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MATERIALS RESEARCH SOCIETY

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E-MRS Spring Meeting 2005

May 31 – June 3, 2005

SYMPOSIUM N

Nuclear Materials

Symposium Organizers:

Claude Degueldre, Paul Scherrer Institute, Villigen, Switzerland

Dolores Gomez Briceno, CIEMAT, Madrid, Spain

Thomas Fanghänel, INE, FzKarlsruhe, Germany

Dominique Warin, CEA, Saclay, France

Papers will be published in journal of nuclear materials

E-MRS 2005 SPRING MEETING

SYMPOSIUM N

Tuesday, May 31, 2005 — Morning
Mardi 31 mai 2005 — Matin

8:30 **Welcome**: Presidency EMRS
8:40 **Introduction**: C. Degueldre (PSI)

Session I: Component materials for advanced fusion/fission systems
Session chairs: Nadine Baluc (EPFL), Dominique Hittner (Framatome-ANP)

N-I.01 09:00 -Invited-

ADVANCED STRUCTURAL MATERIALS FOR NUCLEAR POWER APPLICATIONS

S.J. Zinkle, Oak Ridge National Laboratory, Oak Ridge TN 37831-6138, USA

High performance materials are critical for success in both terrestrial and space nuclear applications. Nuclear power currently accounts for about 24% of the worldwide electricity. Looking to the future, advanced fission ("Generation IV") and fusion reactor systems are proposed to meet the growing worldwide energy demand and to reduce reliance on fossil fuel energy sources that produce greenhouse gases. In response to increasing scientific payload electricity demands for proposed space missions, NASA recently initiated an advanced technology program that will enable several nuclear space reactor missions including orbiter exploration of the moons of Jupiter. This presentation will compare and contrast the performance requirements and summarize candidate structural materials in various existing and proposed nuclear power systems. A common theme for all of these proposed future nuclear power systems is high proposed operating temperatures. An additional key challenge to the successful development of materials for fission and fusion systems is the harsh neutron irradiation environment. Several examples will be given to illustrate how multiscale modeling and advanced experimental test techniques are being used to investigate and resolve key materials issues.

N-I.2 09:20

EFFECTS OF POROSITY CHANGES ON MECHANICAL PROPERTIES OF NUCLEAR GRAPHITE

Ch. Berre, A. Fok, B. Marsden, Nuclear Graphite Research Group, University of Manchester, U.K.

It is well established that changes in the microstructure of a material affect its bulk properties. The aim of this study is to understand the effects of porosity changes on the elastic constants of isotropic Gilsocarbon graphite through detailed FE modelling. A set of 3D micro-tomographic images and nano-indentation test results of the material were used to create detailed FE models using the Simpleware package for analysis with Abaqus. The changes in Young's modulus and Poisson's ratio of graphite are then compared with those predicted by the empirical Knudsen equation. Conditions of linear elasticity are assumed.

N-I.3 09:35

OPTICAL CHARACTERIZATION OF TRISO FUEL PARTICLE CROSS-SECTIONS USING GENERALIZED ELLIPSOMETRY

G.E. Jellison, Jr. and J.D. Hunn, Oak Ridge National Laboratory, Oak Ridge TN 37831-6030, USA

Quantification of preferred orientation of crystallites in the polycrystalline pyrolytic carbon coatings of TRISO (tristructural isotropic) fuel particles has been determined to be an important measurement for quality control. Excessive crystallographic anisotropy leads to unwanted anisotropic dimensional changes during irradiation, which can cause the TRISO coatings to fail. Experimental methods were developed in the 60's and 70's to measure this parameter using the fact that single crystal graphite is optically anisotropic in reflection. Since that time, considerable advancements have been made in the understanding of the effects of optical anisotropy in both experimental and theoretical realms. In this talk, we discuss a new method, based on the two-modulator generalized ellipsometer (2-MGE) to measure the optical anisotropy. This technique has been demonstrated to measure the optical diattenuation to an accuracy of ±0.002-0.005 and the preferred direction of the crystallites to ±1-2° with a spatial resolution of better than 5 microns. Diattenuation "pictures" of the nuclear fuel cross sections reveal that the inner pyrocarbon layer is far from uniform both in the degree of diattenuation and in the direction of the principal axis. The 2-MGE technique is faster, more accurate, and collects considerably more data than previous optical anisotropy measurements of TRISO fuel particles.

* Research was sponsored by the Office of Nuclear Energy, Science and Technology and Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract No. DE-ACO5-00OR22725.

N-I.4 09:50

REVIEW OF CO PRESSURE MEASUREMENTS IN THE U-C-O TERNARY SYSTEM

S. Gossé(a), C. Guéneau(a), S. Chatain(a), C. Chatillon(b), (a)DEN/DPC/SCP -CEA Saclay 91191 Gif-sur-Yvette Cedex, France, (b)LTPCM -CNRS UMR5614, ENSEEG BP75 Grenoble 38402 Saint-Martin d'Hères Cedex, France

For HTR (High Temperature Reactors), one of the future Generation IV system, the high level of fuel operating temperature in normal and accidental conditions requires the thermodynamic assessment of the fuel components and their interactions with structural materials.

Among the concerns of the TRISO fuel particle thermomecanical behaviour, it is necessary to better understand the carbon monoxide formation due to chemical interactions at the UO_{2+x} kernel and graphite buffer's interface. Some of the published data on the equilibrium CO gas pressure measurements of the U-C-O ternary system have been critically reviewed. The discrepancies between the results can be explained (i) by the different gaseous flow rates used for different experiments and (ii) by the location of the measuring pressure gauge from the reaction site. Experimental values have been corrected (i) from the gaseous flow type (molecular, transitional or viscous) defined by the Knudsen number and (ii) from the thermal transpiration effect due to temperature gradient inside the experimental vessels. Taking account of these selected and corrected values improves greatly the consistency of the original set of measurements.

