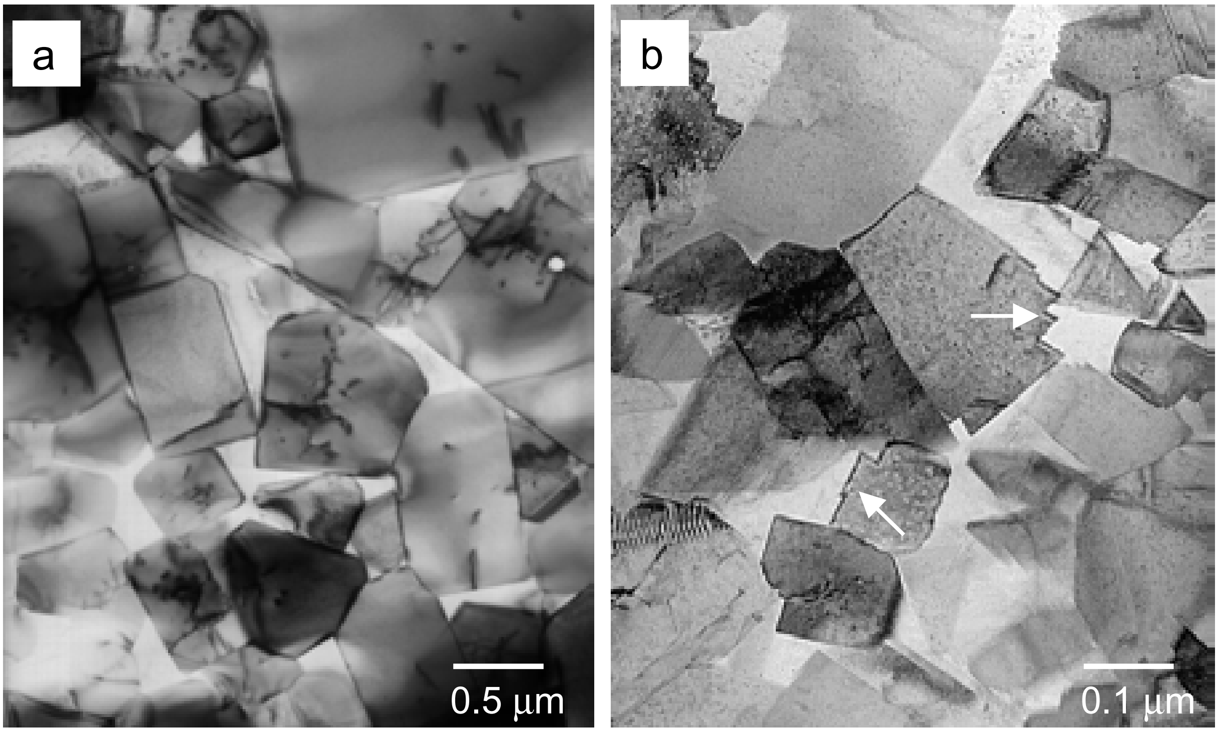

Figure 1: TEM images of two different hard metals sintered at 1350°C; a. hard metal with micrometer sized grains; b. hard metal doped with vanadium carbide with sub-micrometer tungsten carbide crystals revealing growth steps.

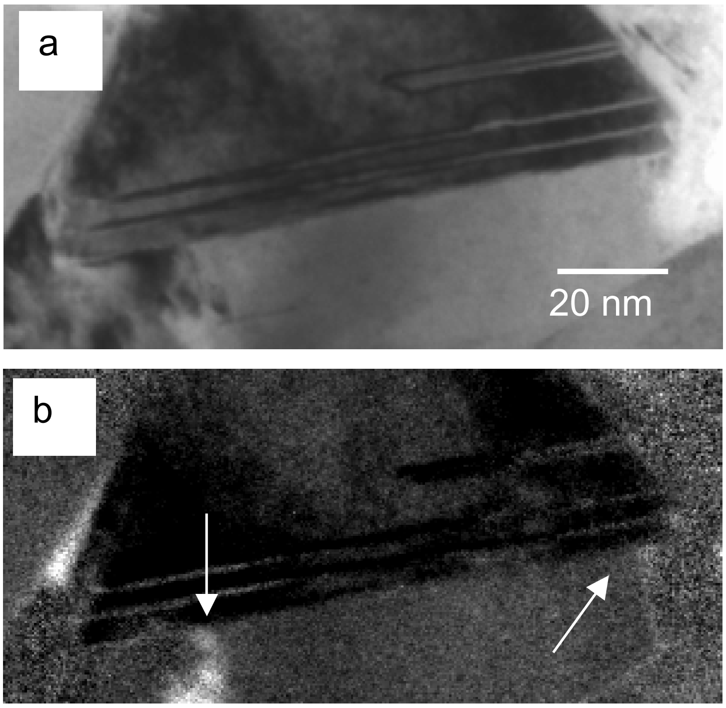

Figure 2:
EFTEM investigation of a cemented carbide doped with VC and Cr_3C_2;
a. TEM image of facetted WC crystal;
b. V jump ratio map recorded with V $L_{2,3}$ edge reveals vanadium enrichments along the WC/Co interfaces.

Synthesis and Characterization of Graphitelike BC_2N Ternary Crystals

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Ternary materials containing the elements boron, carbon, and nitrogen are expected to have interesting electrical and mechanical properties. The cubic form is related to diamond and is potentially ultrahard. The graphitelike material should behave in a manner intermediately between that of semimetal graphite and the electrically insulating hexagonal boron nitride (h-BN), with a band gap depending on the composition. Efforts to produce ternary B/C/N materials has mainly resulted in turbostratically disordered graphitelike phases, which may be either ternary or mixtures of turbostratic graphite and h-BN. In this paper, we present clear evidence for a three-dimensionally ordered graphitelike BC_2N ternary crystals [1].

The samples were prepared with a high-pressure, high temperature reaction in a belt apparatus, between two opposite conical anvils. The pressure medium was soft-fired pyrophyllite. The reaction temperature was achieved with a graphite resistance furmace, in the high-pressure cell. Ternary B/C/N starting materials were prepared by pyrolysis of elementorganic precursors (piperazine-borane). X-ray diffraction (XRD) patterns were measured using a transmission geometry diffractometer. TEM investigation was performed with a Philips CM20 (LaB_6, 200kV) equipped with a Gatan imaging filter; the EELS-spectra were quantified following a procedure described previously [2].

At least two of the four possible phases, g-BC_2N, h-BN, graphite and turbostratically disordered t-B/C/N, were observed by XRD in each of the recovered samples. The cell parameters of the hexagonal phases identified as graphite (a=2.461A, c=6.7076A) and h-BN (a=2.5035, c=6.660A) agree with standards in the literature. A third phase which exhibits general hkl reflections and may thus, be considered three-dimensionally ordered, has the cell parameters a=2.4820A and c=6.620A. Vegard's law was used to calculate the composition of this phase. The BN:C_2 ratio is exactly 1:1; therefore, the composition can be described as BC_2N.

TEM investigation of a sample prepared with 1200°C, 5 GPa (144 h reaction time) revealed crystals of graphitelike structure. The presence of boron, carbon and nitrogen was confirmed by EELS-analysis of a single crystal. Each element showed evidence of K-shell-to-π^* transitions, followed by K-shell-to-σ^* transitions, as observed for carbon in graphite. The background was modelled using a power-law function. The quantification of EELS-spectra recorded from different specimen regions was found to be in good agreement with the nominal composition. In combination with the XRD results, this finding proves that g-BC_2N is, indeed, a ternary graphitelike phase.

The crystals synthesized between 1200° and 1500°C, in the pressure range 3-5 GPa, always have the composition BC_2N, implying a pronounced thermodynamic stability of this phase. The interlayer lattice constant c is significantly shorter than any reported so far for graphitelike structures. Indirect evidence points to an orthorhombic arrangement of boron, carbon and nitrogen atoms in the crystals structure.

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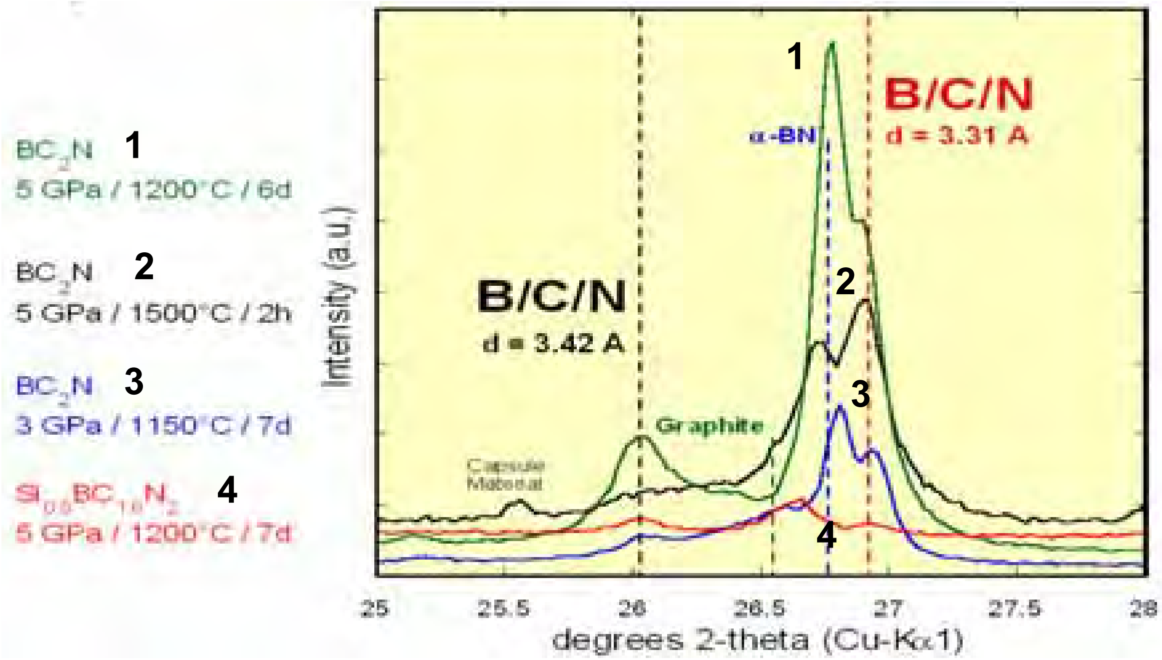


Fig.1 XRD diffraction pattern of various B/C/N samples; all the peaks displayed in this range are (002) reflections of graphite like phases, with the exception of a minor impurity of Al_2O_3 from the capsule material.

