IGC Newsletter

IN THIS ISSUE

Technical Articles

- Equilibrium and Kinetics of Adsorption of Di-Butyl Phosphate on Activated Alumina

- Knowledge Management Initiatives at IGCAR

Young Officer's Forum

- Fabrication of Nanoporous Alumina Membranes by Single Step Anodization
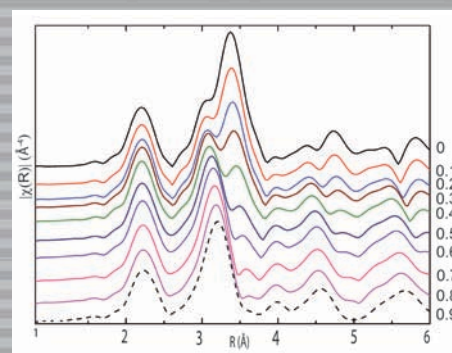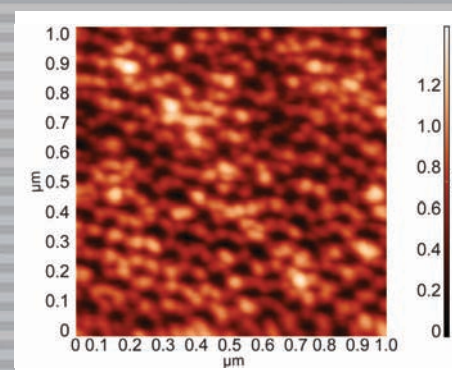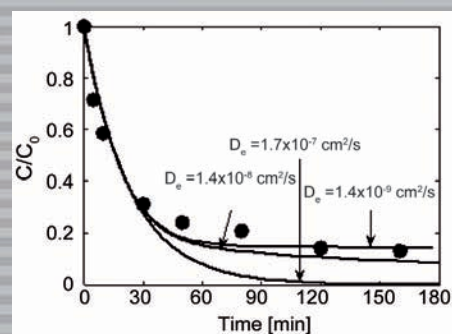
Young Researcher's Forum

- Structural and Optical properties of Wide Band Gap Tunable Compound Semiconducting Oxide: $Cd_{1-x}Ca_xO$

Conference/Meeting Highlights

- 6th International Conference on Creep, Fatigue and Creep-Fatigue Interaction

- Theme Meeting on Novel and Innovative Measurements in Non Destructive Evaluation (NIM-NDE-2012)

Visit of Dignitaries

Awards & Honours

From the Editor

Dear Reader

It is my pleasant privilege to forward a copy of the latest issue of IGC Newsletter (Volume 92, April 2012).

In the Director's Desk, Shri S. C. Chetal, Director, IGCAR has highlighted the R&D activities in Metallurgy and Materials Group taken up towards innovation of improvised materials for future fast reactors, associated fuel cycle facilities, fusion reactors, reprocessing plants, clad tubes for metal-fuel pins and high-temperature boiler for Advanced Ultra Super-Critical Power Plants. The development of Indian Fast Reactor Cladding-1 (IFAC-1) for fuel cladding tubes with improved swelling resistance, is benchmark in this research.

Shri N. K. Pandey and his colleagues have experimentally investigated the fundamental aspects of adsorption equilibrium and kinetics of di-butyl phosphate on activated alumina. The observed experimental adsorption kinetic data has been subsequently interpreted using pore diffusion model. The pore diffusion coefficient and intraparticle effective diffusivity of di-butyl phosphate on activated alumina have also been estimated from the experimental data.

In the second technical article, Shri K. K. Kuriakose and his colleagues have given an account of the knowledge management initiatives at IGCAR. As a step towards this initiative tacit knowledge of senior officers are being elicited through video/audio recordings and this information is made available in the knowledge management portal. As a part of this initiative taxonomy pertaining to the domain knowledge of Computer Division and a knowledge management maturity model have been developed.

In the Young Officer's forum, Dr. S.C.Vanithakumari shares her excitement in the fabrication of nanoporous alumina membranes by single step anodization. Shri Srihari Velaga has presented his study on the structural and optical properties of wide band gap tunable compound semiconducting oxide in the Young Researcher's forum.
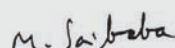
This newsletter carries reports on the 6th International Conference on Creep, Fatigue and Creep-Fatigue Interaction, Indo-French meeting and two-day theme meeting on Novel and Innovative Measurements in Non-Destructive Evaluation (NIM-NDE-2012).

Shri V. Narayanasamy, Honourable Member of Parliament, Minister of State, Prime Minister's Office, Personnel, Public Greviences and Pension, Dr. Barun Mukherjee, Honourable Member of Parliament from West Bengal, Shri Dinkar Khullar, Ambassador and Permanent Representative of India, Vienna, Austria, Dr. Alexander Bychkov, Deputy Director General and Head of the Department of Nuclear Energy, IAEA, Shri Viacheslav Gutkov, IAEA and delegates from UK visited the Centre during the last quarter. Prof. Balraj Sehgal from Royal Institute of Technology, Sweden and Prof. W. Arnold, Physikalisches Institut, University of Goettingen and Department of Material Science and Technology, Saarland University, Saarbruecken, Germany delivered IGC Colloquiums during their visit to IGCAR. A brief report of these visits are covered in this issue.

We are happy to share with you the awards, honours and distinctions earned by our colleagues. We look forward to your comments, continued guidance and support.

With my best wishes and personal regards,

Yours sincerely

M. Saibaba

(M. Sai Baba)
Chairman, Editorial Committee, IGC Newsletter
　　　　　　　　　　&
Associate Director, Resources Management Group

Director's Desk

R&D related to Metallurgy and Materials at IGCAR

Metallurgy and Materials Group pursues a wide range of research programmes of the Centre that encompasses both basic and applied aspects of the development of structural materials for sodium-cooled fast reactors and associated fuel cycle facilities. The key areas of research and development include materials development and manufacturing technology, materials mechanics and properties, physical metallurgy and characterisation, corrosion science and technology, non-destructive evaluation and in-service inspection, irradiation experiments and post-irradiation examination, robotics, innovative design, engineering and synthesis. In the area of materials development, the important activities currently being pursued are: development of special materials like Oxide Dispersion Strengthened (ODS) ferritic steels and Reduced Activation Ferritic Martensitic (RAFM) steels, Indian Fast Reactor Advanced Cladding-1 (IFAC-1), 9Cr-1Mo steel for wrapper tubes, development of welding consumables, optimisation of thermo-mechanical processes for fabrication, characterisation of microstructures, mechanical properties and their interrelationship, modeling of microstructural stability and phase evolution, corrosion, bio-fouling studies and advanced mechanical property measurements using small specimen techniques etc.

Core Structural Materials

14Cr-15Ni-Ti modified austenitic stainless steel (alloy D9) in 20% cold-worked condition is chosen for fuel cladding and wrapper tubes of the initial core of PFBR with a target peak burn-up of 100 GWd/t. An improved version of alloy D9 containing 0.04% P and 0.75% Si, christened as IFAC-1 (Indian Fast Reactor Advanced Cladding-1), has been developed for future fuel cladding tubes with improved swelling resistance to achieve a target peak burn-up of 150 GWd/t. As IFAC-1, which contains higher levels of low-melting eutectic-phase forming elements, is highly susceptible to solidification cracking, extensive pulsed-TIG welding trials, with different weld and geometrical parameters, were carried out to optimise the welding condition for defect-free welding of 316LN SS end plugs to IFAC-1 cladding tubes. These tubes, with optimised composition, will be manufactured (in collaboration with MIDHANI, Hyderabad and Nuclear Fuel Complex, Hyderabad) and taken up for detailed long-term mechanical property characterisation and for studies using laser welding to assess the relative merits of pulsed TIG and laser welding methods. Similarly, 9Cr-1Mo steel, with improved toughness, has also been developed for use as a wrapper material in future.

To realise the target burn-up of upto 200 GWd/t in future, a ferritic-martensitic ODS steel ($Fe-9Cr-2W-0.1C-0.2Ti-0.35Y_2O_3$), with uniform nano-sized Y_2O_3 dispersoid distribution, has been developed. Using an optimized fabrication flow-sheet, fuel cladding tubes of about 4.2 meter length have been fabricated for the first-time in the world. Irradiation with 5 MeV nickel ions at 600°C with a targeted dpa of 50 did not show any observable changes in dispersoid distribution and size indicating the stability of dispersoids. Efforts are on to develop high-chromium ODS steel considering both reactor and reprocessing requirements. Strategies are being identified to reduce anisotropy in

high-chromium ODS steel by optimizing the thermo-mechanical processing route.

Reactor Structural Materials

Extensive evaluation of the creep and low-cycle fatigue properties of 316LN SS, the principal material for high-temperature structural components of PFBR, including its weld joints, confirmed the adequacy of mechanical properties used in the design. The crack growth studies on the welds under monotonic, cyclic and creep loading conditions at various temperatures and extents of ageing confirmed that they have better crack growth resistance compared to those in the French code RCC-MR A16 for the same class. Creep, low-cycle fatigue and creep-fatigue interaction tests conducted in reactor-grade flowing sodium environment at 600°C showed that there are no detrimental effects of sodium on these properties; in fact, the low-cycle fatigue and creep properties are significantly improved in sodium. Electron-probe microanalysis studies enabled predicting the extent of loss in thickness of the material on exposure to sodium at 525°C for 40 years.

As the specifications for various welding consumables to be used in PFBR are tighter than those available in various standards to enhance reliability of sodium components, consumables meeting these specifications were not commercially available in the market. This necessitated indigenous development of these consumables in association with welding consumable manufacturers in the country with necessary support from designers and quality assurance personnel. This led to successful development of E316-15M electrodes and 16-8-2 filler wires for welding 316LN SS and these indigenous welding consumables have been used for fabrication of all the PFBR components made of 316LN SS. Also, E9015-15 electrodes for welding modified 9Cr-1Mo steel have been indigenously developed for future use. With a view to increase the design life of structural components of future sodium cooled fast reactors from 40 to 60 years, studies are being carried out to develop a nitrogen-alloyed 316LN SS with superior tensile, creep and low-cycle fatigue properties as compared to 316LN SS containing 0.07% nitrogen. The influence of nitrogen content on the creep and low-cycle fatigue behaviour of 316LN SS has been studied at four different nitrogen levels from 0.07 to 0.22% by keeping the rest of the composition unaltered. Creep rupture strength was found to increase almost ten times with the increase in nitrogen content from 0.07 to 0.22%. The increase in creep strength with nitrogen content was associated with decrease in steady-state creep rate and increase in the time spent in primary and secondary stages, thus leading to the extension of time for the onset of tertiary creep. The low-cycle fatigue life was also found to increase with nitrogen content upto 0.14%. It has been established that the optimum nitrogen level of 0.12-0.14% provides better combination of creep and low-cycle fatigue properties in 316LN SS. Fracture and crack growth studies for these materials are in progress to confirm optimum nitrogen content. Further, welding electrodes containing 0.12-0.15% nitrogen have been developed for welding of these high-nitrogen 316LN SS. The nickel content is maintained at about 10.5% to ensure the minimum required delta-ferrite in the weld metal. The weld joint made by this consumable met all the mechanical property requirements and passed the intergranular corrosion test and cracking susceptibility test, as per PFBR specifications.