N-I.5 10:05

ATOMISTIC SIMULATION OF RAPID COMPRESSION OF FRACTURED SILICON CARBIDE

A. Romano(a), Ju Li(b), S. Yip(c), (a)Laboratory of Reactor Physics and Systems Behaviour, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, (b)Department of Materials Science and Engineering, Ohio State University, Columbus OH 43210, USA, (c)Department of Nuclear Science and Engineering and Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge MA 02139, USA

Deformation mechanisms of a crack in silicon carbide (SiC) under high-rate compression are investigated by molecular dynamics (MD) simulation using the Tersoff potential. The penny-shaped crack is in tension throughout the simulation (to keep it open) while a variable compression is applied in the orthogonal direction. The simulations are run for hundreds of picoseconds in order to follow the evolution of failure of the specimen. The results reveal two different mechanisms of crack-tip response depending on the initial level of tension imposed on the crack. (1) At low tension, a disordered band is observed to form on the crack surface in the direction orthogonal to the compression. The band grows as the compressional force is increased in a manner suggesting a stress-induced transition from an ordered to a disordered phase. Moreover the crack is observed to close. (2) At a tension sufficient to allow the crack to remain open, application of a compressional stress yields formation of disordered regions along the boundaries of the opened crack, which grow and merge into a band as the compression proceeds. This process is driven by a rotation of the initial crack, which transforms into a curved slit. This mechanism induces incorporation of fragments of perfect crystal into the disordered band. Similar mechanisms have been experimentally observed to occur in porous SiC under high-strain rate compressions. When the compressed powder particles are fine, formation of a well bounded shear band (analogous to mechanism 1) was found; however, as the powder particle size increased the shear localization mechanism is driven by particle break-up and grinding and the formation of a shear band containing particle fragments (analogous to mechanism 2).

10:20 **BREAK**

N-I.6 10:35

IN-SITU CREEP UNDER HELIUM IMPLANTATION OF TiAl ALLOY

J. Chen(a), P. Jung(b), M. Nazmy(c) and W. Hoffelner(a), (a)Department of Nuclear Energy and Safety, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, (b)Foschungszentrum Jülich, 52425 Jülich, Germany, (c)ALSTOM POWER, Haseltrasse, 5401 Baden, Switzerland

A Ti-47Al-2W-0.5Si alloy has been homogeneously implanted with helium under uniaxial tensile stresses from 100 MPa to 350 MPa to a maximum dose of about 0.12 dpa (1000 appm-He) with displacement damage rates of $1.8x10^{-6}$ dpa/s at temperatures of 300°C and 500°C. Straining of the miniaturized dog-bone specimen under implantation was monitored by LVDT measurement, while resistance was derived by four-pole technique. Subsequently the changes of microstructures were investigated by TEM. Creep compliance, i.e creep rate per dose rate and stress, was almost independent of temperature in the investigated region. The resistance of TiAl samples increased with dose and showed a tendency to saturate above 0.05 dpa, reaching total changes of 50% at 300°C and 30% at 500°C. These results are explained by a decrease of short range ordering in the ordered alloy.

N-I.7 10:50

MULTISCALE MODELING OF DEFECT KINETICS IN ELECTRON IRRADIATED IRON

Chu-Chun Fu, J. Dalla Torre, Fr. Willaime, J.- L. Bocquet and A. Barbu, Service de Recherches de Métallurgie Physique CEA/Saclay, 91191 Gif-sur-Yvette, France

Changes in microstructure of nuclear materials are governed by the kinetics of defects produced by irradiation. The population of vacancies, interstitials, and their clusters can however be followed only indirectly, e.g. by macroscopic resistivity measurements. The information on the mobility, recombination, clustering or dissociation of defects provided by such experiments is both extremely rich and difficult to interpret. By combining ab initio and kinetic Monte Carlo methods, we successfully reproduce the abrupt resistivity changes -- so called recovery stages -- observed upon annealing after electron irradiation in pure iron. New features in the mechanisms responsible for these stages are revealed. We show that small vacancy clusters and tri-interstitials contribute to the stages attributed to mono-vacancy and di-interstitial migration respectively, predict the effect of the unexpected low migration barriers found for tri- and quadri-vacancies. The influence of carbon atoms on the recovery stages is also discussed.

N-I.8 11:05

ATOMIC SIMULATIONS OF IRRADIATED NANOCRYSTALLINE FE CONTAINING PRE-EXISITNG VOIDS

M. Samaras(a), P.M. Derlet(a), H. Van Swygenhoven(a), W. Hoffelner(a), M. Victoria(b,c), (a)Paul Scherrer Institute, NUM/ASQ, 5232 Villigen-PSI, Switzerland, (b)Lawrence Livermore National Laboratory, California, USA, (c)Polytechnic University of Madrid, Spain

A better understanding of life assessments of high temperature materials components for future gas cooled reactors under conditions of irradiation and creep requires an understanding of damage defect structure at the microscopic level. The atomic simulation of nanocrystalline Fe under irradiation is therefore undertaken as a first step in studying ODS ferritic materials.

Experimental studies of ion irradiated nanocrystalline materials have revealed that the high density of grain boundaries present in these materials can affect the final damage production. Voids along grain boundaries which can lead to crack formation are typical of creep damage in metals. In this work, void structures have been simulated within a nanoscale grain structure at the grain boundary and are irradiated in order to assess the affect of pre-existing void structures on the microstructure of the sample produce during the primary damage state. Cascade overlap simulations in the vicinity of the pre- existing void structure are also discussed.

N-I.9 11:20

AB INITIO STUDY OF DISSOLUTION, MIGRATION AND CLUSTERING OF HELIUM IN ALPHA-IRON

Chu-Chun Fu and Fr. Willaime, Service de Recherches de Métallurgie Physique, CEA/Saclay, 91191 Gif-sur-Yvette, France

Ferritic steels are proposed as first wall material in fusion reactors.

