ExtreMat
New Materials for Extreme Environments

project | news

issue | 2

Midterm - Achievements and Prospects

Two years after its launch, the ExtreMat Integrated Project is well on its way to create new multifunctional materials for top-end applications in extremely challenging environments.

This issue of the ExtreMat Project News provides a status of the four ExtreMat sub-projects.

Self-passivating Protection Materials

The objective of this subproject is the development of radically new protection materials, able to withstand temperatures up to 2000 °C as well as transient heat flux pulses and cool-down shocks up to 1000 K/s.

The materials shall offer self-passivating effect when exposed to physico-chemically aggressive media (e.g. hydrogen, oxygen or chemically active radicals) and passive stability by surface regeneration processes.

Doped carbon-based materials for fusion first wall applications are being developed within ExtreMat. The aim of doping is to add resistance to chemical erosion by hydrogen while improving at the same time the thermal shock resistance of these materials and especially avoiding particle emission from heat loaded surfaces.

The results obtained with Ti-doped graphites are especially promising. It was demonstrated that Ti-doping reduces the chemical erosion of graphites by hydrogen by factors of 5...10, depending on the temperature. The mechanism of this reduction consists basically on a TiC-enrichment at the surface due to preferential erosion of carbon by hydrogen until a steady state is reached. By this way a self-passivation of the material against hydrogen is achieved.

Particle emissions under high thermal loads can also be suppressed by Ti-doping. This was demonstrated by high heat flux tests of the Ti-doped materials with surface heat loads of 2.4 GW/m^2 during 4 ms pulses, showing a significant reduction of the particle emission compared to undoped graphites. This mainly results from the higher thermal conductivity of the Ti-doped graphite material, which in turn is a consequence of the catalytic effect of the TiC particles on the formation of the graphite structure during the thermal treatment at more than 2700°C at manufacturing.

Concerning potential applications, the joining technology of Ti-doped graphite to copper heat sinks by brazing is under development. Another important topic is the use of sub-µm scale metal-doped C as matrix material in CFC (Carbon Fibre reinforced Carbon) materials in order to provide these highly thermal shock resistant materials with additional self-passivation against hydrogen.

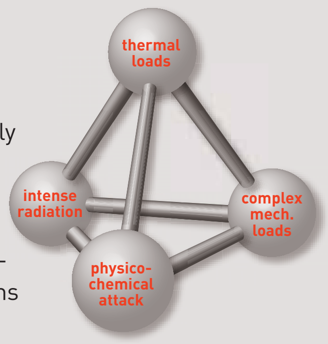
Reduced particle emission by Ti-doping of graphite (picture: FZJ)

SiC-based multilayer ceramics manufactured by tape casting and subsequent sintering are being developed as thermal protection for nose and wing leading

ExtreMat in a Nutshell

ExtreMat is a joint research project of 37 renowned industrial and scientific partners, co-funded by the European Community under the Sixth Framework Programme for Research and Technological Development as a so-called 'Integrated Project'. It targets at development and industrialisation of new knowledge-based materials for top-end applications in extreme environments, characterized by:

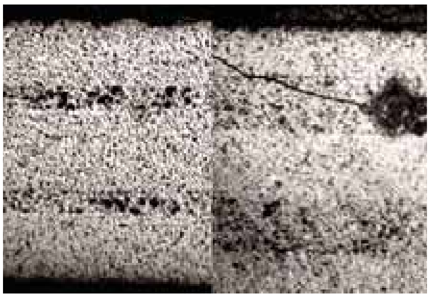
- High temperatures and heat fluxes with frequent, rapid changes
- Complex mechanical loads, e. g. by thermally induced strains in compounds or actively cooled parts
- Physico-chemical attacks by aggressive media, e. g. oxygen and hydrogen radicals, atoms
- Strong irradiation causing structural changes and defects



Typical application fields are high power / high temperature eletronics, aerospace engines and thrusters, heat shields for re-entry vehicles and hypersonic aircrafts, components for advanced fusion and fission reactors, as well as further spin-off applications like high power brake systems, gas turbines combustion chambers, components for thermo-chemical hydrogen generation etc.

edges of space vehicles. At these positions oxidation resistance at temperatures as high as 1900°C is required.