Development of coatings to avoid self-welding, galling and fretting wear of mating surfaces in flowing sodium is another technology that has been developed successfully in close association with Indian industries and successfully implemented during fabrication of various PFBR components. Nickel-base hardfacing alloy Colmonoy-5 was chosen for hardfacing applications based on detailed studies carried out on high-temperature stability of the alloy, effect of dilution on its properties and extensive induced-activity calculation for each of the reactor components that would require hardfacing.

The technology for Teflon coating on large diameter shells was developed in collaboration with Indian industry and was demonstrated on a two-metre diameter scaled-down bearing support ring of large and small rotatable plugs of PFBR. The technology for Teflon coating on carbon steel was transferred to the industry and was successfully used for large rotatable plug and small components of PFBR.

Reprocessing Plant Materials

For dissimilar joining of 304 SS piping to titanium dissolver vessel, required as for the fast reactor fuel reprocessing plant, various joining techniques were studied and the explosive cladding route was selected. This dissimilar joint has been characterised for the mechanical property requirements and nitric acid corrosion. A Ti-Ta-Nb alloy has been developed as a candidate dissolver material for future. The corrosion resistance in boiling nitric acid was optimised by tailoring the microstructure through appropriate heat treatment. Filler wire of this Ti-Ta-Nb alloy has been developed and used for welding of the dissolver. Explosive welding of the Titanium with 304 SS has also been successfully established.

To establish the reprocessing technology for metallic fuels by the pyrochemical route, identification, development, testing and qualification of reliable corrosion resistant materials and coatings for service in corrosive molten lithium-chloride–potassium-chloride (LiCl-KCl) salt and molten uranium environment operating at 600 to 1300°C are necessary. Molten salt test

assembly for testing materials and coatings in molten LiCl-KCl salt under controlled ultra-high-purity argon environment at high temperatures has been designed, fabricated, commissioned and tests have been carried out on various candidate materials and coatings. These studies indicated that yttria-stabilized zirconia (YSZ) coating and pyrolytic graphite have superior corrosion resistance in molten LiCl-KCl salt at 600°C upto 2000 hours exposure. Surface modification techniques like laser remelting and laser shock processing were used to consolidate the coatings and improve their high temperature performance. Coating integrity studies using dielectric electrochemical analysis and thermal cycling established that, compared to plain 9Cr-1Mo steel, YSZ-coated 9Cr-1Mo steel performed better at 200–950°C. Development of simulated metal waste form (MWF) alloys of solid waste including anode basket and clad hulls with zirconium addition was undertaken. Further, characterisation of these alloys, including microstructures, microhardness, electrochemical, corrosion and leachability in simulated geological repository medium have been carried out.

Fusion Reactor Materials

Realization of fusion reactor technology depends largely on the development of materials resistant to the simultaneous effects of high-energy (about 14.1 MeV) neutron irradiation and intense thermo-mechanical loads. An India-specific Reduced Activation Ferritic-Martensitic (RAFM) steel for the Indian Test Blanket Module for ITER has been successfully developed by tailoring the chemical composition of conventional modified 9Cr-1Mo steel by substituting the elements having long half-life transmutants with comparatively lower activation counterparts and by reducing trace elements. The contents of tungsten and tantalum were optimised for achieving better combination of toughness, tensile strength and ductility, creep rupture strength and fatigue resistance. Fracture and fatigue crack growth properties of the RAFM steel at ambient and elevated temperatures were established to be matching with or even better than international versions of similar steels.

Metal-Fuel FBR Related Materials

Modified 9Cr-1Mo steel clad tubes for metal-fuel pins have been developed, in collaboration with MIDHANI, Hyderabad and Nuclear Fuel Complex, Hyderabad. Thermo-mechanical treatments were carried out to optimize the process route. Phase transformations and associated thermo-physical properties in U-Zr alloys have also been studied. The thermodynamics of structural phase changes in these alloys has been modelled using the data on variation of thermal properties in U-Zr alloys with temperature established using calorimetry.

Advanced Ultra Super-Critical Power Plant Materials

Establishment of indigenous technology for Advanced Ultra Super-Critical power plants with steam parameters of 300 kg/cm² / 700°C / 700°C, has been taken up in collaboration with BHEL and NTPC. As part of this programme, IGCAR has taken up the development of advanced high-temperature boiler materials and their fabrication technologies. Boiler tubes of two advanced austenitic materials used in high temperature applications, 304HCu SS and Alloy 617, have been manufactured indigenously for the first time in collaboration with MIDHANI, Hyderabad and Nuclear Fuel Complex, Hyderabad. The assessment of mechanical properties of these indigenously produced materials is under progress. Optimisation of welding procedures for both these materials, including development of welding consumables is also being pursued.

Basic Research and Materials Modelling

Research in the area of physical metallurgy includes identification of optimum treatment for mitigating grain boundary embrittlement in modified 9Cr-1Mo steel through systematic grain boundary engineering approaches involving SEM-EBSD based studies. This approach involves a two-stage normalising treatment by which refinement of austenite grain size is achieved, resulting in a reduction of ductile-to-brittle transition temperature by 15°C, and improvement of upper-shelf (Charpy-V) energy by 35 Joules. Grain boundary engineering approaches are also being pursued for improved resistance to stress corrosion cracking in stainless steels and radiation induced segregation in D9 alloy. In the case of D9 alloy, a low-strain thermo-mechanical (one-step and iterative) processing has been adopted to enhance $\Sigma 3n$ boundaries, low energy special boundaries, A two-step iterative processing comprising of 10% deformation followed by annealing at 1000°C for 30 minutes was found to be the optimum thermo-mechanical processing route to achieve upto about 73% of $\Sigma 3n$ boundaries in alloy D9. Methods combining both simulation and advanced high-resolution TEM imaging are being developed to characterise the spatial and size distributions of the nanometre-sized dispersoids, which is a crucial input in the development of ODS steels. Simulation studies to understand the effect of titanium in the matrix as a function of thermal processing are carried out. Yttria coatings deposited on alloy D9 substrates have been investigated to understand the phase stability and chemical reaction of yttria with titanium during high-temperature exposures. Thermodynamic calculations have been carried out to identify the range of composition of different elements in iron, which would favour the formation of Laves phase as an aid to understanding the embrittlement in ferritic steels due to formation of this phase.

In the area of welding research, hot-cracking susceptibility of austenitic stainless steels has been extensively investigated leading to significant improvement in the understanding of the effect of composition, solidification mode, delta ferrite content and applied strain on cracking susceptibility. Artificial neural network techniques were used to predict delta-ferrite content in the weld metal from the composition, and the prediction made by this procedure has been found to be more accurate compared to other techniques available currently in the literature. A new method for measuring diffusible hydrogen content in the welds using electrochemical sensor was developed and patented.

A unified approach has been developed to describe the inter-relationship between the primary, secondary and tertiary creep behaviour and has been tested on the creep data obtained on 304 SS and 9Cr-1Mo steel. A new relationship has been proposed between the parameters of the constitutive equations, which enable easy determination of crucial inputs for analysis of hot-working which otherwise is computationally intensive. This methodology has been tested for the compression tests data obtained on modified 9Cr-1Mo steel over a wide range of strain rates and temperatures for prediction of flow stresses during hot deformation.

PFBR and Future Fast Reactors Related R&D

Aiming at reduced volume of shielding and better economics, advanced shielding materials based on ferro-boron is being developed for possible use in future fast reactors. Measurement of high-temperature thermo-physical properties up to melting point confirmed the high-temperature phase stability of ferro-boron. The metallurgical interaction between ferro-boron and 304L SS clad has been simulated at temperatures of 550-800°C for reaction times up to 10,000 hours. The ferro-boron was found to be compatible with the 304L SS cladding of shielding sub-assemblies.

In the area of metal forming, microstructurally validated processing maps were developed for a large number of materials, such as SS 304, 304L, 316, 316L, 316LN, alloy D9, modified 9Cr-1Mo steel and modified alloy 617. The Zerrili-Armstrong constitutive model was modified to develop rate-dependent constitutive model for austenitic stainless steels. A full-scale finite-element method process model for multiple-curvature forming of thick plate has been developed and validation with full-scale petal forming trials is planned.

In addition to evaluating the fracture mechanics data on PFBR materials including welds required for integrity assessment of components, the materials mechanics studies being pursued, include development of many novel testing and analysis methods aimed at determining these properties with increased reliability and at the same time reducing the test burden. A new procedure combining experiments and analytical methods was developed for estimating the crack-tip shielding during fatigue crack growth, which led to better understanding of the crack-tip damage processes. Master Curve concept was extended to dynamic conditions and methodologies were established to determine the Master Curve from Charpy-V notch specimens (without pre-cracking) to economise testing procedure. Also, employing the Master Curve methodology, fracture-toughness based reference-temperatures were determined for different ferritic steels and their welds for fast reactor applications. Robust correlations between fracture toughness and Charpy-V energy were established such that reliable toughness values could be estimated from simple Charpy-V test data. A procedure to determine the crack-arrest length in Charpy-V impact test was established and successfully applied for determining crack-arrest toughness of modified 9Cr-1Mo steel.

Fluxes that can provide depth of penetration up to 10 mm for austenitic stainless steels without any deterioration in the properties of the weld have been developed for using in activated TIG (A-TIG) process. A-TIG process is also being developed for welding of titanium alloys, ferritic steels and RAFM steel. Infra-red thermography has been successfully employed for online monitoring of the TIG welding process. Artificial intelligence techniques have been successfully used to process the thermography data for weld defect identification and provide feedback control to welding power source to alter the welding parameters that would avoid the welding defects. This system, after full development and field trials, will find application for remote repair of cracks in critical components. Studies are also in progress for optimisation of post-weld heat treatment procedure for steam generator and sodium-to-air heat exchanger considering cold cracking and delayed cracking.