When submitted to 14 MeV neutron irradiation, not only self-defects but also helium and hydrogen atoms are created. Quantitative studies are required to predict the effect of helium on microstructural and mechanical properties of these materials Density Functional Theory calculations have been performed to study the dissolution and migration of helium in alpha-iron, and the stability of small helium-vacancy clusters. Substitutional and interstitial configurations of helium are found to have similar stabilities. The tetrahedral configuration is more stable than the octahedral one by 0.18 eV. The migration energy of interstitial helium is very low, 0.06 eV. The migration of substitutional helium by the vacancy mechanism is governed by the migration of the di-helium-vacancy complex, with an energy barrier of 1.08 eV. The activation energies for helium diffusion by the dissociation and vacancy mechanisms are determined both when thermal vacancies dominate and in excess of vacancies. The trends of the binding energies of vacancy and helium to vacancy-helium clusters are discussed. The corresponding dissociation energies give new insight into the interpretation of thermal desorption spectra.

N-I.10 11:35

ODS STEEL IRRADIATION WITH HE

M.A. Pouchon, J.-Ch. Chen, W. Hoffelner, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

Oxide dispersed strengthened (ODS) ferritic-martensitic steels are investigated as possible structural material for the future generation of High Temperature Gas Cooled Nuclear Reactors. ODS-steels are considered to replace other high temperature materials for tubing or structural parts. The oxide particles serve for interfacial pinning of moving dislocations. Therefore the creep resistance is improved. In case of the usage of these materials in reactor, the behaviour under irradiation must be further clarified. In this paper the effects induced by He implantation into the Plansee ODS steel PM2000 are investigated. A tandem accelerator is used to generate an implantation which reaches from 0.5 to 2.5 µm in depth. The induced swelling is measured and the mechanical behaviour of the irradiated surface is investigated. A cross sectional cut is performed by FIB and investigated by TEM. The defect density identified on the TEM micrographs coincidences well with the TRIM calculations. A detailed analysis of the defects is given in the paper. The implantation is performed at RT and at 570 K, the former ones are investigated as is and after a post thermal treatment at different temperatures.

11:50 **DISCUSSION**

12:05 **LUNCH**

13:30-14:30 POSTER SESSION

14:45 Poster session briefing
Christine Guéneau (CEA Saclay), Alvin Solomon (University Purdue)

Session II: Structural materials for thermal reactors
Session chairs: Peter Rudling (ANT), Margaret McGrath (OECD, Halden)

N-II.1 15:00 -Invited-

THREE DIMENSIONAL OBSERVATIONS AND MODELLING OF INTERGRANULAR STRESS CORROSION CRACKING IN AUSTENITIC STAINLESS STEEL

T.J. Marrow, L. Babout, A Jivkov, P. Wood, D. Engelberg, N. Stevens, **P.J. Withers**, School of Materials, University of Manchester, UK and R.C. Newman, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada

Stress corrosion cracking is a life-limiting factor in many components of nuclear power plant in which failure of structural components presents a substantial hazard to both safety and economic performance. Uncertainties in the kinetics of short crack behaviour can have a strong influence on lifetime prediction, and arise due both to the complexity of the mechanisms and to the difficulties of making experimental observations. This paper reports an on-going research programme into the dynamics and morphology of intergranular stress corrosion cracking in austenitic stainless steels in simulated light water environments, which makes use of new analytical techniques.
In-situ, high resolution X-ray tomographic observations of intergranular stress corrosion crack nucleation and growth in sensitised austenitic stainless steel provide evidence for the development of crack bridging ligaments, caused by the resistance of non-sensitised special grain boundaries. A simple two-dimensional grain bridging model, introduced to quantify the effect of crack bridging on crack development, has been assessed in thermo-mechanically processed microstructures via statically loaded room temperature simulant solution tests and high temperature/pressure autoclave studies. Thermomechanical treatments modify the grain size, grain boundary character and triple junction density distributions, with a consequent effect on crack behaviour. Two and three-dimensional finite element models of intergranular crack propagation have been developed, to investigate the development of crack bridging and its effects on crack percolation and crack coalescence.

N-II.2 15:20

UNDERSTANDING OF RADIATION DAMAGE IN REACTOR PRESSURE VESSEL STEELS FOR LONG TERM EVOLUTION MODELLING

Ph. Pareige and B. Radiguet, Equipe de Recherche Technologique n°1000, GPM UMR CNRS 6634, A. Barbu, CEA, Saclay, France

Neutron irradiation results in the formation of ultrafine (2 nm in diameter) solute clusters in reactor pressure vessel (RPV) steels. These clusters contain a supersaturated element (copper) and some soluble solutes (Mn, Ni, Si and P). The aim of this work is to understand the basic processes at the origin of the formation of these clusters and to obtain information about the effect of the different solutes.
The microstructure of model alloys, after different irradiation experiments (electron, ion) is characterised by 3D atom probe. The comparison between experimental results and results obtained by mean field modelling (evolution of point defects under irradiation)shows that the precipitation of the solute clusters is heterogeneous, on point defects clusters initiated by displacement cascades. Precipitation kinetics is slowed down by solutes other than copper. These results are in excellent agreement with what is observed in actual RPV steels under neutron irradiation.

N-II.3 15:35

MODEL-ORIENTED EXPERIMENTS TO VALIDATE MULTISCALE MODELING OF RADIATION DAMAGE BEHAVIOUR OF REACTOR PRESSURE VESSEL STEELS

M. Hernández-Mayoral, D. Gómez-Briceño, CIEMAT, Department of Technology, Materials Division, Avenida Complutense, 22, 28040-Madrid, Spain

Reliable experimental data are needed to perform the experimental validation of multiscale models as well as to propose mechanisms about the evolution of irradiation damage of Reactor Pressure Vessel (RPV) steels. With this objective, different irradiation experiments (neutron and ion) of model alloys, carried out under well known and controlled conditions, have been performed. Microstructural characterization after irradiation has been performed by TEM. This technique provides useful information such as defect density, size distribution, as well as their nature characterization.

Neutron irradiations of model alloys that approximate RPV steels compositions, have been performed in a test reactor at 300ºC. To study dose effect, specimens with an accumulated fluence from 0.025 to 0.2 dpa were examined, whereas the flux effect from $3x10^{12}$ n/cm^{2}s to 6.78 $x10^{14}$ n/cm^{2}s was studied at 0.05 dpa.