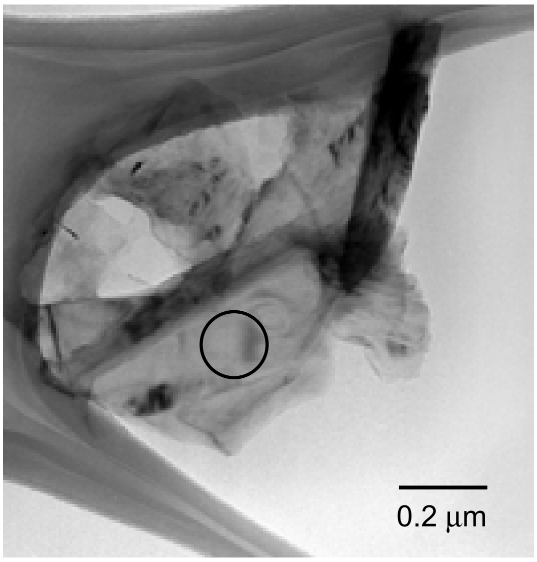
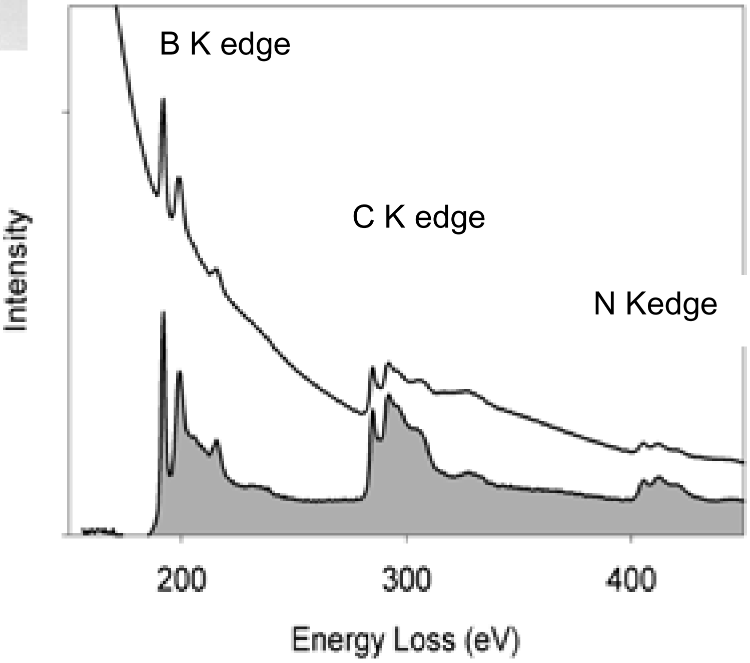


Fig.2 TEM image of a BC_2N particle, recorded on holey carbon film.

Fig.3
Electron energy-loss spectrum of graphite like crystal from specimen region shown in fig.2;
with background subtracted below the B K edge and deconvoluted with Fourier-ratio method;
quantification reveals 24 at% B, 53 at% C and 23 at% N, which closely corresponds to BC_2N.



Microstructure and Properties of Nanocomposite Ti-B-N and Ti-B-C Coatings

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Nanocomposite coating materials have recently attracted increasing interest due to the possibility of the synthesis of materials with unique properties, e.g. superhardness, combined with high hardness and toughness, or hardness and low friction (1). The origins of the attractive properties of these materials are not completely understood. This lack stems not only from the poorly understood micromechanical mechanisms, but also from the difficulty of characterizing these materials consisting of nanoparticles.

The aim of this investigation was to study the microstructure of nanocomposite coatings with a typical thickness of 3 µm and with different compositions in the quasi-binary systems TiN-TiB_2 and TiC-TiB_2, which were deposited onto austenitic stainless steel sheets by means of unbalanced d.c. magnetron co-sputtering system using TiN/TiB_2 (2), and TiC/TiB_2 targets (3).

Chemical composition, structural and mechanical properties were investigated using electron-probe microanalysis (EPMA), scanning electron microscopy (SEM) and energy-filtering transmission electron microscopy (EFTEM), X-ray diffraction (XRD), and depth-sensing nanoindentation. TEM specimens were prepared by cross-sectioning the coatings and ion-milling. The investigation was performed with a Philips CM20 TEM/STEM with a LaB_6 cathode, operated at 200 kV and equipped with a Gatan Imaging Filter (GIF).

In case of single-phase TiN and TiC coatings, SEM characterization revealed the well-known columnar structures and increasing boron content leads to the formation of fracture-amorphous structures. From XRD patterns, a gradual shift from the line positions of the TiN phase to that of TiB_2 can be observed (Fig.1) indicating the formation of both TiN and TiB_2.

From TEM cross-sections and selected area electron diffraction (SAED) patterns the crystal size of both the TiN-TiB_2 and the TiC-TiB_2 coatings was estimated to approximately 3 to 5 nm (Fig.2). X-ray and electron diffraction only reveal the occurrence of nanosized TiN particles, but it is not possible to get any information on the TiB_2-phase.

The electron energy-loss spectrum (fig.3) reveals the occurrence of boron, nitrogen, titanium and oxygen; quantification of this spectrum gives 28 at% Ti, 32 at% N, 20 at% B, 20 at% O.

It is well known that the near-edge fine structures of the ionisation edges reveal chemical bonding information and therefore information on the chemical phases (4). By comparing the fine structures of the B K, N K and O K edges with reference edges measured from TiN, TiB_2, B_2O_3 and TiO_2 standards, we can assume that the nanocomposite coating consists mainly of TiN crystals with an average diameter of several nanometers which are embedded in a quasi-amorphous phase consisting of TiB_x and B_2O_3.

From these results it can be concluded that not only the nanoscale grain size, but also the interfacial arrangement and the interface strength play important roles in determining coating properties.

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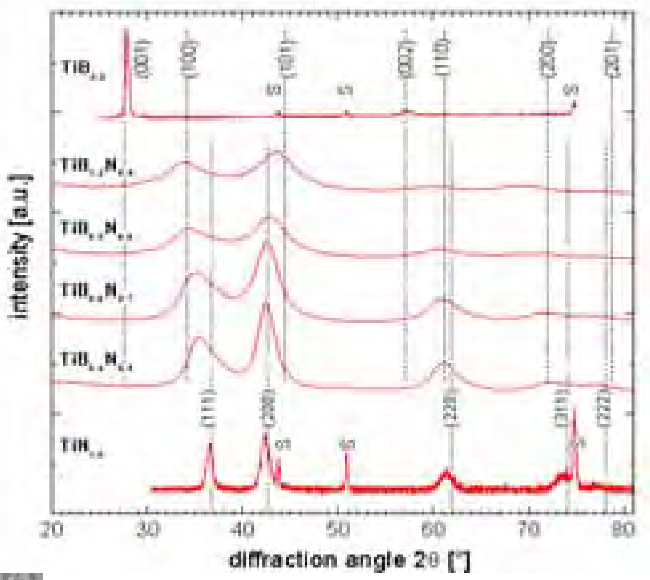
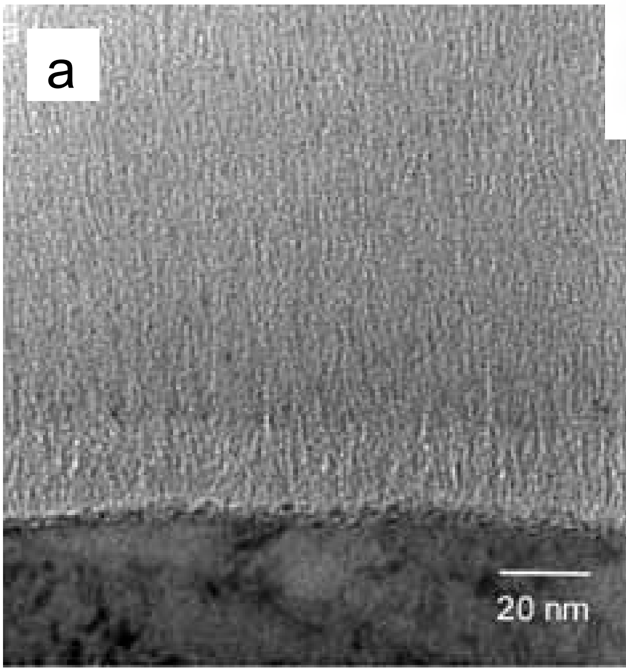
Fig.1 XRD patterns of Ti-B-N coatings of different compositions on molybdenum substrates





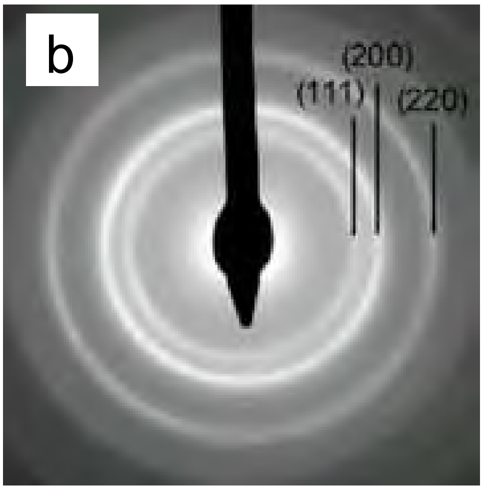


Fig.2 TEM cross-section of a coating with the composition $TiB_{0.6}N_{0.7}$, deposited onto an austenitic stainless steel substrate; a. TEM bright field image, b. corresponding selected area diffraction pattern indicating TiN particles.

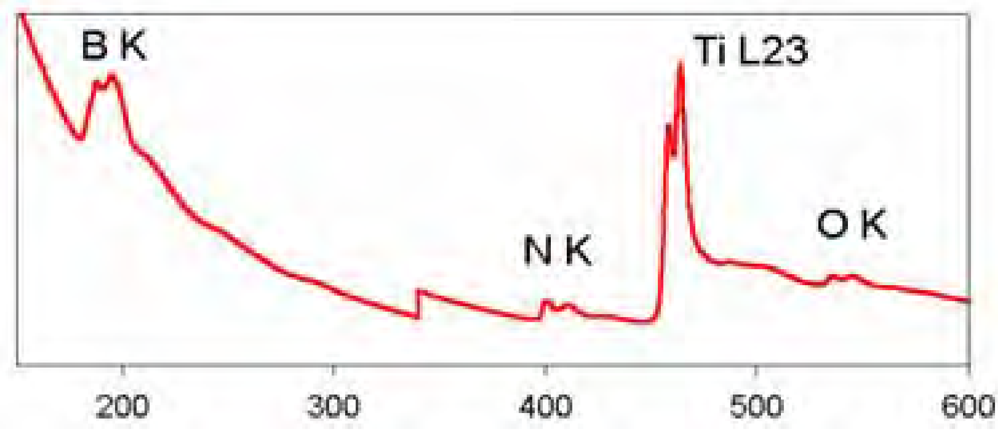


Fig.3 EELS-spectrum of a coating with the average composition $TiB_{0.6}N_{0.7}$ (shown in fig.1); quantification of the spectrum and the near-edge fine structures exhibit the occurrence of TiN, TiB_x and B_2O_3.