Several R&D projects have been taken up towards realisation of material for future FBRs. A cobalt-based alloy with curie-point temperature of 630°C has been developed, in collaboration with Hindustan Aeronautics Limited, Bengaluru, for the electromagnets for passive shutdown mechanism. R&D is in an advanced stage towards development of modified 9Cr-1Mo steel with boron-addition (to reduce susceptibility to Type IV cracking) for steam generator applications and also for power plant piping.

S. C. Chetal
Director, IGCAR

Equilibrium and Kinetics of Adsorption of Di-Butyl Phosphate on Activated Alumina

The PUREX process has been widely used for the reprocessing of irradiated nuclear fuel elements. This process is based on multistage counter current solvent extraction to separate uranium and plutonium from fission products. Uranium and plutonium are extracted into an organic phase (30 vol.% tributyl phosphate in a hydrocarbon diluent), leaving the bulk of fission products in the aqueous raffinate. It is well known that tributyl phosphate (TBP) and hydrocarbon diluents are degraded due to hydrolytic and radiolytic reactions, forming activity-binding degradation products that can cause product losses, poor separation efficiencies and emulsions which could interfere with process operations. The primary degradation products (dibutyl phosphate, monobutyl phosphate, phosphoric acid and butanol) are produced from the hydrolytic and dealkylation reactions of TBP when contacted with nitric acid at relatively high temperatures. The secondary degradation products (nitro paraffins, aldehydes, ketones and carboxylic acids) on the other hand are originated from the radiolytic reactions of diluents when exposed to intensive radiation. In the PUREX process, the spent solvent is continuously regenerated by scrubbing with sodium carbonate/hydroxide and phosphoric acid solutions after each pass through the process and most of the radioactivity belonging to primary degradation products is removed. Residual activity due to secondary degradation products, however, cannot be removed by these washing solutions as these long-chain soluble organic compounds tend to remain in the solvent even after scrubbing with carbonate washing solutions which will again complex with fission products when the solvent is recycled. Other methods such as vacuum distillation, steam stripping and flash distillation have been reported to be effective techniques, but they are limited by the maximum allowable distillation temperature that could lead to significant decomposition of TBP as tar residues. Adsorption-based solvent cleanup process has been studied by several investigators to improve the performance of the recycled solvent. These studies revealed that solid adsorbents such as activated alumina and base-treated silica gel have the potential to remove some of the activity-binding degradation products.

Adsorption is one of the most reliable and versatile physical treatments, whose effectiveness and economic sustainability are related to the type of sorbent. Activated Alumina is the most widely used adsorbent for many applications because of the chemical properties of its surface. It is highly porous in nature and has high surface area (150 – 350 m^2/g). Alumina, owing to its amphoteric properties provides chromatographers an able adsorbent to separate a multitude of compounds.

In the present study, fundamental aspects of adsorption equilibrium and kinetics of DBP on activated alumina have been investigated to show the mechanistic aspect of the process. Sorption data were correlated with the Langmuir and Freundlich isotherm models. Experiments were conducted to determine the adsorption kinetics for di-butyl phosphate and pore diffusion model was used to interpret the observed experimental adsorption kinetic data. Based on the results, pore diffusion coefficient and intraparticle effective diffusivity of DBP in activated alumina have been estimated.

Transport Mechanism of Solute in Sorbent

Adsorption is a surface phenomenon, but it also involves the transfer of solute from one phase to another. Various adsorption kinetic models have been adopted to describe the behaviour of batch sorption process. Sorption kinetics are however, controlled by the following steps: (1) external mass transfer of solute from bulk solution to the outer surface of particles (film diffusion), (2) diffusion of solute from the sorbent surface to the pores of the particles and (3) the adsorption of solute on the active sites of the pore surface. A non-linear concentration profile is expected within the sorbent phase because adsorption and diffusion occur simultaneously inside the particle.

Adsorption Isotherm

Equilibrium data are generally reported in the form of an isotherm, which is a diagram showing the variation of the equilibrium adsorbent phase concentration with the fluid phase concentration at a fixed temperature. Two commonly used mathematical expressions to describe the adsorption equilibria namely, Langmuir and the Freundlich isotherm models were tested with the experimental data. The Langmuir model of isotherm was found to fit the experimental data better than Fruendlich model as is observed from Figure 1.

Mathematical Model for the Transport of Solute from the Solution into Adsorbent Phase

Development of model equations is based on the following assumptions: (1) diffusivity is constant at a fixed temperature and pressure, (2) activated alumina grains are considered as spherical and porous, (3) the adsorption sites are uniformly distributed throughout the grains and (4) the external mass transfer coefficient and diffusivity are constant for the range of solute concentrations under consideration.

The rate of change of di-butyl phosphate concentration in the bulk solution is proportional to the concentration difference between the bulk phase and the outer surface of the particle. The mass balance in the bulk liquid phase describes the relation between the decreasing solute concentration in the solution phase and mass transfer into the solid phase and can be written as

$$-\frac{\partial C}{\partial t} = \frac{3M_p k_f}{VR\rho_p}(C - C_s) \qquad (1)$$
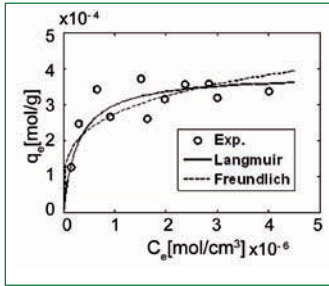
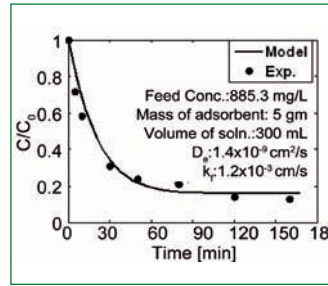Figure 1: Equilibrium data of DBP on activated alumina

Figure 2: Comparison of experimental data and simulation results for DBP adsorption on activated alumina
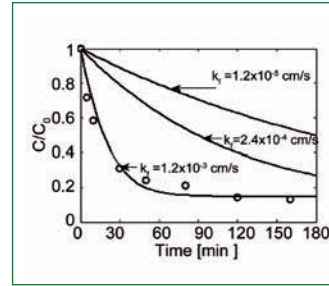

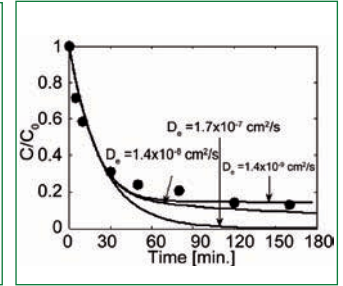Figure 3: Effect of external mass transfer coefficient on model prediction

Figure 4: Effect of effective diffusivity on model prediction

where C is the bulk concentration of solute in the solution phase and C_s is the concentration of solute at the outer surface of the spherical particle. R represents the radius of the particle, ρ_p is the density, M_p is the total mass of the particle, V is the volume used in the batch reactor and k_f is the external mass-transfer coefficient. The mass balance of DBP within a spherical particle is given as

$$\varepsilon_p \frac{\partial C_r}{\partial t} + \rho_p \frac{\partial q_r}{\partial t} = D_e \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \quad (2)$$

where D_e is the effective diffusivity of solute within the particle, ε_p is the porosity, C_r is the solution concentration of DBP within the pores of alumina particle and q_r is the solid phase concentration of DBP.

The Langmuir isotherm $\left(q_r = \dfrac{q_m K_L C_r}{1 + K_L C_r}\right)$ can be used for the correlation of C_r and q_r. Then equation (2) becomes

$$\frac{\partial C_r}{\partial t} = \frac{D_e}{\varepsilon_p + (\rho_p K_L q_m)/(1 + K_L C_r)^2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \quad (3)$$

The initial and boundary conditions can be written as

$$t = 0: C = C_0 , C_r = 0 \quad (4)$$

$$r = 0 : \left(\frac{\partial C_r}{\partial r}\right)_{r=0} = 0 \quad (5)$$

$$r = R : k_f(C - C_S) = D_e\left(\frac{\partial C_r}{\partial r}\right)_{r=R} \quad (6)$$

The model (equation 6) describing the transport of DBP from the solution phase to activated alumina particles was converted into the finite difference equation and was solved numerically by using the fourth order Runge-Kutta method using ODE-45 solver of MATLAB software. The agreement between the experimental results and the model predicted values (as illustrated in Figure 2 is found to be good. The external mass transfer (k_f) and the effective diffusivity (D_e) are the two unknown parameters which are estimated by superimposing the experimental data on to the

diagrams of numerical solution of model equations. The following algorithm was employed to find out D_e and k_f: at the first step the value $k_f = k_f(0)$ was fixed and D_e value was varied to obtain the best fit of the results of numerical solution of equations (3) to (6) with the experimental curves for batch adsorption and $D_e(1)$ was determined. Subsequently, $D_e = D_e(1)$ was fixed and the value of k_f was varied to obtain the best fit again to the experimental curves to obtain $k_f(1)$. In the second step $k_f = k_f(1)$ was fixed in the same way to define $D_e(2)$ and $k_f(2)$. This step was repeated until an acceptable accuracy is attained to get the optimal D_e and k_f values. The value of effective diffusivity (D_e) was determined to be 1.4×10^{-9} cm^2/s.

Sensitivity analysis for the changes of k_f and D_e was performed. Figure 3 represents the effect of k_f on model prediction results. If k_f is 10-100 times smaller than the estimated value of 1.2×10^{-3} cm/s, then the initial removal rate of DBP is slower.

However, when k_f value exceeds the estimated value, the removal rate remains unchanged. As the external mass transfer is sufficiently fast for DBP removal, the increase in the external mass transfer coefficient has no influence on the entire removal process.

Figure 4 shows the effect of diffusivity. If D_e value is 10 – 100 times higher than the specified value (1.4×10^{-7} cm^2/s), then the removal rate becomes faster. However, when D_e is smaller than the estimated value, the removal rate is almost similar to that of the estimated value. Thus, from simulation it was observed that the effect of D_e on removal rate is less sensitive in comparison to the external mass transfer coefficient.

Equilibrium and kinetics of sorption of DBP on activated alumina for the removal from the organic solvent (30 vol.% TBP in n-dodecane) was carried out experimentally. Theoretical models were evolved to explain the experimental data.