In addition, ion irradiation of ultra high purity iron (UHP-Fe), UHP-Fe + 100 ppm C and a commercial purity iron has been also carried out with iron ions of 150 keV. In this experiment, dose and temperature effect in specimens irradiated from 0.05 dpa to 1 dpa at temperatures from room temperature to 300ºC has been examined. TEM examination of these materials will allow to gain some insight into the effect of dose, flux, temperature and impurity content on the microstructural features of irradiated model alloys.

N-II.4 15:50

ASSESSMENT OF THE CONSTITUTIVE LAW BY INVERSE METHODOLOGY

J. Isselin(a), A. Iost(a), J. Golek(a), M. Bigerelle(a,b), (a)Laboratoire de Métallurgie Physique et Génie des Matériaux, CNRS UMR 8517, Equipe Surfaces et Interfaces; ENSAM, 8 Boulevard Louis XIV, 59046 Lille Cedex France, (b)Laboratoire Roberval, FRE CNRS 2833, UTC Centre de Recherches de Royalliey BP 20529, 60205 Compiègne France

Characterization of the power plant component mechanical properties required by an increase of the life time exploitation becomes more and more difficult since available samples which were placed in-situ are drastically diminishing. Thus, in these conditions small-scale specimen techniques or non-destructive tests are more and more attractive to characterize the mechanical properties and the in service degradation of the material. The material investigated in this study is a 15 Mn Mo V steel with a banded ferrite - bainite structure. Samples were taken from a steam vessel of the power plant of Montereau after 145000 hours at 340°C in use. Such samples were used to assess the validity of two methods for determining the constitutive behaviour of the material and the applicability for irradiated materials. First the small ball punch test is performed and the load deflection curve is compared with finite element calculation using Forge 2 Standard code. As a result the yield stress and the strain hardening coefficient were determined by using an inverse methodology (Simplex method) and a two parameters (Hollomon) constitutive law. It can also be shown that a three parameters constitutive law such as the Ludwick Hollomon' one leads to an indetermination since the parameters are connected. The second method consists in performing instrumented ball indentations (like the ABI method) to calculate the true stress strain curve. Both the two methods give results in good agreement with the true stress strain curve obtained by classical tensile test, and we concluded with the applicability of the method to nuclear materials.

16:05 **BREAK**

N-II.5 16:20

THE STUDY OF OXIDE FILMS OBTAINING ON THE SURFACE OF NUCLEAR METALLIC MATERIALS BY XRD AND SYNCHROTRON RADIATION ANALYSIS

V. Malinovschi(a), C. Ducu(a), N. Aldea(b), (a)University of Pitesti, Research Centre for Advanced Materials, Targul din Vale Street, no.1, Pitesti, Romania, (b)National Institute for Research and Development for Isotopic and Molecular Technologies, P.O.B 700, 3400 Cluj-Napoca, Romania

To predict the behaviour of structural metallic materials in to the CANDU nuclear reactor, the oxide films on the surface were growth in a controlled manner. For simulated the environment specific into the nuclear reactor, the autoclaved was used. In order, to establish the structural modifications of the oxide films, the XRD and synchrotron radiation analysis were performed. The qualitative and quantitative phase analysis shown differences between the samples exposed in different conditions correspond to inner, respectively outer CANDU nuclear reactor zones. The mechanical properties of the surface oxide films were correlated with the microstructures parameters determined by XRD and synchrotron radiation analysis. The crystallite size, the microstrains, the probability of the faults and microstrain distributions functions were obtained by the whole pattern fitting methods and by peak profile analysis based on the generalized Fermi function (GFF) facilities. The theoretical considerations of these two methods were presented. The agreement between the results obtained by these methods was discussed according to the structural model of the surface.

N-II.6 16:35

XAFS STUDY OF NB IN ZIRCONIUM ALLOY CORROSION LAYERS

K. Dardenne, INE, Forschungszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, C. Degueldre, LWV, Paul Scherrer Institut, 5232 Villigen, Switzerland

In reactor systems, zirconium based alloys used as cladding corrode steadily in contact with reactor water. To improve the corrosion resistance, new cladding variants are tested and introduced. It has been shown that among these, the (Zr,Nb) alloys corrode less rapidly than current Zr alloys. This is assumed to be due to specific reactions involving Nb species in the corrosion layer. In order to understand the role of Nb for corrosion inhibition, the valence states of this element need to be characterised for both inactive and active (irradiated) samples. The purpose of this study is to evaluate the feasibility of XAFS analysis for Nb speciation in the corrosion layer. The challenge of the work is that the small intensity Nb edge is located just after the very large Zr edge which does interfere in Nb analysis In this study XAFS has been applied at the ANKA-XAS beam-line for a zirconia film obtained by (Zr,Nb) alloy corrosion at 415^{o}C in water steam yielding a10 µm $(Zr,Nb)O_2$ film. We were able to record Nb K XANES in fluorescence Grazing Incidence (GI) mode with quasi-orthogonal detection utilising a 5 elements LE-Ge detector. The Nb XANES spectrum reveals interesting features. The position of the edge taken at the first inflexion point is shifted of 1.4 eV compared to the metal. No change occurs in the spectra during the measurements indicating that the oxidation state of Nb stays stable under irradiation. The white line intensity is rather small compared to what is expected for Nb oxides. The reduction of white line is likely a manifestation of the degree of distortion. This should be expected for a high amount of disorder such as for Zr. In the corrosion sample the line decrease suggests a large disorder and large density of nano porous features. This is also the case for any corrosion of Zry samples independently of the production process (contact with liquid or vapour).