Characterization of a NiO/Pt Interface with EFTEM and EELS

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Summary: Transmission electron microscopy (TEM) in combination with spectroscopical techniques (EFTEM, EELS and EDXS) has been used for the characterization of the interface between a nickel oxide single crystal and a platinum layer. Elemental distribution images of O, Ni and Pt as well as energy loss spectra (EELS) linescans are recorded at the NiO/Pt interface and reveal the presence of nanoscale interfacial reaction layers of different chemical composition. The TEM results are discussed in the context of solid state pattern formation and alloy oxidation.

Metal-ceramic interfaces are involved in many fields of current technology, such as composites, thin films, and solid state electrochemical devices [1]. In particular, phenomena correlating with interfaces or interlayers, respectively, are of great importance as they can essentially determine the materials properties. Owing to micro- and nanometre dimensions at the interfaces, different methods of electron microscopy are crucial tools for interface characterization.

In this contribution we report on investigations of both the microstructure and microchemistry of a NiO/Pt interface using transmission electron microscopy in combination with analytical techniques (EFTEM, EDXS and EELS) [2]. The NiO/Pt interface had formed *in situ* during a long-term NiO coulometric titration experiment [3]. Investigations were performed on a Philips CM20/STEM operated at 200 kV (LaB_6 cathode), equipped with a Gatan imaging filter (GIF) and a Noran EDX system with HPGe-detector. The cross-sectional specimen was prepared using standard TEM preparation techniques with final low angle argon-ion milling. First TEM investigations revealed the presence of nanoscale interfacial layers between the NiO single crystal and the platinum layer (Fig. 1a). Initial EDXS spot analyses showed that these layers were of different O, Ni and Pt contents.

Electron energy filtered images of the interface were recorded at energy losses below and right at the core loss energies of oxygen, platinum and nickel (using the O-K, Pt-$M_{4,5}$ and Ni-$L_{2,3}$ edges in the electron energy loss spectrum), followed by image processing to extract the elemental maps. The elemental distribution images (Figs. 1b-1d) confirmed the EDXS results.

Additionally, electron energy-loss spectra (EELS) linescans across the interface were acquired in order to obtain analytical information at a nanometre scale and make even small composition fluctuations within the various layers visible. As the areas under the characteristic ionization edges in the EEL spectra are a measure of the number of excited atoms of the elements detected, it is possible to obtain quantitative compositional profiles of O, Ni and Pt with high lateral resolution. The medium energy loss range of these linescans covering the ionization edges of O and Ni is shown in Fig. 2. The quantitative analysis of the linescans (also including the information about Pt) gives insight into the intricate reaction mechanisms at the interface (Fig. 3).

The complex nanostructure at the NiO/Pt interface can be explained in terms of solid state pattern formation and the oxidation of alloys. The NiO crystal as well as the periodic patterns developed due to similar mechanistic principles, whereby Liesegang-like mechanisms involving local supersaturation and depletion are considered among the most important aspects for the presented sample.

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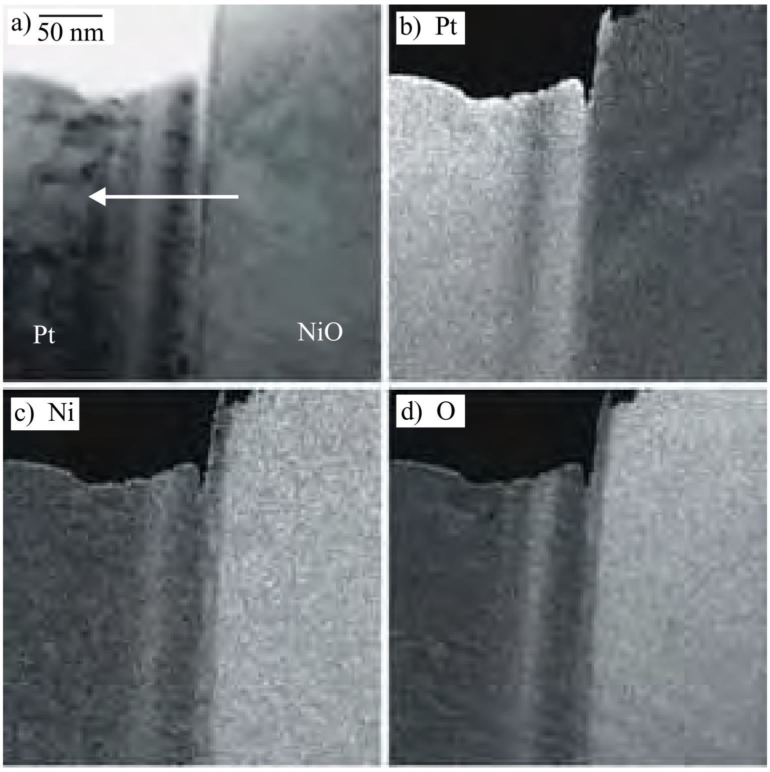


Fig.1a. TEM bright field image of the NiO/Pt interface (with the position of the EELS linescans indicated), b. Pt jump ratio image (Pt-$M_{4,5}$ edge), c. Ni jump ratio image (Ni-$L_{2,3}$ edge), d. O jump ratio image (O-K edge).

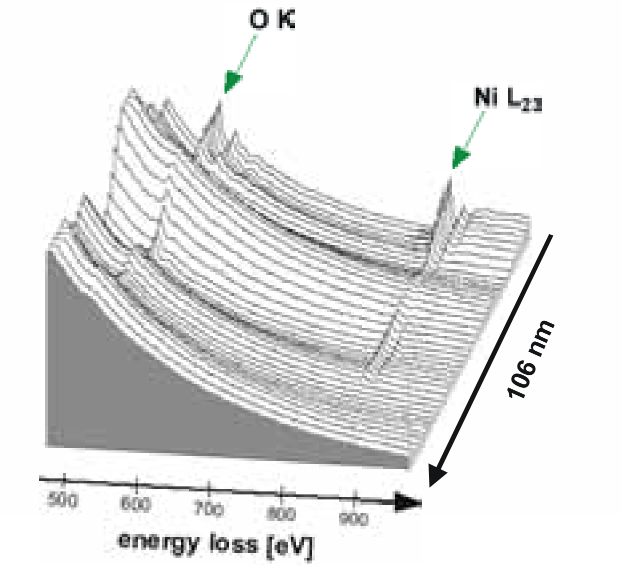
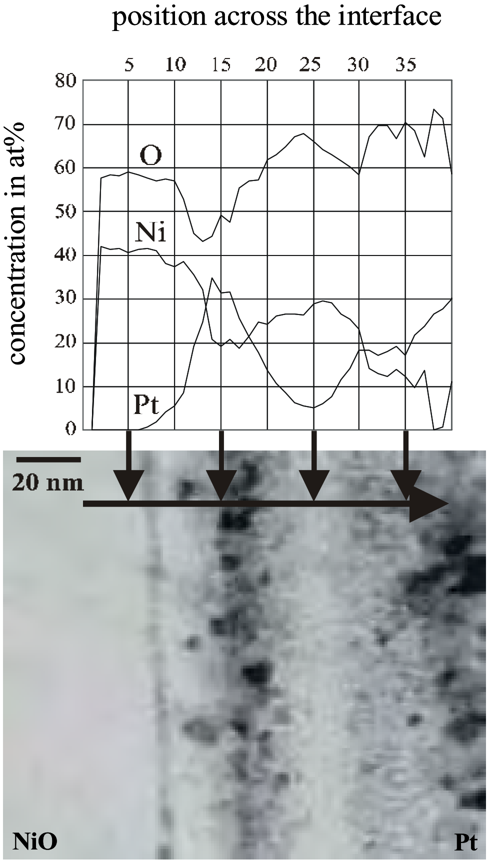


Fig. 2: EELS linescans across the NiO/Pt interface (for the position of the linescans see Fig.1a. showing the medium energy loss range (O-K and Ni-$L_{2,3}$ ionization edges).

Fig. 3: Concentration profiles of O, Ni and Pt across the interface as obtained from EELS linescans.



EFTEM Reveals the Microstructure of Fe-Nd-B Alloys Tailored to Approach Theoretical Coercivity Limits

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Performance of permanent magnets for a variety of applications is often determined by the maximum energy product $(BH)_{max}$. In order to obtain high $(BH)_{max}$ permanent magnetic materials have to have large coercivity. In theory the coercive field of ideally oriented, non-interacting, single domain, magnetic particles, assuming K_1 is much bigger than K_2, was shown to be $H_c = 2K_1/M_s - N.M_s$, where K_1 and K_2 are the magnetocrystalline anisotropy constants, M_s is the spontaneous magnetization and N is the demagnetisation factor. For randomly oriented non-interacting particles the Stoner-Wohlfarth model predicts that the value of H_c decreases to about to half. However, experimentally obtained values of the coercitive fields in permanent magnets are 3 to 10 and 2 times smaller for well oriented and randomly oriented samples, respectively. This discrepancy was attributed to inter-particle interaction and the microstructure of the permanent magnets. In order to understand the difference between the theoretically predicted and experimentally obtained results for H_c we prepared rapidly quenched, Nd-rich, $Nd_xFe_{14}B$ $(2<x<150)$ ribbons. The motivation is to obtain randomly oriented, magnetically single domain, $Nd_2Fe_{14}B$ particles embedded in a non-magnetic Nd matrix. By changing the amount of the non-magnetic Nd matrix the strength between $Nd_2Fe_{14}B$ particles was tailored ranging from strongly magnetically interacting particles in pure $Nd_2Fe_{14}B$ to nearly non-interacting $Nd_2Fe_{14}B$ particles in $Nd_{150}Fe_{14}B$. The latter is expected to approach the high coercivity field predicted by the model.

Preparation details are published in [1]. However, the dependence of coercivity in NdxFe14B as a function of the ND matrix concentration at room temperature is summarized in fig.1; the inset shows a typical hystersis curve with a coercivity of 2.75 T.

Here, we focus on elucidating the details of the microstructure and correlating it with the observed magnetic behaviour. All the work was carried on a CM20/LaB_6 transmission electron microscope equipped with a Gatan imaging filter and a Link x-ray detector.

The electron energy-loss spectrum of a $Nd_2Fe_{14}B$ particle reveals the Fe $L_{2,3}$ and the Nd $M_{4,5}$ edge, but the EELS-spectrum of the matrix only exhibits the Nd $M_{4,5}$ edge (fig.2). In the TEM bright field image (fig.3a), it is almost impossible to visualize the particles and to resolve the particle morphology (shape, size and their distributions). In order to visualize the $Nd_2Fe_{14}B$ particles we recorded EFTEM elemental maps and jump ratio images using the Nd $M_{4,5}$ and the Fe $L_{2,3}$ edges [2]. In figure 3b and 3c we present the jump ratio images, because these maps are not as disturbed by diffraction effects as the elemental maps. Although the jump ratio images do not give quantitative information of the elemental distributions, they clearly reveal the particle morphology and their distribution. The results show that the majority of the $Nd_2Fe_{14}B$ particles, distributed in the pure non-magnetic Nd matrix, are partially elongated in shape with a narrow size distribution.