Reported by N.K. Pandey & Colleagues
Reprocessing Research & Development Division
Reprocessing Group

Knowledge Management Initiatives at IGCAR

Formal knowledge management initiatives at IGCAR were started a few years back. The broad objective was to meet the growing demands of the Research Centre, through performance improvement and breakthrough innovation, by leveraging on the collective knowledge of various organizational entities. Some of the initiatives are highlighted in this article.

Knowledge Management Policy

Recognizing the importance of knowledge management, our Centre has formulated and adopted a policy to create, share, utilize and leverage the organizational knowledge to achieve world class leadership in the fields of fast reactor technology and associated closed fuel cycles. The policy aims to achieve higher quality, productivity and better collaboration through the synergy of knowledge, resources, facilities and employees, in spite of attrition. The policy statement is given below:

"Indira Gandhi Centre for Atomic Research will consistently endeavor through concerted efforts of all it's employees to generate, archive, manage and disseminate the valuable knowledge for improving it's productivity and achieve & sustain world class leadership in all it's scientific & technological research and development activities."

Knowledge Management Portal

A knowledge management portal (Figure 1) has been developed and made available on the intranet, to meet the needs of the entire organization, with the diverse activities like research, design, development, project execution, support services etc. This initiative is to provide the right knowledge to the right person in right time and in right form. Currently knowledge management servers installed in all the Groups are interlinked. Knowledge modules in the form of design reports, publications, presentations, activities, facilities etc. are made available through the server. Regular knowledge sharing sessions are held in various Divisions/ Groups and those details including the presentations are made available through the server. Some of the Groups have implemented pointers to tacit knowledge in the form of expertise and contact details. Also collaboration features are implemented by some Groups.

Tacit Knowledge Elicitation

Tacit knowledge of senior officers are being elicited through

video / audio recordings and documents. The elicited knowledge modules are made available in the in the knowledge management portal with necessary meta data and are being accessed by the employees.

Taxonomy Development

As a part of knowledge management initiative a taxonomy pertaining to the domain knowledge of Computer Division was developed and implemented. The knowledge is classified into nine categories viz., advanced visualization, application software, computational intelligence, knowledge management, networking & communication, scientific computing, simulation & modeling, wireless sensor networking and general. Under each domain the knowledge documents are classified into publications, presentations, design reports, elicited knowledge, frequently asked questions, tech bits and general. Knowledge quality rating for documents and participants are being implemented.

Knowledge Management Awareness

In order to improve awareness of knowledge management among the employees, knowledge management awareness seminars were conducted in various groups of IGCAR. The discussions during the awareness seminar were audio recorded and made available on the knowledge management portal. Also feedbacks were collected from two hundred and forty five participants. The analysis of the feedbacks indicate that though awareness is good, there is scope for further improvement.

Knowledge Management Maturity Model

Knowledge management maturity model is driven by the necessity to have a clear cut road map for any organization that is embarking on knowledge management implementation. It provides the clear vision with a description of the path ahead. Knowledge management maturity models can be considered as an application of structured approach to knowledge management implementation. In other words development of a knowledge management maturity model is nothing, but engineering of knowledge management. Hence knowledge management maturity model can be defined as the "application of systematic, disciplined, quantifiable approach- that is, an *engineering* approach to development, implementation and successive progression to attain maturity in knowledge management".

A knowledge management maturity model was developed which

Figure 1: Knowledge Management Portal

has six maturity levels (level 0 to level 5). The maturity levels are named as 'Default', 'Initial', 'Qualitative development', 'Quantitative development', 'Maturity' and 'Extended-Organizational maturity'. The model identifies five key areas viz., people, process, technology, knowledge and return on investment. It also identifies twenty parameters(key parameters) for all the key areas (people-6, process-4, technology-6, knowledge-3, return on investment-1). The parameters for people key area are awareness, participation, reward & recognition scheme, knowledge management roles, communities of practice and mentoring & succession planning. The parameters for process key area are knowledge management policy, knowledge management strategy, knowledge management processes and process integration. The parameters for technology key area are network, data & information management, explicit knowledge management, tacit knowledge management, artificial intelligence & knowledge engineering techniques and technology integration. The parameters for knowledge key area are knowledge classification, knowledge capability areas and knowledge organization. Employee satisfaction is the only parameter for return on investment. The parameters can have different values called key values, which can be either qualitative values (Low, Medium and High) or quantitative values (0-100%). The value 'Nil' indicates that, either the parameter is not applicable, or it is not assessed or the value is negligible. Each maturity level is identified by a group of key maturity indicators, which is a combination of key areas, key parameters and key values.

For an organization to be in a specific maturity level all the key maturity indicators pertaining to that level and all preceding levels need to be satisfied. No levels can be skipped. If an organization satisfies all the key maturity indicators pertaining to one level, say level 1 and at least one key maturity indicator pertaining to the next level for each key area, then the organization can be considered to be in a level 1+. Similarly if the organization satisfies at least 50% of the key maturity indicators pertaining to level 2 for each key area, then that organization can be considered to be in a level of 1++. Also if the organization satisfies all key maturity indicators of level 1 and satisfies at least one key maturity indicator or at least 50 % of the key maturity indicators of level 2 in one or more specific key areas alone, then the organization is considered to be in level 1 in the over all maturity and 1+ or 1++ in the specific key areas alone.

The maturity levels of IGCAR and various groups were assessed based on the above model. Recommendation for improving the maturity level is being prepared.

The success of knowledge management depends on the active participation of all employees. In order to improve the participation, several measures such as public recognition, annual knowledge management day etc. are planned.

Reported by K. K. Kuriakose and colleagues
Computer Division
Electronics and Instrumentation Group

Young Officer's FORUM

Fabrication of Nanoporous Alumina Membranes by Single Step Anodization

Dr. S. C. Vanithakumari obtained her Ph. D. in Materials Science from the Indian Institute of Science, Bengaluru in 2009, and joined the Corrosion Science and Technology Group, MMG as Scientific Officer (D) in 2010. She is currently involved in the synthesis of oxide nanostructures, porous ceramic membranes, superhydrophobic coatings and characterization of materials and coatings using atomic force microscopy.

Membranes play a vital role in the nuclear reprocessing cycle in which there is recovery of useful materials as well as separation of fission products from waste. Most of the nuclear industries around the world employ membrane based methods for low level liquid radioactive waste treatment which in turn, reduce the activity concentration of liquid radioactive waste to a level at which they are allowed to be discharged according to national regulations. Liquid radioactive waste treatment involves reverse osmosis, nanofiltration and ultrafiltration. Porous ceramic membranes are useful for micro or nano-filtration purpose as they have high thermal stability and are resistant in aggressive media. Unlike organic polymer membranes, inorganic solid-state membranes exhibit no plastic deformation and immediately regain their shape when the pressure is removed. Moreover inorganic membranes are more resistant to radioactive media, and the most important fission products in the radioactive effluents such as ^{137}Cs and ^{90}Sr are co-precipitated and removed by filtering through ceramic membranes. The most frequently used ceramic membranes are Al_2O_3, ZrO_2, CeO_2 and TiO_2 fabricated by various techniques such as aerosol flame deposition, sol-gel, combined phase inversion/sintering and electrochemical anodization, to name a few. We have employed single step anodization to fabricate porous alumina membranes from aluminium. Anodic aluminium oxide membrane having uniform distribution of pores is highly stable in extreme chemical and thermal environments. Due to this reason, porous alumina is being considered as filtration membrane in nuclear industry. In order to optimize the conditions for pore formation, a systematic study was carried out in which the parameters such as surface pre-treatment, electrolyte concentration, applied voltage and time duration are varied during the single step anodization process employed.

Aluminium sheet of 99.9% purity was used as the substrate to synthesize nanoporous alumina membranes. The experimental set up for anodization consists of electrolyte, anode, cathode and a DC power supply. The aluminium coupons were degreased in acetone to remove dust particles from the surface. Electropolishing was carried out using perchloric acid/ethanol (1:3) electrolyte mixture at 20 V for four minutes at a temperature below 10ºC. After electropolishing, smooth scratch free and mirror like surface was obtained, as confirmed from the atomic force microscopy (AFM) and scanning electron microscopy (SEM) images.

The electropolished aluminium samples were then anodized in a beaker containing 0.4M oxalic acid at an applied voltage of 30 V. The applied voltage was gradually increased to 30 V in order to avoid oxide layer breakdown and was maintained for different time durations (15, 60 and 90 minutes) at temperature below 10ºC. High speed magnetic stirrer was used for agitation of the electrolyte to ensure the homogeneity of temperature throughout the electrolyte during anodization. After anodization process, a porous anodic aluminium oxide was formed on aluminium substrate. The as-formed porous layer has to be isolated by simple chemical removal method. To simplify the isolation process, one side of the aluminium coupon was coated with varnish in order to prevent the other side from anodizing. After characterizing the anodized aluminium sample by AFM and SEM, the next step was to isolate the nanoporous alumina membrane using $CuCl_2$ solution. The varnish coating on the other side of the anodized surface was dissolved in acetone and then varnish was applied on the porous layer (anodized) side to prevent the reaction of $CuCl_2$ on porous layer. In order to avoid the precipitation of $AlCl_3$ on the oxide layer, the anodized sample was immersed in $CuCl_2$ solution only for a duration of 15 minutes. During this immersion, large amount of fumes and heat were produced due to exothermic reactions. After the completion of exothermic reaction, the isolated layer was rinsed in ultra pure water and subsequently in acetone to remove the varnish coating on the porous layer side. The isolated layer was taken out and washed with ultrapure water and ethanol and dried at room temperature. As this layer was very brittle, it was carefully preserved for further characterization.