A milestone regarding thermal protection was achieved mainly by the integration of porous SiC layers in a multilayer architecture. Porous layers lower down the thermal conductivity and provide a mechanism for crack deviation at the interfaces which positively affects the toughness. Thermal loads up to 380 MW/m^2 during 4 ms pulses were successfully sustained by the multilayered SiC. It also survived 100 laboratory space re-entries simulations in terms of thermal cycle, temperature gradients, pressure and composition of the gaseous atmosphere without suffering significant degradation.



Integrated porous SiC layers, crack deviation at interface (picture: Polito)

The self-passivating behavior of the multilayers against oxidation has been demonstrated by the exposure to air at 1600°C during 30 h, at which a thin SiO_2 protective layer formed at the surface.

For the application of these multilayer ceramics as thermal protection of turbine engine components, chemical stability against water vapor attack is required. For this purpose, a passivating coating on rare earth basis has been successfully deposited on the multilayer system by spray combustion synthesis. These multilayer ceramics, exhibiting self passivating behavior, high thermal stability and good thermal shock resistance, represent an economically attractive alternative to conventional CVD coated CMCs. In particular multilayer SiC does not need surface coatings for oxide protection that suffer degradation owing to thermal shocks.

Tungsten-based materials are foreseen as protection materials for the first wall of present and future fusion devices. A main concern is their high oxidation rates at temperatures above 600°C leading to the formation of volatile radioactive metal oxides in case of accidental loss of coolant with additional air ingress. The work performed during this period demonstrates that doping of tungsten with oxide forming elements represents a promising way for obtaining a self-passivating behavior against oxidation. Alloying of W with Si resulted in a reduction of the oxidation rate by several orders of magnitude compared to pure tungsten. By the addition of chromium as a third chemical element the oxidation rate could be further strongly reduced to values of 0.1% to 1% of the oxidation of pure tungsten.

Heat Sink Materials

Further development in many technical fields is strongly crimped with raising problem of thermal management. At present overheating causes more than 50 % failures of electronic devices and the high temperature becomes a limiting factor also in construction of heat exchangers, fusion reactors, thrusters chambers, brake systems, aircraft engine parts etc.

New developments requiring the dissipation of up to 20 MW/m^2 will only be possible with heat sinks made of materials possessing extremely high thermal conductivity (~600 W/mK), ability to withstand large temperature changes without disintegration and deterioration of properties and capability to reduce complex thermo-mechanical stresses after bonding to supporting or protecting structures by tailoring of their thermal expansion in the range of 4-9 ppm / K. The development of such materials is a main objective of SP2.

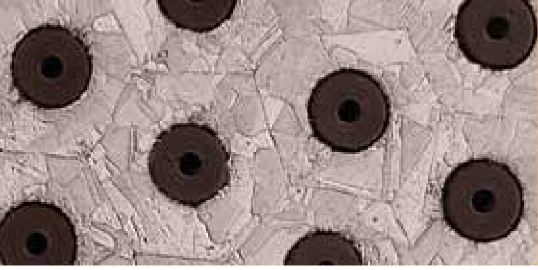
In the first phases of project performance experimental studies were performed on more than 40 promising material systems in order to evaluate their feasibility for targeted applications. Two main material groups were investigated:

- copper alloys reinforced with fibres or (nano)particles for heat sinks working mostly in reactors and engines where performance at high temperatures (up to 1000 °C) and dimensional stability play primary role
- metal matrix composites based on highly conductive phases such as diamond, highly graphitised carbon fibres and flakes, carbon nanotubes, etc. for use in advanced electronic applications

After systematic assessment performed by industrial partners, selected composites were further optimised in phase 3 of the project. For their preparation several advanced technological methods, incl. gas pressure infiltration of melts, squeeze casting, isostatic pressing, rapid sintering, PVD and plasma coating, were utilised. The development of composites was supported by tailoring of interfaces between constituents at nanoscopic level in order to stabilise them in the whole range of working temperatures without degradation of thermal conductivity.