In summary, the coercivity can be enhanced more than two times by fully separating the $Nd_2Fe_{14}B$ single domain particle. The largest coercivity, 27.5 kOe, ever reported for the ternary Nd-Fe-B system (about 80% of the ideal value obtained from the model) at room temperature was obtained for the $Nd_{150}Fe_{14}B$ samples. Thus, the magnetic interaction between single domain particle represents a key factor in determining coercivity of hard magnetic materials [3].

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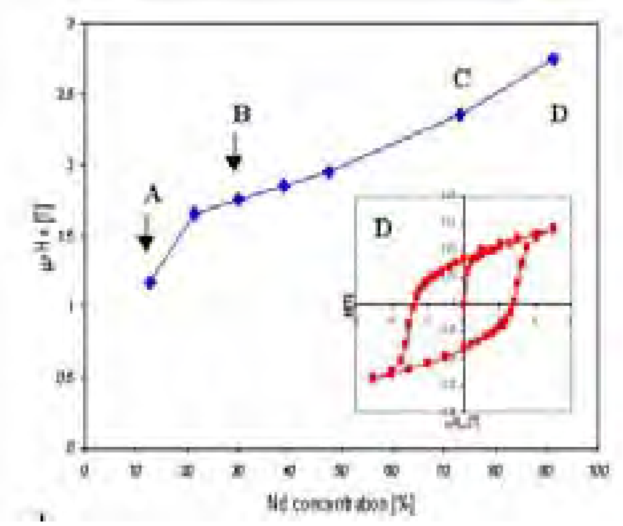
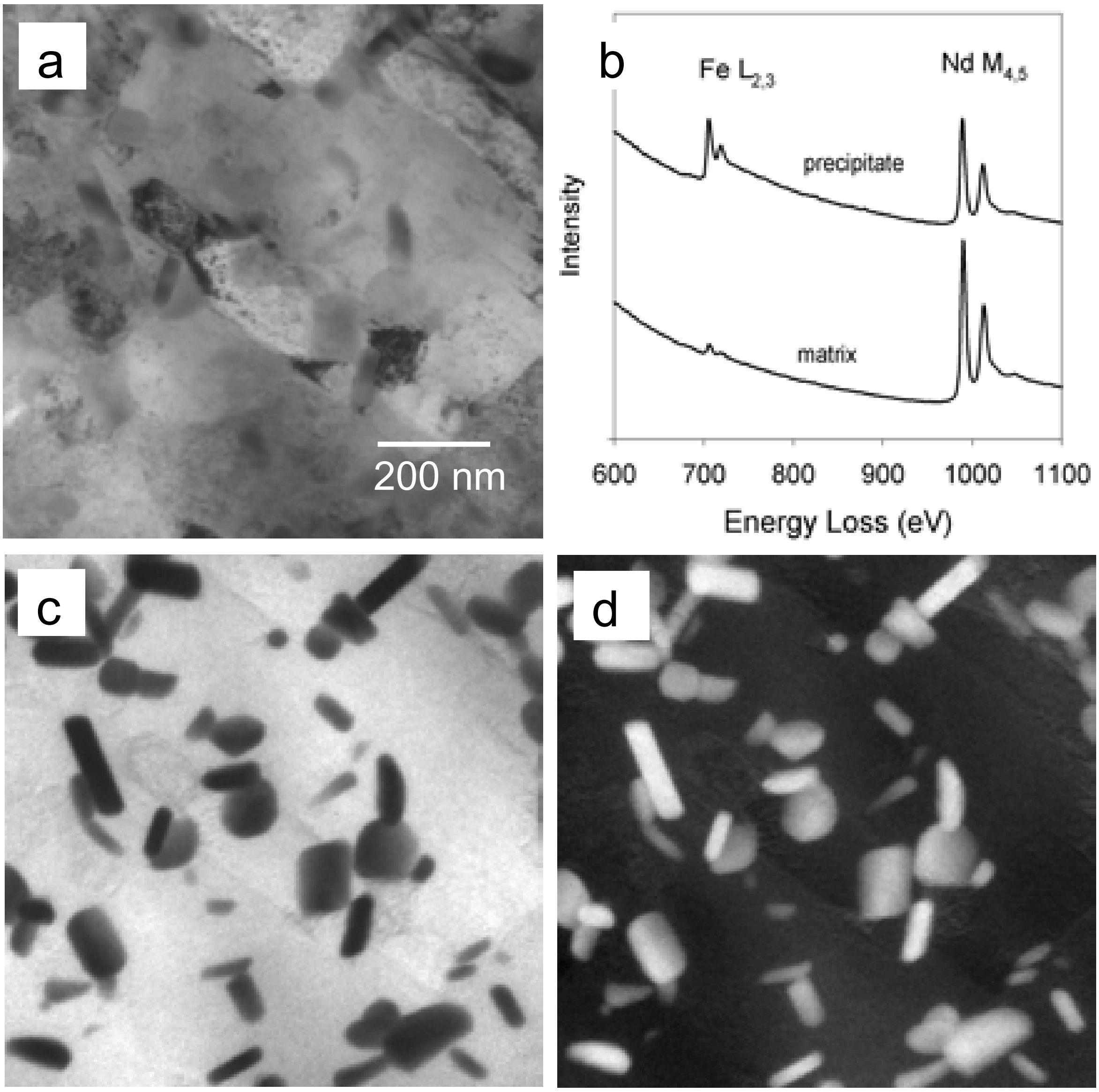


Fig.1 Dependence of coercivity in $Nd_xFe_{14}B$ as a function of the Nd-matrix concentration (room temperature).

Fig.2a. TEM bright field image of $Fe_xNd_{14}B$ alloy; b. EELS-spectrum of matrix and $Fe_2Nd_{14}B$ crystals; c. Nd-$N_{4,5}$ jump ratio image; d. Fe-$M_{2,3}$ jump ratio image revealing the distribution of the single domain $Fe_2Nd_{14}B$ crystals.



Investigation of the Effect of "Magnetic Dilution" in Spinels

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Compounds with spinel structure, e.g. chromites or chromium chalcogenides are of great technological interest. Recently, $CdCr_2O_4$ has been introduced as oxide electrode in an NO/NO_2 sensor. At the same time these materials constitute ideal model systems for investigations of the effect of magnetic dilution on their physical properties, thereby providing valuable hints about the magnetic interactions prevailing in the material.

$CdCr_2O_4$ is antiferromagnetic with a Neel temperature of 9 K. In the course of our investigation the paramagnetic Cr^{3+} ions were gradually replaced by diamagnetic In^{3+} ions. In this way magnetic exchange pathways in the structure were disrupted. It was found that the magnetic behaviour of the material could be continuously tuned over a certain concentration range of the diamagnetic ion. In figure 1 the molar magnetic susceptibility (calculated per mole Cr^{3+}) of $CdCr_{2-x}In_xO_4$ with x from 0 to 0.5 is given as a function of temperature. The gradual change from antiferromagnetic to paramagnetic behaviour is clearly seen. The x-values refer to the batch compositions. It is of utmost importance for a sensible interpretation of such experimental results that the actual chromium and indium contents of the fine crystalline powders are known with fair accuracy. To achieve this analytical transmission electron microscopy (AEM) proved to be a powerful tool.

Structural properties and chemical composition were investigated using X-ray diffraction (XRD), electron diffraction and AEM. TEM specimens were prepared by embedding the powder samples in resin and by thinning the samples to electron transparency by ion-milling. The investigation was performed with a Philips CM20 TEM/STEM (LaB_6 cathode, 200 kV) equipped with a Gatan Imaging Filter (GIF) and an EDX detector (HPGe, Noran).

The results of a TEM investigation of a sample with the nominal composition $CdCr_{1.5}In_{0.5}O_4$ are shown in fig.2. The corresponding EFTEM elemental map of indium has been recorded using the In-$M_{4,5}$ edge and under rocking beam illumination in order to reduce unwanted electron diffraction contrast [2]. This map exhibits the occurrence of two different phases: an In-poor phase (region 1) and an In-rich phase (region 2). However, the $M_{4,5}$ edges of In, Cd and the Cr $L_{2,3}$ edge overlap thus hindering quantitative analysis. Therefore, EFTEM results were further confirmed by EDX analyses. Quantification of the EDX spectra reveals the composition of phase 1 (Cr=60.4, Cd=30.7, In=8.9) and phase 2 (Cr=14.7, Cd=32.8, In=52.5) in at-% of the cations. The XRD pattern of this sample showed broadened lines also indicating two different phases. The calculated lattice parameters a suggest In^{3+}-substituted $CdCr_2O_4$ and Cr^{3+}-doped $CdIn_2O_4$ spinel structures (confirmed by electron diffraction).

Although it is well known that powder XRD is the primary characterization technique for phase homogeneity, it has its limitations for indicating the occurrence of (unwanted) additional phases in the material, such as due to problems with overlapping peaks, eventual low concentration of the secondary phases, small crystallite sizes, amorphous phases and compositional fluctuations within a given phase. In all these cases EFTEM provides detailed information on the chemical composition and structure of technologically important materials ranging from micrometer to nanometer regions [2].

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Fig.1
Molar magnetic susceptibility (calculated per mole Cr^{3+}) of $CdCr_{2-x}In_xO_4$ with $0 < x < 0.5$ given as a function of temperature