Field emission scanning electron microscopy images of aluminium anodized at 10ºC with the anodization durations of 15, 60, and
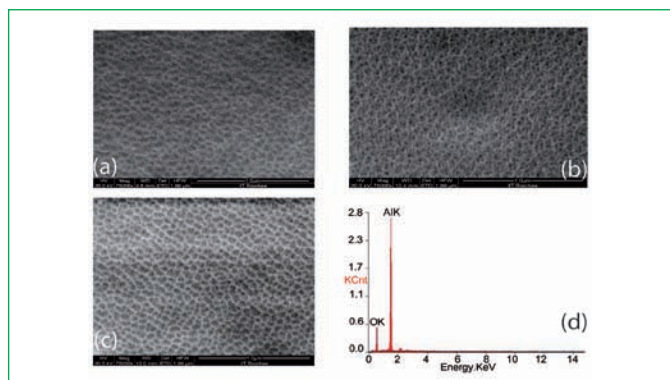
Figure 1: (a-c) SEM images of aluminium anodized for a duration of 15, 60 and 90 minutes respectively, (d) a typical EDS spectrum of porous alumina membrane showed the presence of Al and O

Figure 2:AFM images of the nanoporous alumina membrane (scan size 1 μm X 1 μm). Average pore diameter was 40-45 nm

90 minutes showed different surface morphology, as shown in Figures 1 (a-c). The aluminum sample anodized for 15 minutes showed the initiation of pores on the surface but the pores were not formed uniformly throughout the anodized area. The sample anodized for 60 minutes showed thick oxide layers on top surface and porous inner layer. But compared to the sample anodized for 15 minutes, the sample anodized for 60 minutes showed thicker oxide and inner porous layer. It should be noted that the thickness of the oxide layer formed during anodization is directly proportional to the current density and anodizing time in accordance with Faraday's law, leading to thickening of the oxide layer. The sample anodized for 90 minutes showed much better cell arrangement compared to samples anodized for 15 and 60 minutes. In the sample anodized for 90 minutes, the pores are well aligned and formed throughout the anodized area. This showed that the prolonged anodization resulted in homogeneous pore arrangement and increase in pore depth. The phase and the composition of the anodized samples were analyzed by energy dispersive X-ray spectroscopy (EDS) and grazing incidence X-ray diffraction (GIXRD) techniques. EDS spectrum of anodized aluminium with the atomic and weight percentages of Al and O is shown in Figure 1(d). The graph showed only Al and O peaks and no other elements. When the XRD patterns of the as-received and anodized aluminium were compared, it was found that the anodized aluminum was non-crystalline. This result confirmed the amorphous nature of alumina at room temperature. XRD pattern of isolated layer also showed amorphous phase alumina at room temperature. AFM images showed ordered nanopores formed on the surface of the anodized aluminium. The 2D and 3D images over the scanning area 1 μm X 1 μm are shown in Figure 2.The high resolution AFM images showed the dense regular array of pores and also the thick oxide layer around the pores. It could be clearly seen that the oxide at the junction of three pores was very thick. The pore size analysis was performed with NOVA software which showed that the average pore diameter was 40-45 nm.
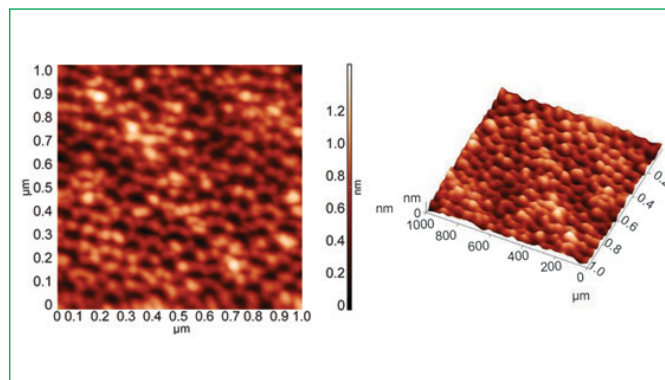
The porous alumina membranes developed will be utilized to fabricate biological ceramic composites that can act as selective metal binding filters. For this purpose, microbial S-layer protein nanostructures are isolated from microorganisms growing in uranium mining waste. This will be embedded in porous alumina membranes to produce a porous filter matrix with a homogeneous structure and completely immobilized biocomponents and is called a biocer. Bacterial S-layer proteins are glycoprotein subunits that possess the intrinsic property of being able to re-crystallize into two-dimensional linear arrays at various technologically important substrates like ceramics, metals by in vitro molecular reassembly. These recrystallized microbial S-layers act as molecular adhesives or sieves for specific and selective removal as well as recovery of lanthanides and simulated actinides from radioactive waste. Ceramic alumina matrix provides the mechanical and thermal stability to the biocers. In addition to this, the porosity of the alumina membrane is very crucial for the degree of immobilization of biocomponents and efficient diffusion processes. Thus the main thrust of our work is to optimize pore size and homogeneous distribution of pores by varying the anodization parameters. The literature does not provide any desired pore size range, since the fabrication and application of biocers is a new field of research and there are only a very few reports on nanoporous alumina and S-layers being used in nuclear waste management. Currently, such biocers are being developed for waste treatment, and the as-prepared alumina membranes would be useful for this purpose.

To conclude, nanoporous alumina membranes with homogeneous pore arrangement were synthesized by anodization. Biocers fabricated using S-layer proteins recrystallized with nanoporous alumina membranes could be used as filters in reprocessing and waste management units of nuclear industry and the efficiency of these filters has to be examined in detail.

Reported by S.C. Vanithakumari
Corrosion Science and Technology Group
Metallurgy and Materials Group

Young Researcher's FORUM

Structural and Optical properties of Wide Band Gap Tunable Compound Semiconducting Oxide: $Cd_{1-x}Ca_xO$

Shri Srihari Velaga did his Masters in Physics from Andhra University, Visakhapatnam. He joined X-ray Scattering and Crystal Growth Section, CMPD, MSG, IGCAR as a DAE research fellow on 19th February 2006. He has submitted his doctoral thesis titled "Investigation on CdO - CaO Solid Solution with Wide Band Gap Tunability: Macroscopic Structure, Vibrational and Local Structural Studies at Atomic Scale" in October 2011 to University of Madras under the guidance of Dr. H. K. Sahu.

Alloying of materials has been a subject of great interest since ancient times in order to attain good mechanical strength and other needful material properties. From the middle of the last century semiconducting alloys were explored for manufacturing of light emitting diodes (LED) with various colours. Subsequently, these semiconducting alloys have found applications in various fields such as electronics, optoelectronics etc. (as tunable lasers, both optical and nuclear radiation detectors over a very wide spectral range). In this context, it is highly desirable to have a system with a tunable band gap and with appropriate useful physical properties such as high electron mobility, strong room-temperature luminescence, high breakdown voltage, low electronic noise at high-temperature and high-power operation. Thus, the search for new materials with favorable properties and methods of engineering band gap in semiconductors have come to the forefront of research activities both in electronic and in materials science. This trend is continuing to date with renewed emphasis.

In recent years, oxide based semiconductors are emerging as a possible and preferred alternatives to the conventional semiconductors in many applications. Oxide semiconductors are safe and environmental-friendly materials and possess a variety of desirable optical, electrical and magnetic properties. Further, the exploration of new oxide semiconductors can lead to evolution of novel functions and devices. Among others, ZnO, TiO_2, SnO_2, In doped SnO_2, CdO, Ga_2O_3 and their alloys with various compounds have been extensively investigated. In most of the alloys, tuning the physical properties is attempted on thermodynamically unstable (immiscible solid solutions) compounds, which is quite undesirable. The quest for finding thermodynamically stable solid solutions having wide range of band gaps has motivated the present study of searching possible materials to tune the physical properties of CdO in a controlled manner.

Calcium is identified as a thermodynamically suitable candidate for tuning the band gap of CdO in a controlled manner as oxide of calcium is iso-structural with CdO. Both CdO and CaO crystallize in rock salt structure with ~2.5% difference in lattice parameter.

CaO having a band gap of 7.1 eV, provide scope for tuning the band gap of CdO from 2.23 to 7.1 eV, which is quite a large range and covers the entire visible range of the electromagnetic spectrum. Solid solution of $Cd_{1-x}Ca_xO$ was prepared by solid state reaction. Chemical composition of the prepared ternary compound was confirmed using energy-dispersive X-ray spectrometer (EDAX). Crystal structure of the $Cd_{1-x}Ca_xO$ system was studied with X-ray diffraction (XRD) technique followed by Rietveld refinement analysis of the XRD patterns. As shown in Figure 1 the diffraction peaks shifts to smaller 2θ values, indicating lattice expansion on substituting calcium for Cadmium and the change in the relative intensity of the diffraction peaks. The lattice dilation on substituting calcium is consistent with the larger ionic radius of Ca^{2+} and the change in the relative intensity of the diffraction peaks is due to the smaller Z (number of electrons) value of calcium.

Though the difference in lattice parameter between CdO and CaO is small, the lattice parameter of the ternary compounds deviates (Figure 2) from the linear interpolation of the lattice parameter of CdO and CaO (Vegard's law). Three-dimensional electronic density maps (not shown) in a unit cell were reconstructed using maximum entropy method (MEM) analysis of the powder XRD data, which shows that the bonding nature between Cd/Ca-O changes from covalent like to ionic as the concentration of calcium increases. Band gap of the material was estimated
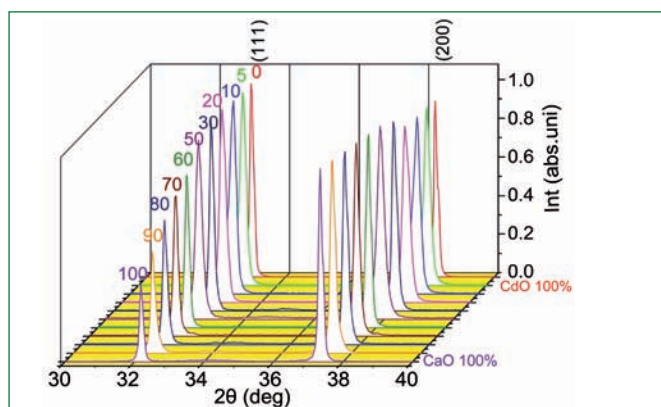

Figure 1: XRD patterns of the CdO-CaO solid solution showing variation of intensity of (111) and (200) peaks as a function of the Ca concentration

from diffuse reflectance spectroscopic (DRS) measurement. The absorption edge estimated for x = 0 to 80 at.% are shown in Figure 3. The band gap estimated was plotted as a function of calcium concentration in Figure 4. It is seen from Figure 4 that the band gap of the ternary compound with x ≤ 30 at.% is less than that of CdO and increases to 3.9 eV on further increase in x up to 80 at.%. However, band gap of the material with x > 80 at.% could not be estimated due to limited range of diffuse reflectance spectroscopy.

The observed deviation in lattice parameter and band gap of the $Cd_{1-x}Ca_xO$ system from linear interpolation of the lattice parameter and band gap of the end members was fitted with a second order equation. The amount of deviation from the linear interpolation of the end members in both lattice parameter (0.03088 (2) Å) and band gap (8.90 eV) of the $Cd_{1-x}Ca_xO$ system was found to be larger compared to similar systems in literature. In order to understand these observations detailed band structure calculation was undertaken using Density Functional Theory (DFT), which shows similar results. Various contributions to optical bowing parameter such as structural relaxation, volume change and charge transfer were calculated. From the relative magnitude of these factors, it is seen that contribution of structural relaxation is most significant as is found in many of the semiconducting systems. Contribution from volume change is expected since there is a difference between the cell volumes of CdO and CaO. Least contribution comes from charge transfer, which arises due to change in the bond characteristics.