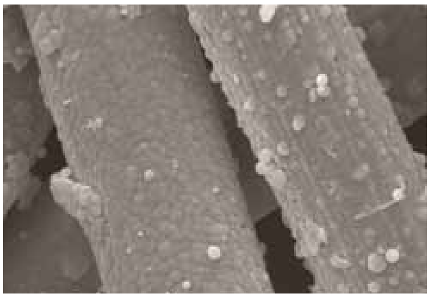
Aluminium-diamond composite (picture: EMPA)

A set of (SiC, W, C) fibre reinforced copper matrix composites has been produced and submitted to neutron irradiation testing to evaluate their feasibility for fusion applications. Regarding materials for electronics, thermal conductivities in the range 600-700 W/(m K) have already been achieved with diamond and pitch based carbon fibres reinforced metals. The technology for con-



tinuous manufacturing of Cu-SiC-fibre monolayers in industrial scale and also industrially applicable technique for gas pressure infiltration of particle/fibrous preforms were developed to support future industrialisation of obtained knowledge. Several patent applications were filed based on the achieved findings.

In next phases of the project the developed materials will undergo a large application oriented testing programme, which should yield data to allow assessment of their behaviour at irradiation, heat flux and thermo-mechanical loading.



Coated carbon fibres (picture: TUW)

Various combinations of heat sink and protection materials will be prepared in order to demonstrate and test the mutual joinability and performance of joints under extreme loading. Several experiments already started to evaluate the performance of developed materials as heat sinks in electronic packages, power- and optoelectronic devices and in divertor of fusion reactor. The process techniques will be further developed and adapted to allow their industrial upscaling.

Radiation Resistant Materials

The objective of this subproject is the development of new materials for advanced nuclear applications (e.g. fusion, fission, neutron sources and accelerators) with protective, heat removal and structural functions. The materials shall maintain structural stability under very intense irradiation at lowest possible activation: Metallic materials at neutron doses up to 150 dpa (displacements per atom) and at operation temperatures of up to 700 °C, non-metallic materials at neutron doses up to 10 dpa and at operation temperatures of up to 1000 °C.

Materials under development and investigation are ODS steels and W-based alloys, as well as Carbon- and SiC-based materials.

Research work in this subproject covers the experimental and theoretical investigation of fracture behaviour, radiation damage and radiation effects, the identification of testing parameters for pre-/post-irradiation testing, the selection of most promising material compositions and manufacturing routes, the production of required raw materials and final test specimen, the characterization of their microstructure and their physical and mechanical properties, as well as the planning and implementation of the actual neutron irradiation tests. The following highlights have been achieved:

Modelling of radiation damage and radiation effects: As previous available long-range interatomic potentials for pure tungsten seem to fail to reproduce the correct energy of defects in body centred cubic (bcc) transitions metals, a new long-range interatomic potential for pure tungsten has been developed which is now being used for simulating radiation damage in pure tungsten by molecular dynamics. The fracture behaviour of polycrystalline and single crystalline tungsten has been investigated over a range of temperatures and strain rates, in the view of modelling the ductile-to-brittle transition.

Development of reduced activation, radiation-resistant, oxide dispersion strengthened (ODS) ferritic steels: Small ingots of ODS ferritic steels, with the composition Fe-(12-14)Cr-1.2W-0.3Ti-0.3%Y_2O_3 (in weight percent), have been prepared by mechanical alloying and Hot Isostatic Pressing (HIPping). The density of the ingots is 99.3-99.5% of the theoretical density and the ductile-to-brittle transition temperature (DBTT) of 12Cr ODS ferritic steels is close to 0°C. All ingots contain a homogenous distribution of fine (below 5nm in size) oxide particles. The numerous internal interfaces originating from the presence of oxide particles are expected to act as sinks for the irradiation-induced defects. Such materials shall be used as structural materials in fission and fusion reactors, for instance, up to about 800°C.

Preparation of the ExtreMat neutron irradiation programme: In ExtreMat a large number of different materials are investigated with respect to the influence of neutrons on their physical, mechanical and heat removal properties. About 1000 specimens have been prepared for the irradiation test, comprising materials newly developed in all ExtreMat subprojects. The different material samples will be exposed to individually defined temperatures and accumulated neutron doses. Defining the arrangement of the specimens inside the reactor, as well as performing the pre-irradiation characterization was a major effort in the experiment so far.

High flux test reactor in Petten (picture: NRG)

The irradiation with neutrons will take place in the High Flux Reactor in Petten, The Netherlands for about one year starting in fall 2007.

ExtreMat Compounds

This sub-project targets at the development of new joining processes, interlayer, coatings and integrated diffusion barriers tailored for the new materials developed in the other three subprojects of ExtreMat. Objectives are the improvement of wetting with molten brazing alloys, reduction of residual stress from bonding processes, prevention of embrittlement by suppression of interfacial material diffusion at high temperatures, as well as prevention of hydrogen permeation.