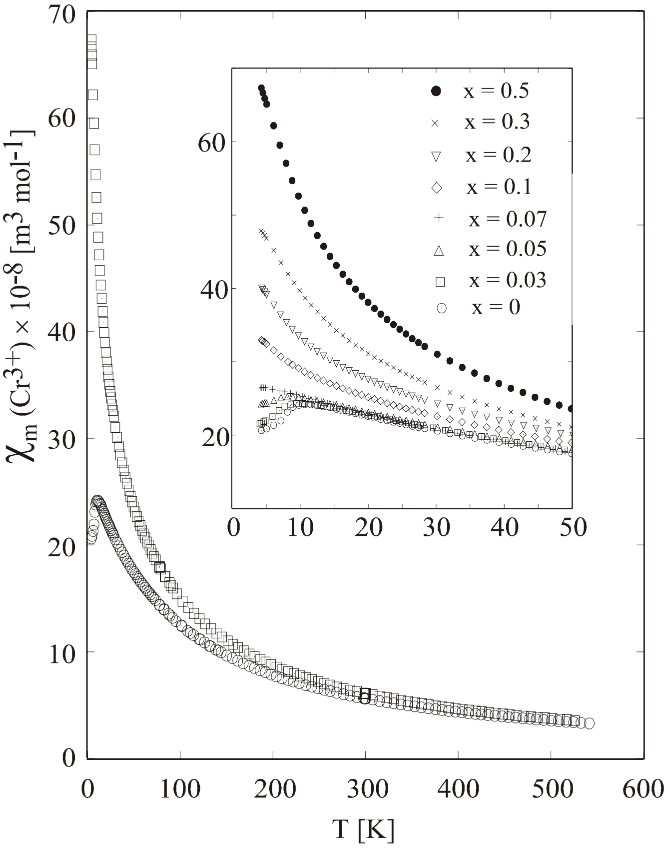
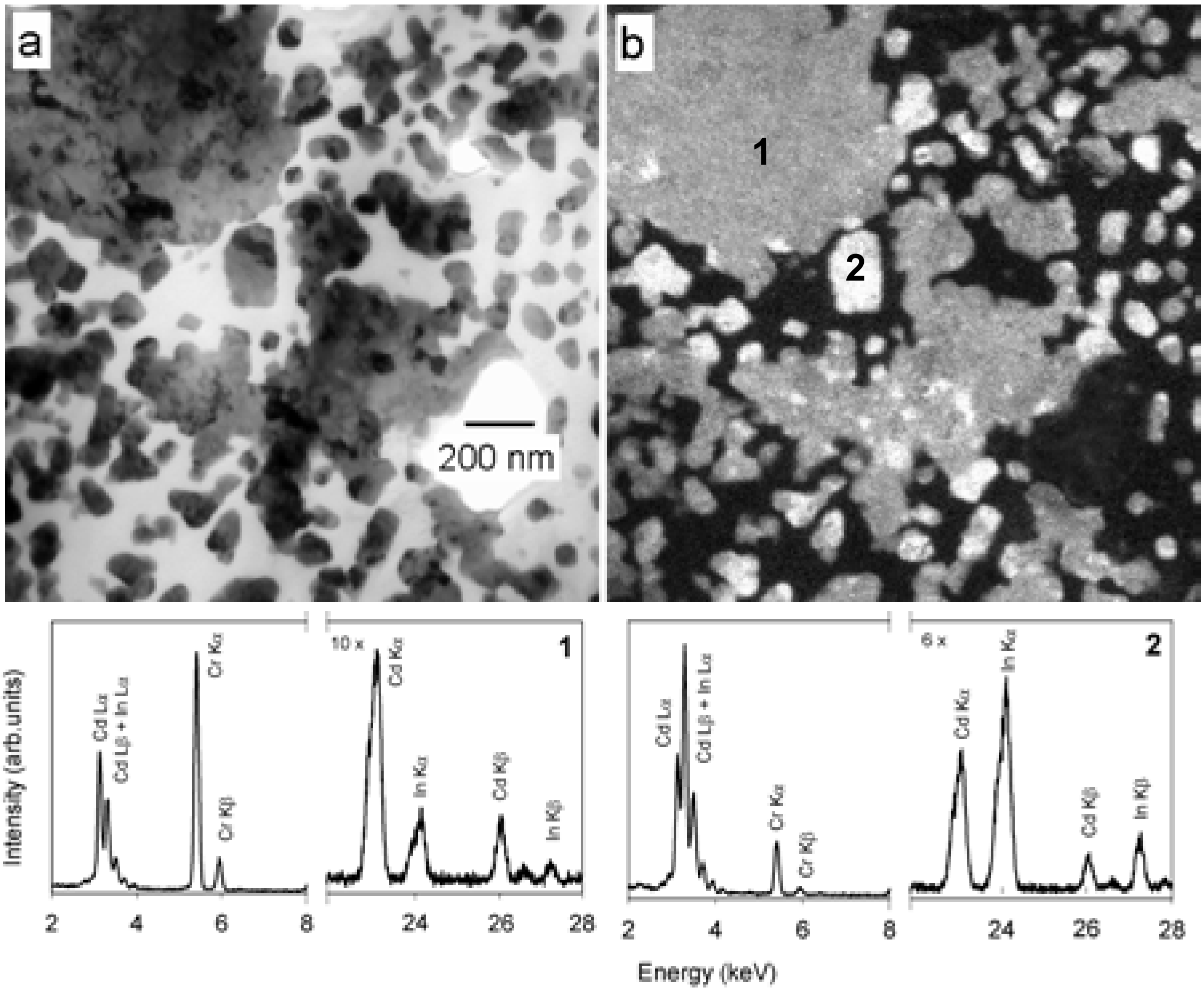


Fig.2 EFTEM investigation: Checking the homogeneity of the complex spinel $CdCr_{1.5}In_{0.5}O_4$ prepared from nitrate precursors; (a) TEM image and (b) In $M_{4,5}$ jump ratio image revealing the occurrence of two phases with different indium concentration, with EDX-spectra recorded from regions 1 and 2



EELS and EFTEM of Titanium-doped Electrolytic Manganese Dioxide

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Introduction

Former investigations of the uncycled titanium-doped electrolytic manganese dioxide (doped with organotitanium compounds) were carried out on powder samples, where the powder was mounted on holey carbon grids following standard TEM preparation procedures. Since EELS and EFTEM are limited to thin specimen-regions it was not possible to verify a homogenous Ti distribution in the interior of the agglomerates [1]. To investigate both the surface and the interior of particle agglomerates powder of the TiO_2-cycled material was embedded in epoxy resin, mechanically grinded and dimpled, and finally argon milled under low angle.

Results and Discussion

Figure 1 represents a TEM cross-section through a big particle agglomerate of the cycled TiO_2-doped material, which consists of small nanometer-sized crystallites. The TEM bright field image in Fig. 2a shows a typical specimen region of the same sample. The absolute thickness of the cross-sectioned specimen falls within a range of 35 and 85nm [2]. Because in this thickness range multiple scattering is not a predominant process [3], EELS and EFTEM can be reliably applied to study elemental distributions within the agglomerates. By comparing the two elemental maps for titanium and manganese from figs. 2c and 2d (Ti-$L_{2,3}$ and Mn-$L_{2,3}$) it becomes clear that there are Ti-richer areas on the surface of the EMD agglomerates. These regions appear bright in the titanium map and consist of Ti-Mn-oxides. However the titanium map also shows a homogenous distribution of titanium in the interior of the agglomerates. A quantitative EELS analysis of a spectrum taken at the interior of these agglomerates (marked region in Fig.2a; Fig.2b) gave a Ti/Mn atomic ratio of about 0.05. This ratio is much higher than that determined for the organotitanium doped EMD [1].

There is clear evidence for titanium enrichment at the surface of the agglomerates as well as in the pores that penetrate into the agglomerates (indicated by the arrows in fig. 2c). A concentration gradient of the dopant within the agglomerates could not be found.

EFTEM elemental mapping is a powerful tool for studying the distribution and concentration of dopants in electrolytically doped manganese dioxides. Ion milling of big EMD agglomerates, which are too thick for electron penetration, enables the visualization of the distribution of the dopants from the surface and the interior. This information cannot be obtained from conventionally prepared TEM specimens.

We gratefully acknowledge financial support from the *Fonds der wissenschaftlichen Forschung* (FWF) within the Special Research Program *Electroactive Materials* and supply with titanium chemicals from the companies Rhodia, Auberville, France, and Millenium, Saint-Denis, France. We thank *Albert Brunegger* and *Peter Warbichler* for the preparation of the TEM specimens.

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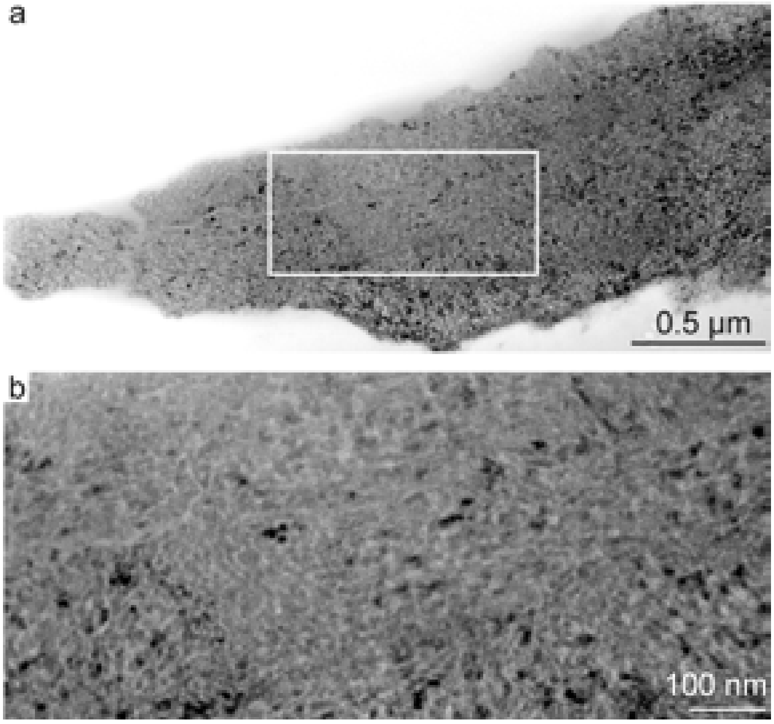

Fig. 1. TEM image of a cross-sectioned EMD agglomerate revealing the internal structure

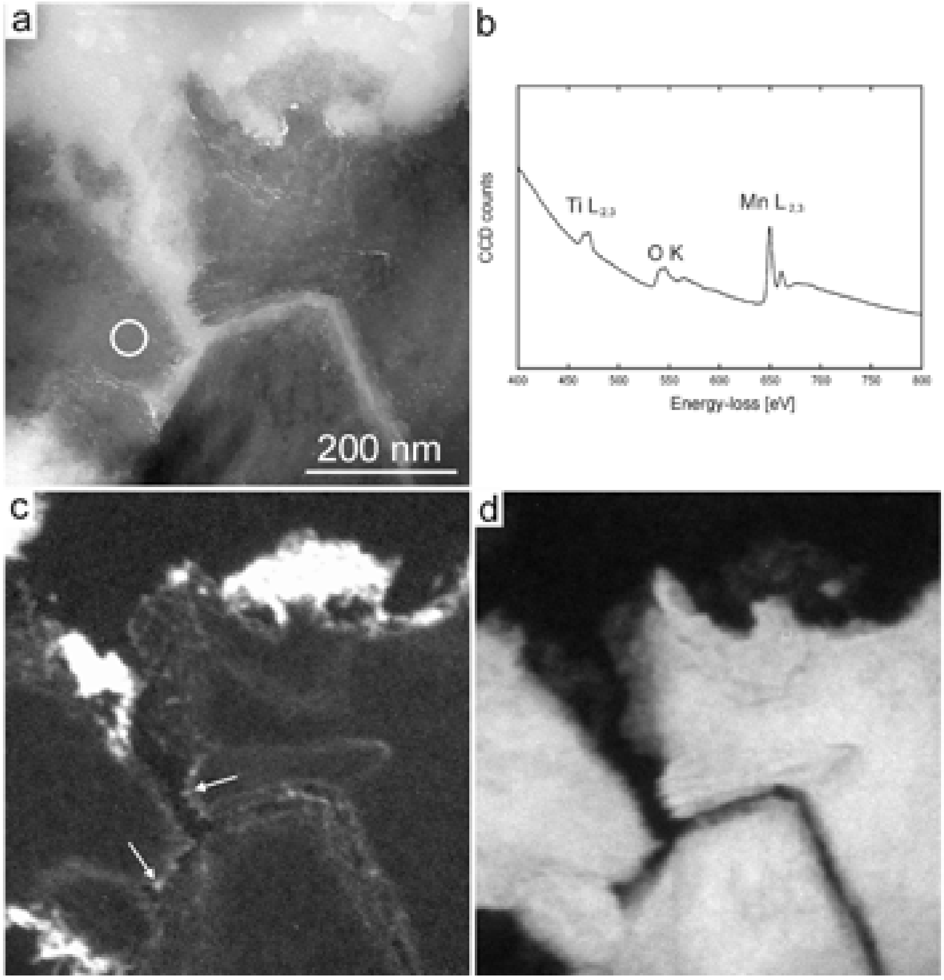

Fig. 2a. TEM image of a cycled titanium doped EMD prepared by cross-sectioning; b. EELS spectrum of specimen region shown in fig.2a; c. titanium distribution map (recorded with Ti-$L_{2,3}$ edge; d. manganese distribution map recorded with the Mn-$L_{2,3}$ edge.