N-II.7 16:50

J-R CURVES DETERMINATION OF TUBE CLADDING MATERIAL

J. Bertsch, W. Hoffelner, Paul Scherrer Institut, Laboratory for Materials Behaviour, 5232 Villigen PSI, Switzerland

Zirconium based alloys have been in use as fuel cladding material since many years in light water reactors. As claddings change their mechanical properties during service, as a result of irradiation induced degradation, oxidation and hydride formation, it is essential for the assessment of mechanical integrity to provide parameters for potential rupture behaviour. Usually, fracture mechanics parameters like the fracture toughness KIC or, for high plastic strains, the J-integral JIC are employed. In claddings with a very small wall thickness the determination of toughness needs the extension of the J-concept beyond the limits given by any standard. In the paper a method based on the traditional J approach is presented. J-R curves were created for unirradiated thin walled Zircaloy and aluminium cladding tube pieces at room temperature using the single sample method. The procedure of creating sharp fatigue starter cracks with respect to optical recording was optimized.

N-II.8 17:05

FEELING DEFECTS IN ZIRCALOY BY XAFS AND muSR

C. Degueldre(a), S. Conradson(b), A. Amato(c), E. Campiteli(a), (a)LWV, PSI Villigen, Switzerland, (b)LANL, Los Alamos, NM, USA, (c)LMS, PSI Villigen, Switzerland

A subnanoscopic view of effects generated by plastic deformation in Zircaloy was depicted using results provided by XAFS and muSR. XAFS was able to visualize the atomic environments such as distortions and indirectly vacancies, defects and their development during plastic deformation in the lattice. The defects are deduced from the coordination of Zr and the next neighbour determination shell per shell provided by the XAFS analysis.

An additional dimension is added with the study of muon properties in the material, namely the possibility of examining different states of the defect centres. Muon spectroscopy has been successfully in characterizing these features, determining the local structures using stability, mobility and interactions of muons in the investigated material. In addition, characterization of trapping centres such vacancies was performed. Combining these techniques allow completing the complex picture yields by defects generated by plastic deformations in Zircaloy.

17:20 **DISCUSSION**

Wednesday, June 1, 2005 Afternoon

Mercredi 1 juin 2005 Après-midi

Session III: Fuel materials

Session chairs: Didier Hass (ITU), Tim Abram (BNFL)

N-III.1 14:30 -Invited-

FUEL MATERIALS FOR GAS COOLED FAST REACTORS

Ph. Martin(a), H. Burlet(b), J.L. Seran(c), (a)CEA/DEN/DEC, Centre de Cadarache, 13108 ST Paul lez Durance, France, (b)CEA/DRT/DTEN, Centre de Grenoble, 17 Rue des Martyrs, 38054 Grenoble, France, (c)CEA/DEN/DMN, Centre de Saclay, 91191 Gif sur Yvette, France

Gas cooled Fast Reactors (G.F.R.) are among the six nuclear reactors concepts selected by the International Generation IV Forum.

The advantages (no phase change and low neutronic weight, chemical inertia, transparency and easy access to components, allowance for high outlet temperatures applications and efficiency…) brought by the choice of a gas as coolant, have consequences on the core design in terms of the volume fraction devoted to the coolant versus structures and fuel, and the need for temperature (normal, incidental, accidental) resistance of materials. Furthermore, the willingness to achieve a fast spectrum, necessary for ensuring a sustainable view of the fuel cycle (self generation of fissile materials, and integral recycling of minor actinides) yields other criteria applicable to materials in terms of neutrons absorption and thermalization.

The consequences of such requirements in terms of materials choices for in core structures and first barrier to radiotoxic species in the G.F.R. core will be drawn. The options for the fissile ceramics will be commented and the classes of other fuel materials to be associated with them justified. It will be shown that specific performances are requested from these materials (mostly ceramic based). Specific R&D tracks liable to lead to acceptable solutions will be presented. Once verified on “fresh” materials, they have to be checked against irradiation conditions. A comprehensive approach of their behaviour and degradation modes based on modelling, is another aspect that will be developed as being recognized to be especially important for safety demonstrations.

N-III.2 14:50

THE EFFECT OF HIGHLY PRESSURISED INTRA-GRANUALAR BUBBLES ON THE MOBILITY AND RELEASE TO GRAIN BOUNDARIES OF DIFFUSING RARE GAS ATOMS IN URANIUM DIOXIDE

P. Garcia(a), P. Martin(a), G. Carlot(a), E. Castelier(a), M. Ripert(a), C. Sabathier(a), C. Valot(a), F. D'Acapito(b), J-L. Hazemann(c), O. Proux(c), V. Nassif(c), (a)CEA-Cadarache, DEN/DEC/SESC/LLCC, Bâtiment 315, 13108 Saint-Paul-lez-Durance cedex, France, (b)GILDA/CRG-ESRF 6 rue Jules Horowitz, B.P. 220 38043 Grenoble, France, (c)CNRS, Laboratoire de Cristallographie, B.P. 166, 38042 Grenoble cedex 09, France

One of the difficulties encountered when modelling the release of fission gases in UO_2 lies in predicting the proportion of rare gas atoms which are isolated in the matrix and that of atoms which form bubbles. In-pile, the accepted picture is that trapping by bubbles of diffusing gas-atoms or irradiation induced bubble nucleation is offset by a radiation induced re-solution phenomenon. However in out of pile annealing experiments, radiation effects can hardly be invoked. In this case, modelling fission gas bubbles as behaving as perfect sinks leads to an underestimation of the fraction of fission gases released. The explanation put forward in the paper lies in the fact that the gas contained in intra-granular bubbles is highly pressurised. It is shown that the high pressures are likely to affect the sink strengths of bubbles with respect to diffusing gas atoms. In the first part of this paper, a review of the experimental data available pertaining to the pressure in intra-granular bubbles is drawn up. This review is complemented with the results from X Ray Absorption Spectroscopy experiments performed on a set of xenon implanted polycrystalline UO_2 samples which were subsequently annealed or re-irradiated with swift heavy ions. The results indicate that the gas precipitates to form highly pressurised inclusions as a result of both temperature anneals at 600°C or low fluence irradiations with 790MeV krypton ions. The pressure estimated in the bubbles is shown to be in the region of 1 to 3Gpa. The consequence of such a phenomenon occurring in-pile is then discussed and a model is given which enables the computation of bubble sink strengths as a function of the geometry of the bubble and physical characteristics of the gas it contains.