Deposition of TiC films on C-based protection materials as wetter promotors for brazing (picture: IPP)

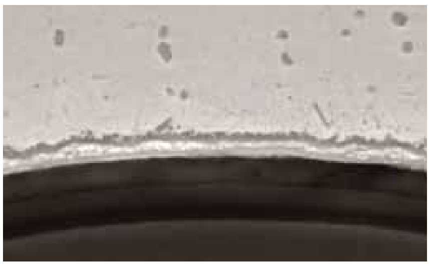
Specific joining and interface techniques for ExtreMat materials were advanced to a significant extent. They can be used in multi-material compound formation (e.g. ceramic interlayers in metallic materials) as well as for joining of materials developed within the other ExtreMat subprojects. In particular:

- → Hydrogen diffusion barriers against tritium diffusion in nuclear fusion applications. Under the specific conditions of metal-cooled fusion reactors, Erbium oxide deposited by chemical vapour deposition on tungsten and steels is showing itself as a suitable alternative to conventional Hydrogen barriers.

- → Electric insulation layers with good thermal conductivity for power electronic applications. Alumina deposited by high velocity oxygen-fuel technique (HVOF) as well as glassy lead-boron oxide coatings by electrophoresis and low temperature sintering, are investigated in different joining concepts to heat sinks. HVOF alumina layers are especially promising, demonstrating dialectric strength up to 30 MV/m (partial discharge < 10 pC), even after 4 weeks of long term high voltage storage at 3 kV. Metallization of the alumina surface for good thermal contact is under development.

- → Surface tailoring techniques which provide compatibility for the joining of ceramic matrix composites to metallic materials, e.g. SiC joined to Cu-based heat sinks. Atomic deposition of thin interface films followed by sophisticated characterization like Rutherford back-scattering and sessile drop technique for in-vacuum wetting angle measurements at high temperature open enhanced operation regimes (temperature, mechanical loads) for compound materials.

- → Improved matching of the coefficient of thermal expansion (CTE) of different constituents of composites for heat sink applications by interlayers. W and Mo, deposited by thermal spray or chemical vapour deposition or implemented as solid sheets, are the main elements used for interlayers with intermediate CTE. As a highlight, W-Cu layers with tailored CTE and an almost 4-times increase of thermal diffusivity could be produced by a combination of plasma spraying and HIPping.



Interface of the CuCrZr/interlayer/SiC composite (picture: DLR)

Outlook

After more than half of the project duration, all four ExtreMat sub-projects are well on their way. Important milestones set for project midterm have been met, e.g. the cross-project neutron irradiation campaign is started. The "Research & Development" project phase will terminate with successful materials concepts which can be taken into the industrialization phase.

The remaining time of the project will be devoted to up-scaling of materials concepts and processes to industry-relevant levels. Planned activities encompass the integration of new materials into compounds by the application of the newly developed joining and bonding technologies.

The public outreach of the ExtreMat project will be intensified by the presence of the project at the Hanover Industry Fair 2008 and through the organization of an "ExtreMat Conference" open for all interested parties in June 2008.

Facts & Figures

ExtreMat is an Integrated Project, co-funded by the European Community under the NMP priority of the Sixth Framework Programme for Research and Technological Development:

Project reference:
NMP3-CT-2004-500253

Start date:	2004-12-01
Duration:	60 Months
Budget:	approx. 35 million €
EU funding:	17.4 million €
Website:	www.extremat.org

Contact:
Prof. Dr. Dr. Harald Bolt
Max-Planck-Institut für Plasmaphysik
Bereich Materialforschung
Boltzmannstrasse 2
85748 Garching
GERMANY

Tel: +49-89-3299-2141
Fax: +49-89-3299-1212
E-Mail: harald.bolt@ipp.mpg.de
URL: www.ipp.mpg.de

Imprint: Published by Bayern Innovativ GmbH, Gewerbemuseumsplatz 2, 90403 Nürnberg, Germany.
Editor: Dr. Uwe Schüssler, Phone: +49-911-20671-310, E-mail: schuessler@bayern-innovativ.de
Authors: C. Garcia-Rosales, CEIT; F. Simancik, IMSAS; N. Baluc, EPFL; C. Gualco, ARI; Ch. Linsmeier, IPP.
Layout: roccas GmbH, Nürnberg.