Raman spectra of $Cd_{1-x}Ca_xO$ measured with 514.5 nm excitation are shown in Figure 5. First order Raman spectra in both CdO and CaO are symmetry forbidden due to the symmetry constraints of the rock salt structure, however weak second order Raman spectra were observed in CdO and CaO. As seen in Figure 5 an additional broad and intense feature appeared in $Cd_{1-x}Ca_xO$ for 20% ≤ x ≤ 90%, which was assigned to the impurity induced Raman mode (can be a first order mode). In order to understand the deviation from the Vegard's law and the observed additional
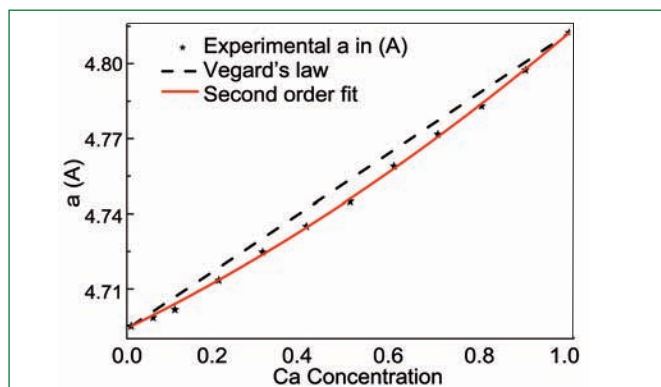

Figure 2: Lattice parameter a (Å) calculated from XRD data by Rietveld analysis vs calcium concentration, (star) experimental data, (continuous line) quadratic fit and (dashed line) Vegard's law variation of lattice parameter with concentration

modes in the Raman spectra local structural studies about Cd atom were carried out by Cd K-edge Extended X-ray Absorption Fine Structures (EXAFS) at Photon Factory Advanced Ring (PF-AR) NW10A synchrotron beam line facility in Tsukuba, Japan.

Figure 6 shows the absolute magnitude of χ (R) derived from the Fourier transform of EXAFS signal χ(k) as a function of radial distance from the absorbing atom. |χ(R)| shows several peaks and sub-structures: a peak at ~2.2 Å corresponding to the 1st nearest neighbor (nn) distance viz., d_{Cd-O} (≈ a/2) and a second peak centered at about ~3.37 Å corresponding to 2nd nn distance viz., d_{Cd-Cd} (≈ a/√2). The shift of the 1st-nn shifts to higher R values with x clearly indicates an increase of d_{Cd-O} (x) with x, confirming the lattice dilation with calcium substitution. Peak at about ~3.37 Å, corresponding to 2nd nn, has an associated shoulder at lower R at ~3.05 Å, even for undoped CdO. This arises from the non-monotonic variation in the back scattered amplitude as a function of the photoelectron wave number, k. The contribution of Ca-back scattering to |χ(R)| is also located close to the location of the shoulder. This implies a bimodal distribution in the 2nd nn interatomic distance as $d_{Cd-Cd} \neq d_{Cd-Ca}$. With increase in calcium substitution, the peak located at about 3.05 Å corresponding to d_{Cd-Ca} expectedly grows
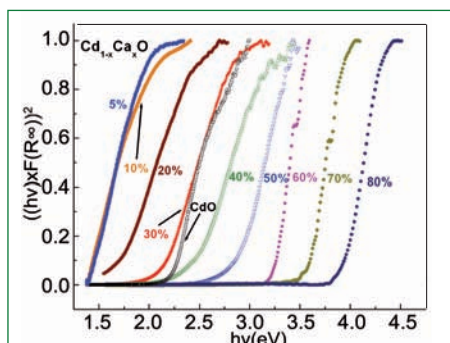

Figure 3: Plot of $((h\nu)xF(R\infty))^2$ vs hν, absorption edge energies are determined by the intercept of linear fit to the absorption edge for the samples with Calcium concentration up to 80 at.%
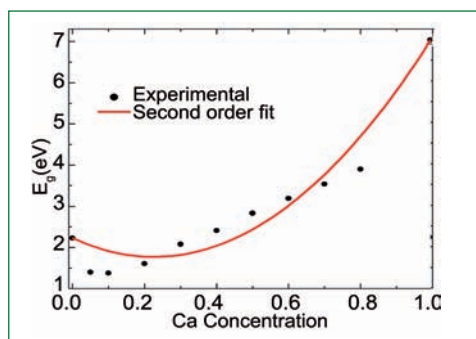

Figure 4: Variation of the band gap with Calcium concentration. The value of E_g for CaO adopted from R.C. Whited. et. al
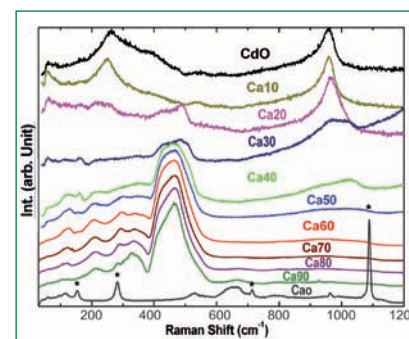

Figure 5: Room temperature Raman spectra of $Cd_{1-x}Ca_xO$ * represents the $CaCO_3$ Raman modes present in CaO (the spectra are vertically displaced for clarity)
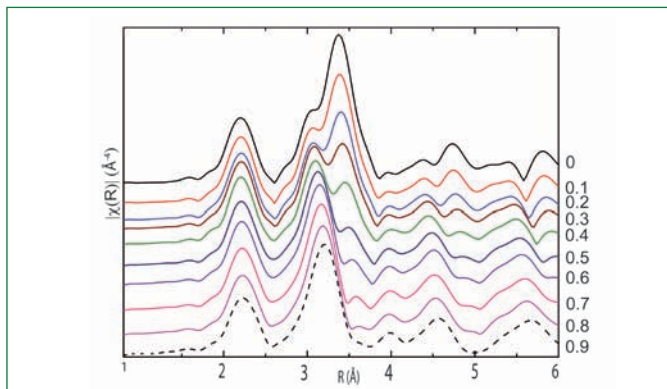
Figure 6: The Fourier transformed $\chi(k)$ signal as a function of radial distance from the central absorbing atom photon energy for $Cd_{1-x}Ca_xO$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9). The curves are vertically displaced for clarity

at the expense of peak located at about 3.37 Å corresponding to d_{Cd-Cd}. Detailed structural modeling of EXAFS, considering the phase difference between the back scatted wave from Cd and Ca atoms, shows that d_{Cd-O} (x) monotonically increases and exhibits a negative deviation from linear behavior as also observed in the case of a(x) from XRD. Variation of d_{Cd-O} was fitted to second order polynomial and the corresponding bowing parameter which compares well with that obtained from XRD. Not withstanding all these, the variation of d_{Cd-O} (x) from EXAFS fails to explain lattice parameter variation with x quantitatively as it is always smaller than d_{Cd-O} (x) from XRD for all values of x, except for x = 0. Hence, it appears necessary to include the contributions of the other Ca-O 1st nn distances, d_{Ca-O} (x), in modeling the EXAFS signal. This could not be done in the present case, because the calcium K-edge EXAFS measurement could not be carried out as it is very close to the L_{III}-edge of Cd. However, the local structure should correspond to the average structure (as obtained from diffraction studies) at larger length scales. In other words, sum of the compositional weighted 1st-nn distances should give the correct lattice parameter.

The 2nd-nn distance, d_{Cd-Cd} (x) and d_{Cd-Ca} (x), almost linearly increases with x and d_{Cd-Cd} (x) d_{Cd-Ca} for all values of x, consistent with the larger ionic radius of Ca^{2+} compared to that of Cd^{2+}. d_{Cd-Cd} (x) obtained from EXAFS and XRD follow the same trend except that it deviates from the same by XRD at higher calcium substitution. Debye-Waller (like) factor σ^2_{Cd-O}, representing the static and thermal disorder, corresponding to d_{Cd-O} (x) increases with x up to x = 0.5 and decreases thereafter. On the other hand, the disorder associated with 2nd-nn, σ^2_{Cd-Cd} and σ^2_{Cd-Ca} are much higher compared to that of 1st-nn and did not exhibit any systematic variation with calcium substitution. In the alloys with the rock salt structure with the $Fm\overline{3}m$ space group, to which $Cd_{1-x}Ca_xO$ system belongs, does not allow for a bond angle variation and results in larger changes in the bond lengths. This leads to smaller value of $\left(d_{cd-o}^{EXAFS}(x) - d_{cd-o}^{XRD}(x) \right)$ compared to that of the systems belonging to Wurzite structure. For those systems where

the lattice parameter variation obeys Vegard's law, the ionicity of the end members (e.g. 0.31 eV for GaAs and 0.357 eV for InAs) are closely matched and changes in the nature of bonding are not expected. The ionicity of CdO and CaO are widely different: 0.785 eV for CdO and 0.913 eV for CaO. Alloying of such end members is expected to bring out a considerable change in the nature of bonding; from more covalent-like for smaller values of calcium concentration to ionic bonding for higher calcium concentration. This, coupled with the rather rigid cubic symmetry, is possibly responsible for the observed bowing in the variation of d_{cd-o}^{EXAFS} and hence in a(x).