N-III.3 15:05

FABRICATION METHOD AND THE VARIATION OF THERMAL CONDUCTIVITY OF Mo-PRECIPITATED UO2 PELLETS

Si-Hyung Kim, Yeon-Gu Kim, Han-Soo Kim, Sang-Ho Na, Young-Woo Lee, Dong-Seong Sohn, Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Daejeon 305-600, South Korea

Thermal conductivity is one of the most important properties of UO_2 fuel pellets, which directly influence the fuel operating temperatures. But, the thermal conductivity of UO_2 is very low compared with U metal, UN or UC and so various efforts have been tried to enhance the thermal conductivity of UO_2 pellets.

This work deals with the fabrication method and the thermal conductivity of Mo-precipitated UO_2 pellets. Mo compounds can be present at Mo metal or Mo oxides(MoO_2 or MoO_3 et al.) according to different oxygen partial pressures at high temperatures. Mo oxides have low melting point and can make not only the large grain UO_2 pellets but also the pellets with the high thermal conductivity. The UO2 powder was mixed with weighed amounts of MoO_3 powder, at concentrations between 0.5wt% and 7wt%, by a Turbula mixer for 1 hour and then successively milled by a planetary mill for 1/2 hour. The milled oxide powders were compacted with a compaction pressure of 300 MPa and the green pellet specimens were sintered between 1573K and 1973K in H_2 or various ratios of CO_2/CO gas. In H_2 atmosphere Mo metal was separately distributed in the UO_2 grain. On the contrary, Mo metal was continuously precipitated along with the UO_2 grain boundary when the UO_2-MoO_3 was sintered at the oxygen potential of about –200 KJ/mole between 1823K and 1923K. The UO_2 pellets with the continuously-precipitated Mo metal showed a higher thermal conductivity compared with pure UO_2 pellets.

N-III.3 15:20

FABRICATION OF DRY PROCESS NUCLEAR FUEL PELLETS BY USING SIMULATED HIGH BURNUP SPENT FUEL

W.K. Kim, W.C. Shin, Jae W. Lee, G.I. Park and J.W. Lee, Korea Atomic Energy Research Institute, PO Box 105, Yusong, Taejon, South Korea

Burnup of nuclear fuel was continuously extended to enhance the economy of nuclear power plants. In 1960's, the burnup of fuel ranged 20,000~30,000 MWd/tU. In 1990's, it reached 60,000 MWd/tU. In this study, simulated dry process fuel pellets were fabricated by using UO_2 powder added by the simulated fission products calculated by ORIGEN-2 code for spent PWR fuel with burnup of 60,000 MWd/tU to investigate the fabrication characteristics of dry process nuclear fuel. The simulated dry process fuel pellets were fabricated by dry recycling fuel fabrication flow including 3 cycle treated OREOX(Oxidation and Reduction of Oxide fuel) process. 0.07~0.2 wt% of dopant such as TiO_2, Nb_2O_5 are added to enhance sinterability of the fuel powder. The sintered densities of the pellets without dopant ranged from 10.04 g/cm^3(94.3 % of T.D.) to 10.32 g/cm^3(96.9 % of T.D.), and the average grain size ranged from 3.4 to 3.8 mm. Both sintered density and grain size did not satisfy CANDU fuel specification. The sintered densities of the pellets doped with TiO_2 or Nb_2O_5 ranged from 10.46 to 10.32 g/cm^3, and the average grain size ranged from 7.3 to 9.9 mm. Sintered density greatly increased by doping TiO_2 and Nb_2O_5. Both of the dopants helped to increase grain size largely. Consequently, a small amount addition of TiO_2 or Nb_2O_5 is effective to enhance the sinterability of dry process nuclear fuel pellets from high burnup spent PWR fuel.

N-III.5 15:35

CALCULATIONS ON GRAIN BOUNDARY DIFFUSION OF XE/KR IN THE HIGH BURNUP STRUCTURE

P. Blair, A. Romano, Ch. Hellwig, Paul Scherrer Institut, 5232 Villigen-PSI, Switzerland

Whilst the fission gas behaviour in fuel with moderate burnup is well understood and various models have been developed, fission gas behaviour in high burnup fuel, especially in the so-called High Burnup Structure (HBS) is still a matter of research. In specific terms, mechanistic models to reliably predict the fission gas behaviour in high burnup fuel are largely missing today. The role of grain boundary diffusion in the HBS is of particular interest due to the huge amount of grain boundaries compared with unrestructured fuel. Quasi-steady state calculations have been performed to evaluate the effect of grain boundary diffusion in the high burnup structure. The calculations assume a lack of bubble growth in the grain boundaries and that as a consequence grain boundary diffusion plays a role in the gas dynamics. The effect of changes in the high burnup structure with particular reference to xenon depletion and gas transport to the pores are examined.

15:50 **BREAK**

N-III.6 16:05

PROTECTED PLUTONIUM PRODUCTION (P^3) FOR PEACE AND SUSTAINABLE PROSPERITY

M. Saito, Research Laboratory for Nuclear Reactors; Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan

The ***"Protected Plutonium Production (P^3)"*** has been proposed to improve the proliferation resistance of plutonium accumulated in the environment of LWRs. The studies focus on the transmutation of MAs such as ^{237}Np and ^{241}Am with large neutron capture cross-sections to increase the fraction of ^{238}Pu, which is a strong source of neutrons from spontaneous fission ($2.6x10^3$ n g^{-1} s^{-1}). This will cause deterioration in the quality of the plutonium nuclear explosive. In addition, the high decay heat of ^{238}Pu (560W kg^{-1}) makes the procedures of nuclear weapon manufacture and maintenance technologically difficult. The protected plutonium production (P^3) has been studied in critical and sub-critical systems. P^3 technology has been extended to studies on the degradation of reactor and weapon grade Pu by fission, spallation, and fusion neutron sources. Advanced nuclear energy systems with inherently protected plutonium production (P^3) make the nuclear fuel cycle more flexible with respect to intermediate plutonium storage for future energy crises because of the plutonium's enhanced proliferation resistance. The main feature of P^3 concerns the treatment of MAs. Instead of their geological disposal or just their burning through fission, they are treated as burnable fertile materials to improve proliferation resistance of the future nuclear energy systems, which opens new possibilities to provide new nuclear markets in the world. The demonstration of P^3 mechanisms in reactors is an event of great historical significance in the second stage of the "Atoms for Peace".