Analytical Electron Microscopy Reveals the Chemistry of Pd Colloids Rinsed with $Na_2S_2O_3$

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During the manufacture of circuit boards, a palladium colloid is absorbed onto an expoxy substrate and serves as a catalyst for the subsequent electroless deposition of copper in nonconductive areas, viz., the drilled holes. Recently, a process has been developed in which the absorbed catalyst is chemically altered by immersion in an aqueous solution of $Na_2S_2O_3$, so that the electroless deposition step is no longer required.
Analytical electron microscopy and FTIR-microscopy were used to characterize palladium colloids before and after activation with a thiosulfate-containing solution and these results are compared with palladium colloids which have been activated with a sulfide-containing solution.

Figure 1 shows the TEM-image of Pd-colloid rinsed with an aqueous solution of $Na_2S_2O_3$ with particles of a mean particle size of about 3 – 6 nm. The electron diffraction pattern (fig.2) exhibits diffuse rings which can be attributed to palladium. For reasons of comparison we include the diffraction patterns of PdS-particles and of a thin metallic Pd-film which corresponds quite well to the Pd-colloid. There is no indication for a Pd-sulfur compound.
In order to detect the thiosulfate ion, we conducted EELS-investigations, where we used the near edge fine structures (ELNES) of the S $L_{2,3}$ ionization edge (figs.3 and 4). Since there is only limited knowledge on the ELNES of sulfur-containing compounds, we recorded ELNES-spectra by using well known reference samples such as $Na_2S_2O_3$, $NaSO_4$ and PdS. The S $L_{2,3}$ ELNES of the Pd-colloid rinsed with thiosulfate shows a close similarity to the S $L_{2,3}$ edge of $Na_2S_2O_3$, but is quite different from the PdS spectrum or from the Pd-colloid rinsed with sulfide. These findings could be confirmed by FTIR-microscopy investigations of the Pd-colloid rinsed with thiosulfate.
Fig. 5 shows EFTEM elemental distribution images: The Pd- and the S-map have been superimposed in the RGB-image thus revealing that at least the larger particles consist of Pd which is covered by a sulfur-rich phase.

From these results we suggest a model for the Pd-colloid rinsed with thiosulfate: The Pd-particles are not altered by treatment with a thiosulfate containing solution, but the surface of the Pd-particles is covered by a sulfur rich phase which probably is the thiosulfate phase found by ELNES and FTIR-microscopy. There is no indication for a phase exhibiting sulfide ions.

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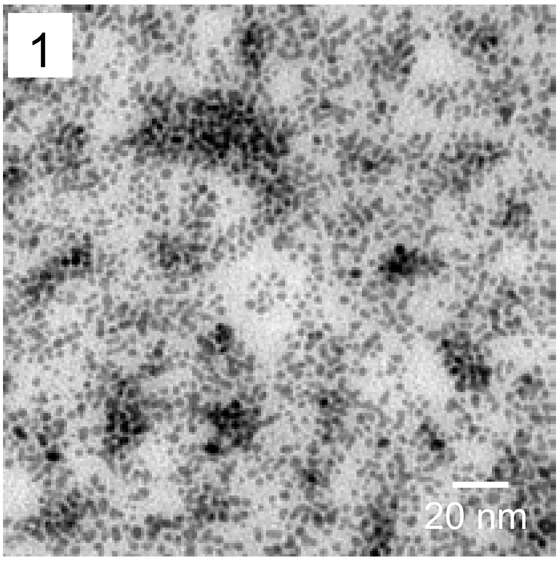

Fig.1 TEM image of Pd-colloid treated with $Na_2S_2O_3$

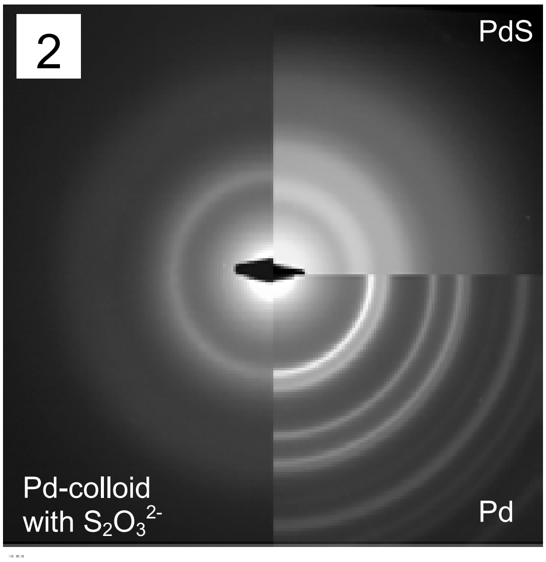

Fig.2 Electron diffraction pattern of Pd-colloid treated with $Na_2S_2O_3$, compared with PdS nanoparticles and a 20 nm thin Pd film.

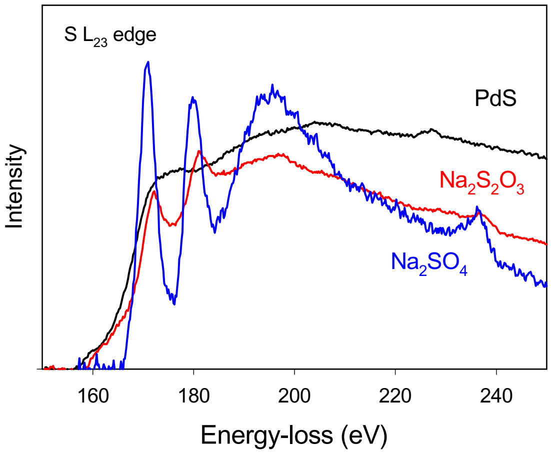

Fig.3 ELNES of the S $L_{2,3}$ edge of reference compounds, background subtracted

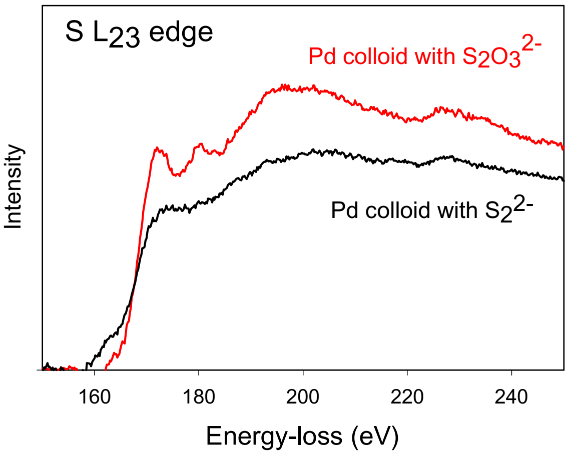

Fig.4 ELNES of the S $L_{2,3}$ edge of Pd-colloids rinsed with thiosulfate and sulfide-containing solutions

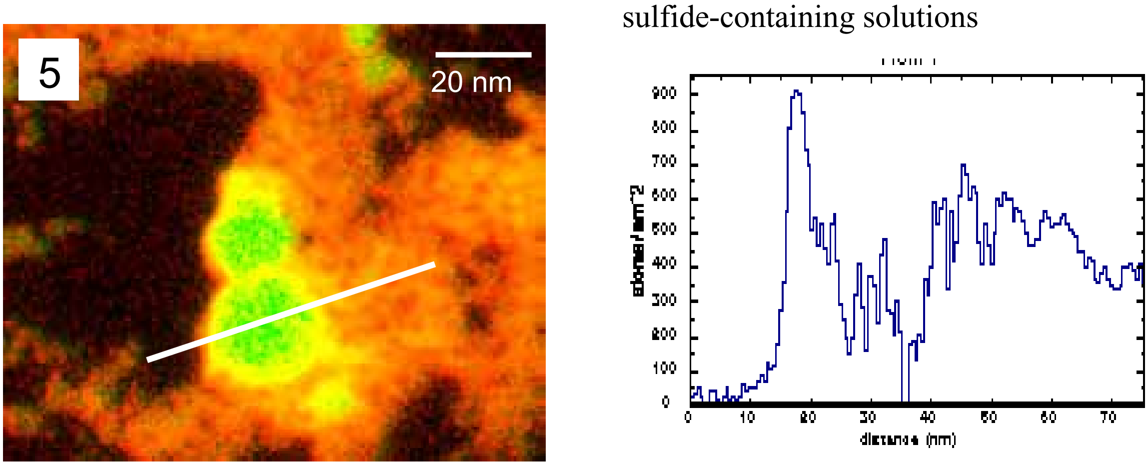

Fig.5 EFTEM elemental maps superimposed in an RGB-map; green = Pd $N_{2,3}$ map, red = S $L_{2,3}$ map, with line scan presenting the number of S-atoms / nm^2

Morphology Investigations of a SCLC-Blockcopolymer

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The creation and characterisation of well defined nanostructured organic materials or organic/inorganic hybrid structures ("nanocomposites") is an area of high technological interest. Therefore great efforts in the generation of nanomaterials have been made in the last years. One possibility to prepare nanostructures is the synthesis of well-defined blockcopolymers, which are able to form microphase-separation if the two covalent bounded blocks are incompatible. In combination with conjugated electrical conductive domains such microphase-separated blockcopolymers are of great interest because of their special electronic properties which can be used for boundary layers or transport-interfaces in electronic devices.

In this abstract an example for a microphase-separated side-chain liquid crystalline blockcopolymer is given. If one of the incompatible partners is a liquid crystalline block, microphase-separation is quasi guaranteed, as the mesogens have a high self-assembling tendency.

In Fig.1. the chemical structure of blockcopolymer **C9-Cy** is shown as an example for a series of polymers under investigation. The blockcopolymer **C9-Cy** was synthesized in two different mol-ratios:

C9-Cy-A, where the mol-ratio of the liquid crystalline block C9 to the partially crystalline polyoctenamer Cy is 1:3

C9-Cy-B, where the mol-ratio of the liquid crystalline block C9 to the partially crystalline polyoctenamer Cy is 3:1.