Thermodynamically stable and homogeneous solid solution of $Cd_{1-x}Ca_xO$ was prepared in the entire composition range; $0 \le x \le 1$. $Cd_{1-x}Ca_xO$ alloys show complete solubility of CaO in CdO, ensuring the samples to be mono-phasic $Cd_{1-x}Ca_xO$ for all values of x. The lattice parameter is seen to monotonically increase as x increases. The increase in the lattice parameter with x exhibits a negative deviation from the linear interpolation of the lattice parameters of the end members as suggested by the Vegard's law for many alloys. Electron charge density distribution in the unit cell, indicate that the nature of bonding between Cd/Ca-O increases in its ionic character with increasing x. The band gap of the $Cd_{1-x}Ca_xO$ solid solution was found to have a non-monotonic variation with x. Wide tunability in band gap was achieved in $Cd_{1-x}Ca_xO$ system from 1.7 to 3.9 eV for $0 \le x \le 0.8$. Raman scattering studies indicate that the system belong to two mode behavior as the vibration modes of the end members remain persist in the intermediate compositions as well. A frozen mode positioned at ~600 cm^{-1} independent of x is reasoned to arise from the large difference between the effective masses of the end members. Local environment around Cd atom in $Cd_{1-x}Ca_xO$ solid solutions was investigated through Cd K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy. Variation of the first nearest neighbour (nn) distance d_{Cd-O} (x) estimated by EXAFS is also nonlinear with a negative curvature having a bowing parameter value comparable to that of d_{Cd-O} (x) estimated by XRD (a(x)/2). However, $d_{cd-o}^{EXAFS}(x)$ was found to be smaller than $d_{cd-o}^{XRD}(x)$ and the difference between them is found to increase with x. The EXAFS Debye-Waller (like) factor σ^2_{Cd-O}, a measure of cumulative static and thermal disorder relative to Cd (absorbing) atom exhibits a symmetric behavior about x = 0.5. This implies that calcium is randomly distributed within the solid solution. The variation in the 2nd-nn distances d_{Cd-Cd} and d_{Cd-Ca} obtained by EXAFS almost follows those from XRD studies. No systematic variation could be observed for the σ^2 (x) of the 2nd-nn. From the deviation of 1st-nn distance from that of average structure it was inferred that the system belongs to persistence type.

Reported by Srihari Velaga
Condensed Matter Physics Division
Materials Science Group

Conference/Meeting Highlights

6th International Conference on Creep, Fatigue and Creep-Fatigue Interaction
January 22-25, 2012

Dr. T. Jayakumar, Director, Metallurgy and Materials Group and Chairman, Local Organising Committee, Shri S.C. Chetal, Director, IGCAR and Chairman, National Organising Committee, Dr. Farhad Tavassoli, Head, Fusion Materials Project, CEA, France and Dr. M. D. Mathew, Head, MMD, MMG, Convener, on the dais during inauguration

The 6th International Conference on Creep, Fatigue and Creep-Fatigue Interaction (CF-6) was held at Hotel Radisson Blu Resort Temple Bay, Mamallapuram during January 22-25, 2012. Shri S.C. Chetal, Director, IGCAR inaugurated the conference. Dr. Farhad Tavassoli, Head, Fusion Materials Project, CEA, France delivered the keynote talk on "Materials for Future Sources of Energy" as a part of the inaugural programme. CF-6 was organized by IGCAR jointly with the Metal Sciences Division and the Kalpakkam Chapter of the Indian Institute of Metals. The conference was sponsored by the Board of Research in Nuclear Sciences and co-sponsored by Society of Materials Science Japan, Korean Institute of Metals and Materials, Japan Society of Mechanical Engineers and Korean Society of Mechanical Engineers.

Forty three invited talks by eminent experts (twelve from India and thirty one from abroad) in the areas of creep, fatigue, creep fatigue interaction, materials development, and high temperature design and assessment were delivered in CF-6. One hundred and sixty contributory papers were also presented. More than three hundred fifty

delegates including seventy five foreign delegates from fifteen countries attended CF-6. The technical programme was structured into twenty sessions which were held in two parallel sessions. Most of the contributory papers were presented as posters. The poster sessions were held on all the three conference days. There was also a separate category on student's posters. The best three posters in the general category and students' category were given awards. There were separate technical sessions on topics such as creep and fatigue deformation and damage, thermal and thermo-mechanical, fatigue, multi-axial and component testing, high temperature design and life assessment, materials for advanced nuclear reactors, oxide dispersion strengthened materials, materials for ultra super critical power plants, innovative testing techniques, deformation and damage modeling. Both in terms of the number of delegates attended and the number of papers presented. Fifty eight academic and research institutions working in the areas of creep and fatigue were represented in CF-6.

Reported by M. D. Mathew, Convener, CF-6

Theme Meeting on Novel and Innovative Measurements
in Non Destructive Evaluation (NIM-NDE-2012)
February 23-24, 2012

Shri S. C. Chetal, Director, IGCAR addressing the delegates of the two-day theme meeting NIM-NDE-2012. Dr. P. R. Vasudeva Rao, Director, Chemistry Group, releasing the NIM-NDE-2012 Souvenir and handing over the copies to Dr. T. Jayakumar, Director, MMG, Dr. C. Babu Rao, Head, UMA section, MMG and Dr. B. P. C. Rao, Head, EMSIS, NDED during inaugural function

A two-day theme meeting on 'Novel and Innovative Measurements in Non Destructive Evaluation (NIM-NDE-2012)' was organised jointly by Indira Gandhi Centre for Atomic Research, Kalpakkam and Board of Research in Nuclear Sciences, Mumbai at Convention Centre, Anupuram during February 23-24, 2012. The meeting started with welcome address by Dr. T. Jayakumar, Chairman, NIM-NDE-2012 and Director, Metallurgy and Materials Group, IGCAR. Dr. Jayakumar highlighted the need for a forum to discuss the recent advances in NDE sensors and measurement technologies for structural integrity assessment of components and welcomed the invited speakers and delegates. He lauded the three decades long novel research contributions of Dr. C. Babu Rao, Head, UMA Section, MMG who later delivered a keynote talk on "Development of novel sensors and NDE methodologies at IGCAR" in which he gave a detailed account of his research in fiber optic sensors, under sodium ultrasonics, eddy current sensor, XRF based zari analysis, medical diagnostics and societal applications. Shri S.C. Chetal, Director, IGCAR gave a special address during the theme meeting and highlighted the vital role of NDE techniques for in-service inspection (ISI) of fast reactor

components, especially main vessel, steam generator and reprocessing plant components. He stressed the need for developing high-temperature fiber optic sensors and NDE technologies for inspection of under-sodium components. Dr. P. R. Vasudeva Rao, Director, Chemistry Group released the souvenir and addressed the gathering. He highlighted the role of NDE technologies for ensuring safety and reliability of components. In the theme meeting, there were twenty eight invited talks by eminent professionals from IISc, IITM, BARC, SERC, CGCRI, NFC, Anna University, LPSC-ISRO and IGCAR highlighting the advances in various NDE techniques. NIM-NDE-2012 was attended by one hundred and forty delegates including thirty five graduate students and Ph.D. scholars pursuing studies in the area of NDE. There were very good scientific interactions during the technical sessions and poster sessions. During the valedictory function, the delegates lauded the efforts of the NIM-NDE-2012 organising committee and thanked the organisers for effectively conducting the theme meeting. Dr. B. P. C. Rao, Convener, NIM-NDE-2012 proposed a vote of thanks.

Reported by B. P. C. Rao, Convener, NIM-NDE-2012

Indo-French Technical Meeting on Thermochemical Modelling
March 7-8, 2012

Dr. Jean-Paul Piron, French Correspondent and Dr. Jean-Christophe Dumas of Fuel Study Department, Nuclear Energy Directorate, CEA, Cadarache, France with Shri S.C. Chetal, Director, IGCAR and senior colleagues of the Centre

A two-day technical meeting on thermochemical modelling was held at IGCAR during March 7-8, 2012. Earlier, IGCAR and CEA, France had entered into an Implementation Agreement on "Thermodynamic Modelling of the Actinide Oxides and Oxy-Carbide Systems" under the existing CEA-DAE cooperation agreement in the field of basic research and modelling of physical phenomena. The objective of the present meeting was to exchange the views and progress on the thermodynamic properties of actinide oxide and oxy-carbide systems and their modelling.

Dr. Jean-Paul Piron, French Correspondent and Dr. Jean-Christophe Dumas of Fuel Study Department, Nuclear Energy Directorate, CEA, Cadarache, France participated in the technical exchange meeting. The technical programme started after a brief meeting of the visitors with Director, IGCAR. Dr. P.R. Vasudeva Rao, Director, Chemistry Group made a presentation on fast reactor programme in India and discussed the scope of the agreement on thermochemical modelling.

Dr. S. Vana Varamban, Indian Correspondent from Materials Chemistry Division, Chemistry Group presented the progress made by IGCAR on thermochemical modelling of oxides and carbides of uranium and plutonium systems. Dr. Jean-Paul Piron and Dr. Jean-Christophe Dumas presented the progress made by CEA on thermochemical modelling of oxides of uranium, plutonium and americium systems and carbides of uranium, plutonium systems.

During discussions, several gaps in the current data, particularly in the carbide systems, were pointed out by the participants. Dr. Vasudeva Rao recommended a few benchmark problems to be solved by both countries and the results to be compared. Director, IGCAR commented on the relevance of thermodynamics in fuel behaviour modelling.

Overall, the technical meeting helped exchange of views between CEA and IGCAR on the subject of thermochemical modelling of actinide oxide and carbide systems.

Reported by S. Vana Varamban,
Materials Chemistry Division, Chemistry Group

News and Events

MoU signed between IGCAR and Korea Atomic Energy Research Institute
January 28, 2012

Shri S. C. Chetal, Director, IGCAR and Dr. Yong Hwan Jeong, Director, Nuclear Materials Development Division, KAERI during the signing up of MoU with KAERI

Consequent to the Nuclear Cooperation Agreement signed on July 25, 2011 between Government of India and the Government of the Republic of Korea, Indira Gandhi Centre for Atomic Research and Korea Atomic Energy Research Institute (KAERI) entered into a Memorandum of Understanding (MoU) on January 28, 2012 at Kalpakkam. This MoU aims at strong mutually supportive research collaborations between IGCAR and KAERI in the fields of science and technology. The immediate areas of collaboration include high temperature mechanical properties, welding technology, high temperature design and life assessment.

Visit of Dignitaries

Dr. Barun Mukherjee, Honourable Member of Parliament from West Bengal with Shri S.C.Chetal, Director, IGCAR during his visit to the Fast Breeder Test Reactor

Dr. Barun Mukherjee, Honourable Member of Parliament (Rajya Sabha) from West Bengal visited the Centre on January 7, 2012. After a meeting with Shri S.C. Chetal, Director, IGCAR, Dr. Prabhat Kumar, Project Director, BHAVINI and Shri K. Ramamurthy, Station Director, Madras Atomic Power Station, Dr. Barun Mukherjee visited the Fast Breeder Test Reactor, Hot Cells and Non Destructive Evaluation Division, Facilities in Fast Reactor Technology Group, Chemistry Group, Structural Mechanics Laboratory, Sodium Fire Facility, Atmospheric Dispersion, Madras Atomic Power Station and the construction site of Prototype Fast Breeder Reactor.