N-III.7 16:20

HEU LEU FUEL BEHAVIOUR COMPARISON FOR THE TRIGA SSR

Gh. Negut(a), N. Danila(b), (a)Institute for Nuclear Research (ICN), 0300 Pitesti, PO Box 78, Romania, (b)University Politehnica Bucharest, Romania

TRIGA SSR core was originally loaded with High Enriched Uranium 93% fuel. Due to the new international regulations it was decided to operate with Low Enriched Uranium fuel under 20% U235 enrichment. Now we operate with a mixed core HEU & LEU fuel. It is necessary to revise the Safety Report to update the data and analysis on LEU fuel. The data provided by LEU manufacturer shows the from the thermal properties point of view there are no differences between HEU and LEU fuel. The neutron and kinetic analysis shows some differences.

Previous analysis show different behaviour of LEU fuel compared with HEU from the point of view of prompt negative reactivity coefficient. For that reason we made some analysis of the TRIGA LEU core behaviour during reactivity insertion accidents using RELAP5 code. It was studied an insertion of dk/k =1% in 0.3 sec presented in SAR. The analysis for the behaviour of the LEU 35 fuel bundles core shows no big differences with the original HEU 29 fuel bundles core. The LEU fuel behaves better for the SAR reactivity accident at low power. For the 14 MW level reactivity accident the LEU peak power seems to be higher due to LEU lower temperature coefficients. But the temperatures reached by the fuel and the clad do not affect fuel integrity. The RELAP one point kinetic model of the TRIGA 14 MW SSR core proved very useful for these investigations. All this analysis is included in the further Safety Analysis Report for the new LEU fuel core.

N-III.8 16:35

FABRICATION, CHARACTERIZATION AND PROPERTY EVALUATION OF MIXED CARBIDE FUEL FOR INDIAN FAST BREEDER TEST REACTOR

S. Majumdar, A.K. Sengupta and H.S. Kamath, Radiometallurgy Division, Bhabha Atomic Research Centre, Mumbai 400085, India

The Fast Breeder Test Reactor (FBTR) at Kalpakkam, India is operating successfully since October 1985 with high plutonium content hyperstoichiometic mixed carbide as driver fuel. The reactor was first made critical with a small core containing (70%PuC – 30% UC) fuel and the core is now being progressively enlarged with addition of fuel containing (55%PuC – 45% UC). The initial fuel has reached a burnup of 130 GWD/T without any fuel pin failure. Establishment of fuel fabrication flow sheet and parameters, characterization techniques, generation of thermophysical & thermomechanical properties data and out of pile Fuel – SS clad – Na coolant compatibility studies were done indigenously, as no reported information were available for this unique fuel composition. The paper gives Indian experience of sustaining a mixed carbide fuel production programme for the last two decades.

N-III.9 16:50

NITRIDES AS A NUCLEAR FUEL OPTION

M. Streit, F. Ingold, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

Nitrides have been proposed to be a suitable material for fast neutronic systems from beginning of the development of nuclear fuel. Starting with the production of uranium nitride and sesquinitrides up to mixed plutonium uranium nitrides, today's developments are inert nitride matrix materials to burn plutonium or to transmute long-lived actinides in accelerator-driven sub-critical systems (ADS) or fast reactors (FR). Several authors proposed zirconium nitride as possible inert matrix material for this reason. Mixed zirconium nitrides can be fabricated by carbothermal nitridation of the oxides in a narrow temperature window. Obtaining high quality material with low carbon and oxygen content is still the major challenge. Producing mixed nitride fuels by special shaping methods, as for example direct coagulation casting or freeze-drying, in comparison to conventional powder compaction enables to use this material in special shapes to optimize burn up. The history of nitride fuels at PSI will be shown up to today's CONFIRM project, dealing with plutonium zirconium nitride fuels.

17:05 **DISCUSSION**

19:00 **AWARD CEREMONY**

The symposium organizers and the candidates to the graduate student award are requested to attend.

CONFERENCE RECEPTION

Thursday, June 2, 2005 Morning
Jeudi 2 juin 2005 Matin

Session IV: Waste form
Session chairs: Bernard Kienzler (INE, FzK), Virginia Oversby (VMO Konsult, Stockholm)

N-IV.1 09:00 -Invited-

THE INFLUENCE OF THE PRODUCTS OF ANOXIC CORROSION OF IRON ON THE RATES OF DISSOLUTION OF SPENT FUEL AND UO_2 DOPED WITH ^{233}U

K. Spahiu and L. Werme, SKB, Brahegatan 47, 102 40 Stockholm, Sweden

In most European disposal concepts, large amounts of dissolved hydrogen are expected to be produced by the anoxic corrosion of massive iron containers. At repository temperatures, hydrogen is quite inert and is not expected to contribute to the redox capacity of the deep groundwaters. In several recent works, a large impact of the products of anoxic corrosion of iron, dissolved hydrogen and Fe(II) ions, on the dissolution of the PWR or MOX fuel and $UO_2(s)$ doped with ^{233}U. For hydrogen concentrations above a certain limit and Fe(II) concentrations typical for European repository concepts, the dissolution rates of these irradiated materials drop to very low values. A discussion of the results of the leaching of spent fuel and MOX fuel in the presence of a range of hydrogen concentrations is presented. Typical for all measurements under such conditions are the very low long term concentrations of uranium and other redox sensitive radionuclides, as Tc and the minor actinides. The concentrations of U are systematically lower than the ones measured during $UO_2(s)$ solubility measurements carried out in the presence of strong reducing agents. Measurements of the radiolytic oxygen after long leaching periods result in values below detection limit. The investigation of the surface of a $UO_2(s)$ pellet doped with 10 % ^{233}U after almost two years testing by XPS indicates the absence of any oxidation. In the case of spent fuel, the kinetics of the release of the non-redox sensitive elements such as Sr and Cs is discussed in some detail. Finally an attempt is made to propose potential mechanisms responsible for such behaviour, based mainly on data from studies on the interaction of adsorbed water on the surface of irradiated metal oxides.