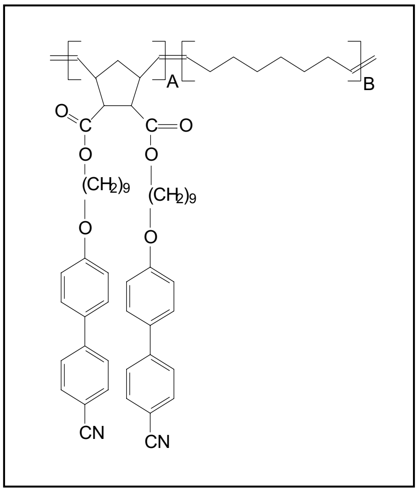


Fig. 1 SCLC-blockcopolymer C9-Cy

The nanostructures were characterized by atomic force microscopy (AFM), small angle X-ray spectroscopy (SAXS) and by transmission electron microscopy (TEM). Thermal characteri-zation was carried out by Differential Scanning Calorimetrie (DSC), (results in table 1).

Polymers	M_w (g/mol)	M_w/M_n	T_g (°C)	T_m(Cy)	T_i (°C)
C9-Cy(1:3)	65328	1.2	28	55	131
C9-Cy(3:1)	67200	1.3	26	55	129

Tab.1 GPC-data and DSC-data of the blockcopolymers **C9-Cy**

The formation of a smectic-A texture (S_{mA}) was ascertained by Polarized Light Microscopy (POM) in combination with a heating stage as shown in the POM-image in Fig. 2 and by X-ray diffraction. The *AFM-picture* of a polymerfilm of **C9-Cy-A** shows a multi-layer-structure, which is caused by the incompatibility of the two covalent bounded blocks. The TEM-image confirms the existence of microphase-separation consisting of domains with a lamellar structure with an interlayer distance of 15 nm. The sample was cut by cryo-ultramicrotomy and afterwards the aromatic biphenyl-units of the mesogens were stained with RuO_4. *SAXS-reflexes* gave a peak for the lamellar phase-separation of the blocks. From this the interlayer distance was calculated to be 154 Å. The second peak confirms the existence of a smectic texture. The distance of the smectic layers within the LC phase is 45 Å.

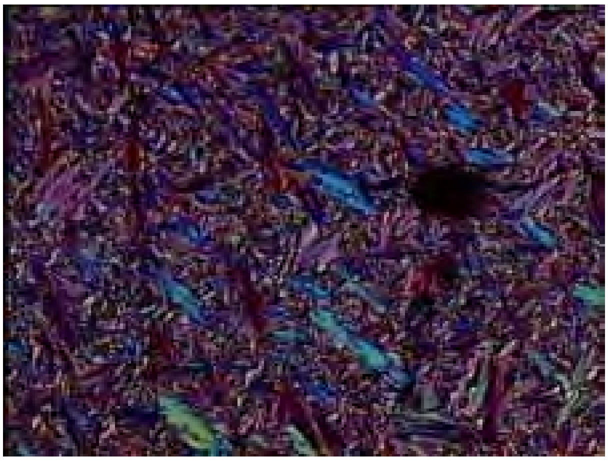
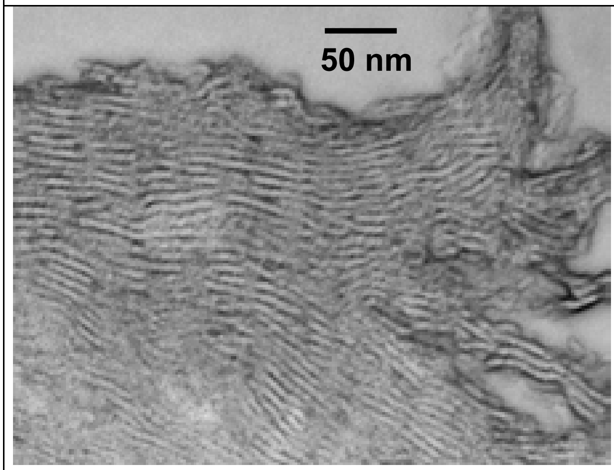
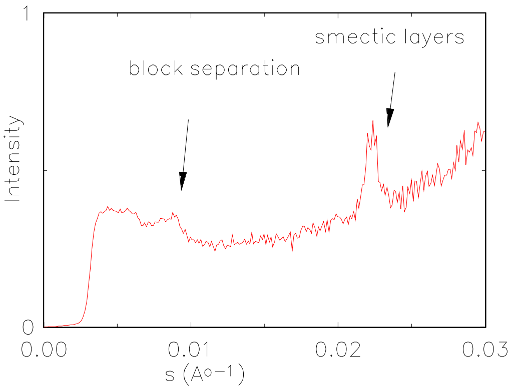
	
POM-image of the blockcopolymer **C9-Cy-A** T=120°C, magn. 100, smectic A	AFM-image of a polymerfilm of **C9-Cy-A**
 	
TEM – image of the blockcopolymer	SAXS-reflexes of the blockcopolymer

Fig. 2 Characterization of the microphase-separation of the blockcopolymer **C9-Cy-A** using different methods

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Electron Microscopy Study of Sn/SnSb Composite Electrodes for Lithium-ion Batteries

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Summary: Electron microscopy (SEM and TEM) in combination with spectroscopical techniques (EFTEM, EDXS and EELS) has been used for the characterization of Sn/SnSb composite electrodes for lithium-ion batteries. Morphology and changes of morphology, which occurred during charge/discharge cycling of the electrode, are given. Furthermore the chemical composition and particularly compositional fluctuations within the composite material are investigated using EFTEM and EDXS.

Alloys of the elements Sn and Sb are interesting electrode materials for lithium-ion batteries due to their high theoretical lithium storage capacities compared to carbonaceous electrode materials. A crucial point is the integrity of the electrode during charge/discharge cycling. Substantial volume changes during insertion/removal of lithium into/from the alloy composite electrode cause mechanical stress and disintegration and therefore reduce the lifetime of the electrode. It is clear that observation of the micro- and nanostructural changes of the composite electrode is of immense importance for further improvements of the cycling performance and coulombic efficiency [1].

In this contribution we report on investigations of the morphology and changes of morphology of Sn/SnSb composite electrodes during cycling using SEM and TEM (including EDXS and EELS analyses). The composite electrodes consist of 82% active material (Sn/SnSb powder), 10% Ni-powder as conductive additive and 8% poly(vinylidene fluoride) (PVDF) acting as a binder. Investigations were performed on a FEG-SEM (DSM 982 Gemini) and a Philips CM20/STEM operated at 200 kV (LaB_6 cathode), equipped with a Gatan imaging filter (GIF) and a Noran EDX system with HPGe-detector. Samples for TEM observation were prepared either following the standard powder preparation techniques or by direct argon-ion milling of the electrode material deposited on a stainless steel grid.

Fig. 1 shows SEM micrographs of an uncycled Sn/SnSb composite electrode (Fig.1a and Fig. 1b) and an electrode after 10 cycles (Fig. 1c). The large round particles represent the polymer binder phase which is found to be dispersed inhomogeneously in the active material. The distribution of the binder and the metallic particles is largely maintained during cycling, although the active material appears to be more amorphous or covered with an amorphous layer.

Cross sectional TEM can provide the inner structure of the particles. Fig. 2a shows a TEM image of an uncycled Sn/SnSb powder sample. EDX spectra measured by a STEM probe (about 2 nm) on particles showing a core-shell structure are given in Fig. 2b. It was found that the core consisted of Sn, whereas the shell contained Sn, Sb and O. A Sn $M_{4,5}$ jump ratio image confirms these results (Fig. 2c). Since the Sn $M_{4,5}$ and Sb $M_{4,5}$ edges overlap, it was necessary to adjust and optimize the position and width of the pre- and post-edge images [2]. The morphology changes during cycling observed by SEM could be confirmed by TEM analyses. Parts of the active material get finer during the initial cycles, furthermore amorphous layers are found in the cycled material [3].

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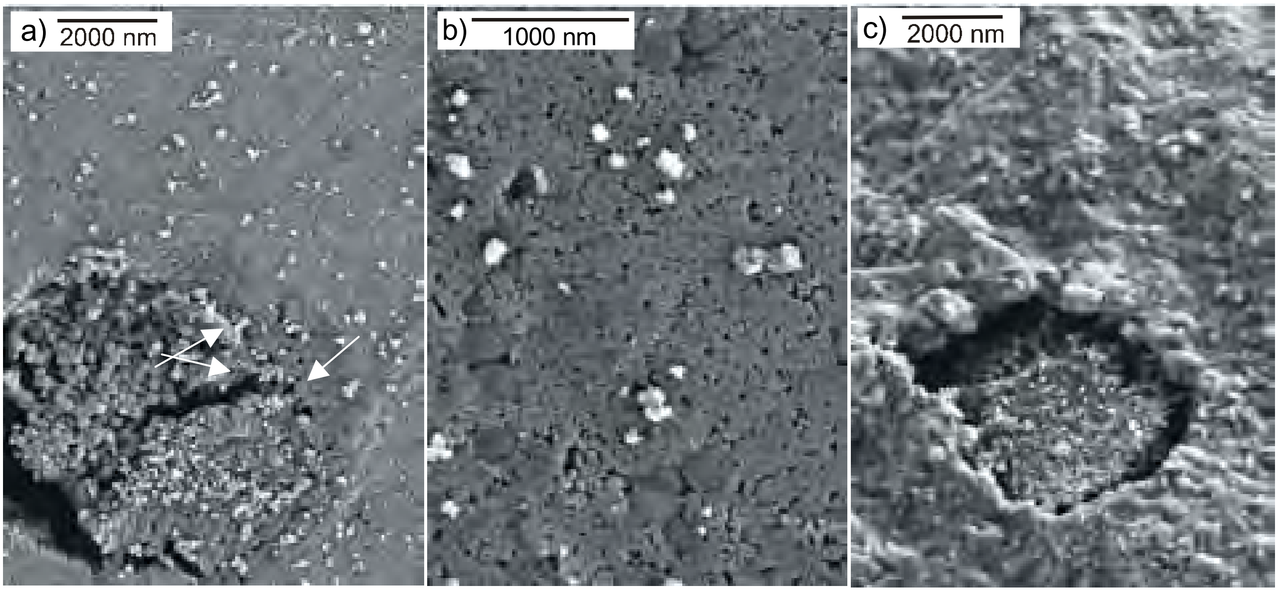

Fig. 1: SEM micrographs of Sn/SnSb composite electrodes (82 wt% Sn/SnSb, 10% Ni, 8% PVDF), a. and b. uncycled electrode, c. electrode after 10 cycles (in the discharged state).