IGC Colloquium on "Fukushima Daiichi Nuclear Accidents" was delivered by Prof. Balraj Sehgal from Royal Institute of Technology, Sweden on January 30, 2012

Prof. Balraj Sehgal from Royal Institute of Technology, Sweden, during his visit to the Centre on January 30, 2012 delivered the IGC Colloquium on "Fukushima Daiichi Nuclear Accidents".

Delegation from UK with Shri S.C. Chetal, Director, IGCAR and other senior colleagues of the Centre

A delegation of academicians from UK, comprising of Professor Chris Grovenor, Head of Department, Materials Department, Oxford University,and   Co-Director, Bristol/Oxford Nuclear Research Centre, Prof. Mike Fitzpatrick, Head, Department of Materials Engineering at the Open University, Milton Keynes and Prof. P John Bouchard, Professor in Materials for Energy, Materials Engineering at the   Open University,   visited IGCAR on February 13, 2012. They had in-depth discussions on the possible collaborations in the areas of life assessment and structural integrity; modelling, simulation and severe accident and nuclear safety, to be funded by EPSRC, UK, under the Indo-UK civil nuclear collaboration. The meeting was chaired by Shri S.C. Chetal, Director, IGCAR, and involved presentations on areas of mutual interests by senior scientists of IGCAR. The UK delegation also visited laboratories in the Metallurgy and Materials Science Groups and also the Structural Mechanics Labaoratory.

Dr. Alexander Bychkov, Deputy Director General and Head of the Department of Nuclear Energy, IAEA and Shri Viacheslav Gutkov with Shri S.C.Chetal, Director, IGCAR and senior colleagues of the Centre

Dr. Alexander Bychkov, Deputy Director General and Head of the Department of Nuclear Energy, IAEA and Shri Viacheslav Gutkov visited the Centre during February 23-26, 2012. During the meeting they were briefed about the Research and Development activities at Indira Gandhi Centre for Atomic Research by Shri S. C. Chetal, Director, IGCAR. After the meeting Dr. Alexander Bychkov and Shri Viacheslav Gutkov visited the Fast Breeder Test Reactor & KAMINI, Hot Cells and Non Destructive Evaluation Division, Facilities in Fast Reactor Technology Group like Steam Generator Test Facility and SADHANA Loop, Sodium Chemistry Laboratories at Chemistry Group, Sodium Fire Facility, Madras Atomic Power Station and the construction site of Prototype Fast Breeder Reactor.

Shri V. Narayanasamy, Honourable Minister of State, Parliamentary Affairs Prime Minister's Office and Shri P. Viswanathan, Honourable Member of Parliament, representing the Kancheepuram Constituency with Shri S.C. Chetal, Director, IGCAR and senior colleagues of the Department

Shri V. Narayanasamy, Honourable Minister of State for Parliamentary Affairs and Prime Minister's Office and Shri P. Viswanathan, Honourable Member of Parliament, representing the Kancheepuram Constituency visited the Centre on March 03, 2012. During the meeting they were briefed about the Research and Development activities of various DAE units at Kalpakkam by Shri S. C. Chetal, Director, IGCAR, Dr. Prabhat Kumar, Project Director, BHAVINI, Shri C. D. Rajput, Chief Superintendent, Madras Atomic Power Station and Shri S. Basu, Facility Director, BARC Facilities.

Prof. W. Arnold, Physikalisches Institut, University of Goettingen, and Department of Material Science and Technology, Saarland University delivering the IGC Colloquium

IGC Colloquium on "SESAME Experiments within the European ROSETTA Mission" was delivered by Prof. W. Arnold, Physikalisches Institut, University of Goettingen, and Department of Material Science and Technology, Saarland University, Saarbruecken, Germany on March 13, 2012, during his visit to the Centre.

Shri Dinkar Khullar, Ambassador and Permanent Representative of India, Vienna, Austria with senior colleagues of the Centre and the Department

Shri Dinkar Khullar, Ambassador and Permanent Representative of India, Vienna, Austria, visited the Centre during March 28-29, 2012. After meeting the senior colleagues of the Centre and the Department, Shri Dinkar Khullar visited the Fast Breeder Test Reactor, Hot Cells and Non-Destructive Evaluation Division, CORAL facility, Kalpakkam Reprocessing Plant, construction site of Prototype Fast Breeder Reactor and Madras Atomic Power Station.

DAE Awards & Honours

Group Achievment Award for 2010

Nitric Acid Loop for Long-Term Corrosion Studies

Dr. U. Kamachi Mudali, MMG, Group Leader

Shri Ravikumar Sole, Shri K. Kamalanathan, Shri A. Ramakrishnan, Shri T. Nandakumar, Shri R. Thiruvalluvan and Shri R. Rajendran from MMG. Shri R. Rajeev, Shri T. Selvan, Shri Geo Mathews and Shri A. Sriramamurthy from RpG.

Best Paper/Poster Awards

Several of our colleagues, research scholars and students, who presented their research work at conferences and seminars, are recognized for their contribution in the form of "Best Paper/Poster Awards". In the this issue the honours received are given:

Constitutive equations to Predict High Temperature Flow Stress in a Ti-modified Austenitic Stainless Steel
Dr. Sumantra Mandal, Shri V. Rakesh, Dr. P. V. Sivaprasad, Dr. S. Venugopal and Shri K.V. Kasi Viswanathan from MMG
Top Cited Author 2011 by Elsevier

Studies on Passive Films of Type 316LN Stainless Steels Using Micro Laser Raman Analysis and Imaging
Dr. S. Ramya, Shri C. Arun Chandran, Dr. Rani P. George and Dr. U. Kamachi Mudali from MMG
National Symposium on Electrochemical Science and Technology (NSEST-2011)
Indian Institute of Science, Bengaluru, August 2011
Best Oral Presentation Award

Laser Surface Melting of Plasma Sprayed Alumina-Titania Coating on High Density Graphite
Shri Jagadeesh Sure, Shri A. Ravi Shankar and Dr. U. Kamachi Mudali from MMG
International Conference on Advanced Materials (ICAM 2011), PSG College of Technology, Coimbatore,
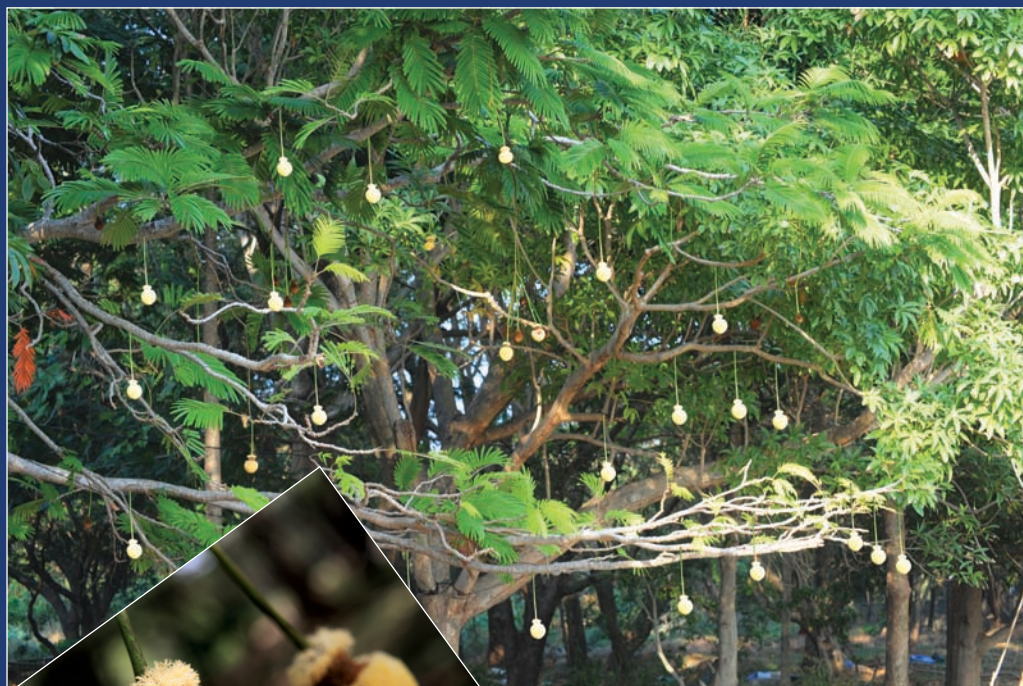December 12-16, 2011
Best Poster Presentation Award

Micro-nano Texturing of Titanium by Anodization - a Step Towards Corrosion Inhibition and Anti-biofouling
Dr. S. C. Vanitha Kumari, Dr. Rani P. George and Dr. U. Kamchi Mudali from MMG
Electrochemical Techniques in Nano Scale Surface Engineering (ECTNSE-2012), BARC, Mumbai, January 5-6, 2012
First Best Poster Award

Laser Raman Analysis and Imaging of Molten Salt Exposed Partially Stabilized Zirconia Coated High Density Graphite
Dr. S. Ramya, Shri Jagadeesh Sure, Dr. A. Ravi Shankar, Dr. Rani P. George and Dr. U. Kamchi Mudali from MMG
Electrochemical Techniques in Nano Scale Surface Engineering (ECTNSE-2012), BARC, Mumbai, January 5-6, 2012
Third Best Poster Award

Nanocontainer Impregnated Self-Healing Surfaces for Corrosion Protection
Shri C. Arunchandran, Dr. S. Ramya, Dr. Rani P. George and Dr. U. Kamchi Mudali from MMG
Electrochemical Techniques in Nano Scale Surface Engineering (ECTNSE-2012), BARC, Mumbai, January 5-6, 2012
Third Best Poster Award

Thermally Activated Deformation of a High-nitrogen Grade 316LN Stainless Steel under Compressive Loading
Ms. Diptimayee Samantaray, Dr. Sumantra Mandal, Dr. S.K. Albert, Dr. A.K. Bhaduri and Dr. T. Jayakumar from MMG
ICAMPS, Thiruvananthapuram, January 19-21, 2012
Third Best Technical Paper Award

Effect of Ceric Ions in the Extraction of Ruthenium into 30% TBP/NPH Systems
Ms. Pravati Swain, Dr. R. Srinivasan, Dr. C. Mallika, Dr. U. Kamachi Mudali and Shri R. Natarajan from RpG
Ms. S. Annapoorani from CG
DAE-BRNS Biennial International Symposium on 'Emerging Trends in Separation Science and Technology (SESTEC-2012)', Mumbai, February 27 - March 01, 2012
Best Poster Presentation Award

Parkia Biglandulosa (Badminton Ball Tree)