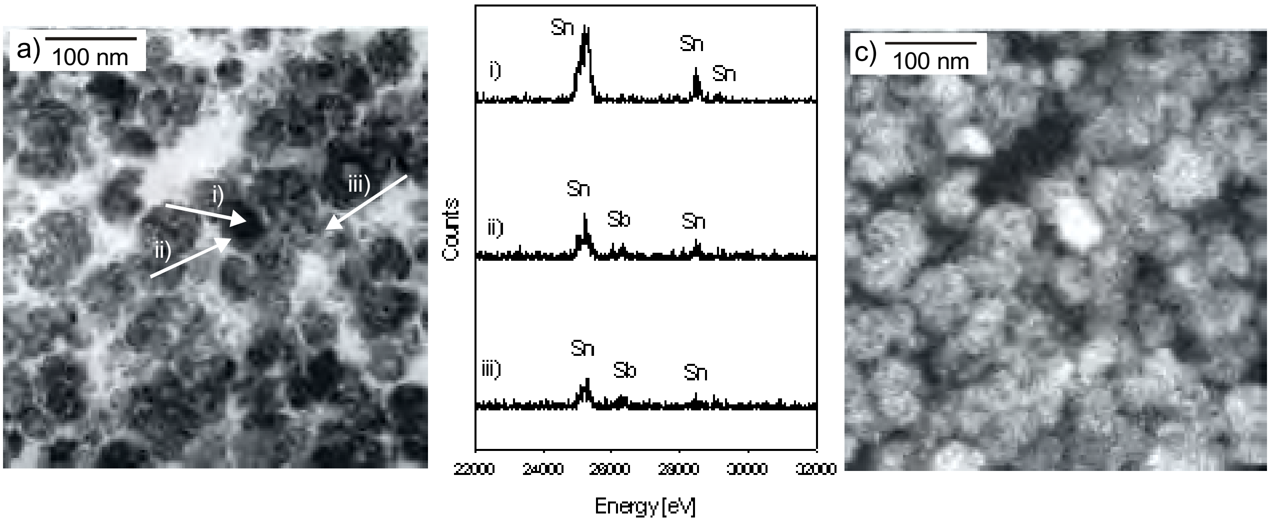

Fig. 2a. TEM brightfield image of Ar-ion milled uncycled Sn/SnSb powder (embedded in epoxy resin); b. EDX analyses of the areas as indicated by arrows in Fig. 2a, (i) core of the particle, (ii) shell of the particle, (iii) fine material; c. Sn $M_{4,5}$ jump ratio image.

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Lung Deposits in the 5300-Year-old Tyrolean Iceman

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In the Tyrolean Ötztal Alps alpinists discovered in 1991 a well-preserved, freeze-dried, Late Neolithic human mummy [1]. This male corpse is one of the oldest human mummy ever found. Since human beings and thus their lungs are exposed to air pollution due to natural reasons, it is of great interest to study the anthracotic areas (which are caused by air pollution) in the lung of this mummy to get information about his living conditions.

Ultrathin sections from epoxy resin embedded lung material were studied by a combination of transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), electron dispersive x-ray spectroscopy (EDXS), energy-filtering TEM (EFTEM) and electron diffraction. This combination of methods gives an overall characterisation of deposits in human lung tissue. EDXS and EELS gave information about the chemical composition of a specimen area. EFTEM showed the distribution of the elements, detected with EDXS and EELS at high spatial resolution and electron diffraction was carried out to find out if the deposit was amorphous or crystalline and to identify a crystalline particle [2].

Lung sections from this mummy contain numerous anthracotic areas consisting of fine-grained particles (Fig.1a). The carbon map shows that these particles are rich in carbon (bright areas in Fig.1b); the EELS-spectrum reveals that these particles consist only of carbon (Fig.1c). The near-edge fine structure of the carbon K-edge and the electron diffraction pattern are typical for soot which probably was inhaled from open fires in houses [3]. Between these soot particles we could detect many tiny mineral crystals, which are made visible in the C K map as black particles. The bright regions in the silicon map (Si $L_{2,3}$ jump ratio image shown in fig.2a) correspond to the bright regions in the oxygen map (O K jump ratio image in fig.2b). Additional information on the composition of these crystals, seen in the EDX-spectrum (fig.2c) and from electron diffraction showed that these and most of the crystals found in anthracotic areas refer to the mineral muscovite. The Ötztal Alps, were the Iceman was found and where he probably lived, are composed of different muscovite containing metamorphic rocks. Mica-rich rocks weather easily and so tiny crystals become airborne and may be inhaled. Beside muscovite various feldspar crystals, illite and quartz particles were also found with the soot. Not only mineral particles were detected in the Iceman's lung; some differently shaped amorphous particles were also inhaled and subsequently deposited in the anthracotic areas. These organic particles could derive from indigestible cell wall materials. As these particles could be threshing residues it can be suggested that he was at least partly working as a farmer.

Beside these findings two kinds of crystals were detected in the lung tissue outside of the anthracotic areas. One of them forms small aggregates (fig.3a) which were identified as iron phosphate crystals (fig.3c). The detailed analysis of the electron diffraction pattern (fig.3b) revealed that these crystals refer to vivianite. The second kind of crystal found outside of the anthracotic areas is hydroxyapatite. As these two kinds of crystals are found separately in the lung tissue and as least compounds of them are also found on the skin of the mummy, we assume that they were not inhaled but were crystallized during the 5300 years of storage of the Tyrolean Iceman in the high mountains.

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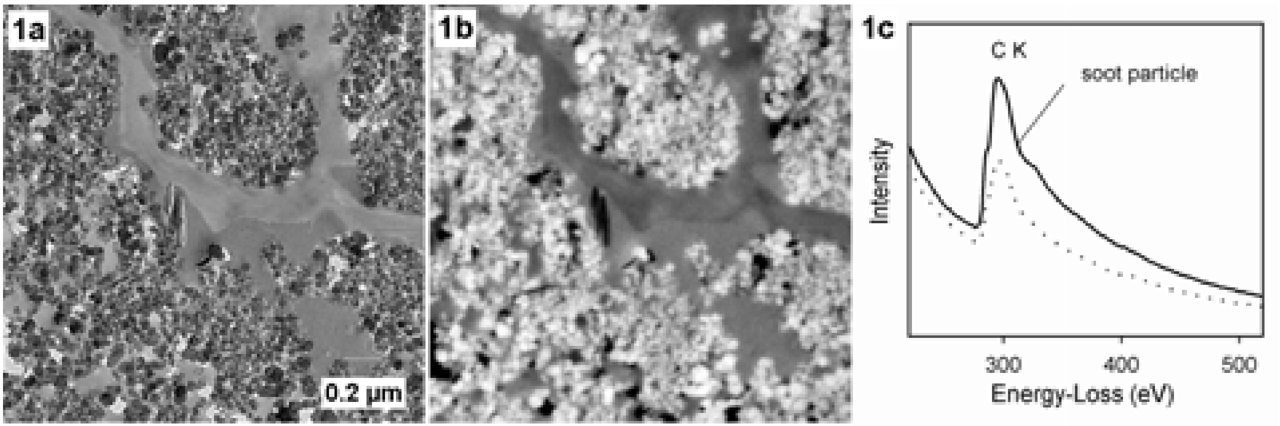

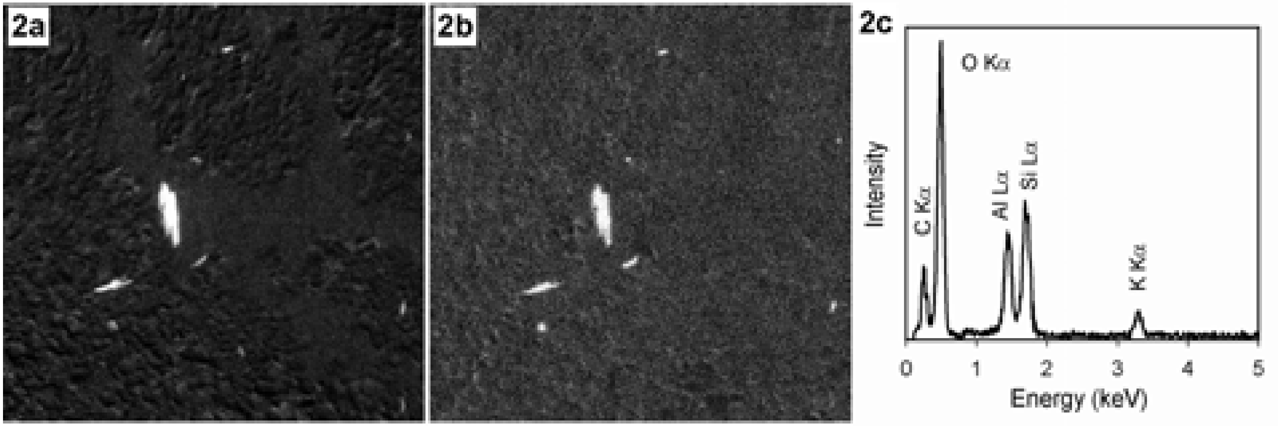

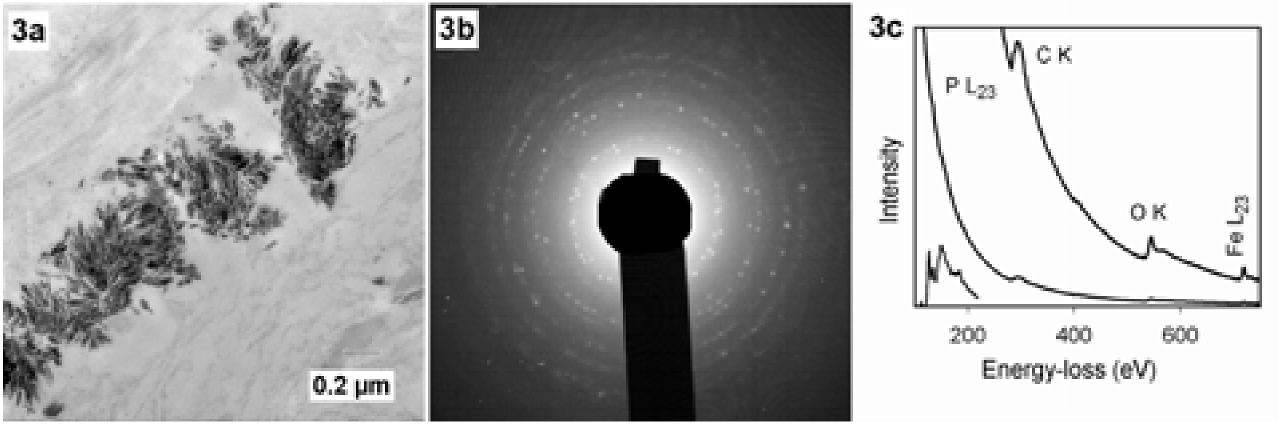

Fig.1a. TEM image of an anthracotic area, b. carbon map (C K elemental map) of this area; c. EELS-spectrum of soot particles and embedding tissue (dashed).
Fig.2a. Silicon map (Si $L_{2,3}$ jump ratio map) of the anthracotic region shown in fig.1a; b. oxygen map (O K jump ratio map); c. EDX-spectrum of a bright particle (= mineral muscovite).
Fig.3a. TEM image of vivianite crystals; b. electron diffraction pattern of these crystals; c. EELS-spectrum of vivianite particle (P $L_{2,3}$ edge also shown with the background subtracted)

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