N-IV.2 09:20

ROLE OF IRRADIATION AND AIR RELATIVE HUMIDITY ON IRON CORROSION

S. Lapuerta(a), N. Bérerd(a), A. Chevarier(a), H. Jaffrézic(a), N. Millard-Pinard(a), N. Moncoffre(a), D. Crusset(b), F. Petit(c), B. Hannoyer(c), (a)Institut de Physique Nucléaire de Lyon, 4, rue Enrico Fermi, 69622 Villeurbanne cedex, France, (b)ANDRA, Parc de la Croix Blanche, 1-7 rue Jean Monnet, 92298 Châtenay-Malabry Cedex, France, (c)LASTSM, Institut des Matériaux de Rouen, Avenue de l'Université - B.P. 12, 76801 Saint Etienne du Rouvray Cedex France

In the context of a long term geological storage, high level nuclear wastes will be embedded in stainless steel and in a low alloyed carbon steel overpack as second barrier. These containers will be exposed to atmospheric corrosion and to gamma irradiation. In this work, the irradiation effect will be studied at room temperature by using MeV proton irradiation characterised mainly by an electronic energy deposition. Since it is known that iron corrosion is enhanced by the double influence of air and humidity, the experiments are performed in a large relative humidity range varying between 0 and 90%. The corrosion depths are measured by Rutherford Backscattering Spectrometry allowing to determine the oxygen mass gain as a function of the irradiation time. Three beam intensities (5, 10 and 20 nA) are studied. The corrosion kinetics are plotted for each proton fluence. A diffusion model of the oxidant species is proposed, taking into account the fact that these oxidant species flux through the surface is dependant on a kinetic factor K. This model put in evidence the dependence of the diffusion coefficient D and of K with the proton beam intensity. A complementary surface characterization is performed by X-ray diffraction analysis.

N-IV.3 09:35

SOLUBILITY IMPROVEMENT OF CERIUM AND PLUTONIUM BY REDUCTION IN BOROSILICATE GLASSES

J.-N. Cachia(a), X. Deschanels(a), C. Denauwer(b), (a)Commissariat à l'Energie Atomique, DEN/DTCD/SECM/LMPA, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France, (b)Commissariat à l'Energie Atomique, DEN/DRCP/SCPS/LCAM, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France

High-level radioactive wastes produced by spent fuel reprocessing containing actinides elements, fission and activation products are incorporated into the French borosilicate glass so-called ‘‘R7T7’’. To ensure optimum radionuclide containment, the resulting glass must be as homogeneous as possible. Any microscopic heterogeneity can arise from various processes including the excess loading of an element exceeded the solubility limits. Currently 0.4 wt% of actinide elements is incorporated into the glass.

Works are in progress in our laboratory to assess the extent of actinide solubility in these glasses, especially for plutonium. In first step, actinides have been simulated by lanthanides and hafnium. Results obtained show that +III-oxidation state elements (La, Gd) exhibit a higher solubility than +IV-oxidation state elements (Pu, Hf). Cerium is an interesting element because its oxidation state tunes from +IV to +III as a function of the processing conditions like temperature or the redox potential of the melt. In order to quantify the benefit in solubility, cerium doped glasses were melted under reducing conditions by adding reducing agent. Thus, solubility observed at 1200°C strongly increase from 0.11 mol% (normal conditions) up to 1.64 mol%. Several reducing compounds have been test. This paper deals with this study and the application to reduce PuIV to PuIII. The reduction state characterisation was performed by XAS (XANES) for plutonium or by chemical analysis for cerium. The material homogeneity was verified by optical and scanning electron microscopy. Preliminary elements about reducing Pu-doped glasses made in hot cells will be also presented.

N-IV.4 09:50

PERLITE FOR THE CONFINEMENT OF Cs

J. Balencie(a), D. Burger(a), J.-L. Rehspringer(a), C. Estournès(a), S. Vilminot(a), M. Richard-Plouet(a), A. Boos(b), (a)IPCMS-GMI, UMR7504, BP43, 67034 Strasbourg Cedex, France, (b)LCAM, UMR7512, ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

Perlite is a metastable amorphous hydrated aluminium silicate. It is mainly used (fillers, filter aid, horticultural aggregate, insulation) as « expanded perlite » obtained by rapid heating of the ground mineral that promotes water loss and formation of a highly porous materials. These properties lead us to consider the possible use of expanded perlite as waste for the confinement of Cs. Cs is introduced as an aqueous solution of its nitrate that fills up the porosity. After water evapouration, the possibility of the formation of a glass was considered but, even at high temperature (1550°C), the liquid was too viscous to be poured in a mould. However, chemical analysis reveal that no Cs loss is observed up to the highest temperatures for Cs contents as high as 50 wt% of Cs_2O whereas Cs oxides are known for their volatility. We therefore considered the sample elaboration by sintering giving rise to a vitroceramics containing pollucite, $CsAlSi_2O_6$, as the crystalline phase. Pollucite is evidenced by X-ray diffraction only for Cs contents higher than 25 wt% of Cs_2O. Numerous samples have been checked by lixiviation technique either on powders or on sintered pellets at a temperature of 85°C with various S/V ratios. Cs, Si and Al were analysed by ICP-MS in the resulting lixiviats and in all cases the analysis reveal a very small dissolution rate below 0.5 mgCs/m^2d for the sintered samples.

N-IV.5 10:05

CHARACTERIZATION OF SIMULATED VITRIFIED INEEL AND HANFORD WASTES PRODUCED IN COLD CRUCIBLE

S.V. Stefanovsky(a), T.N. Lashchenova(a), L.D. Bogomolova(a), C.C. Herman(b), D.F. Bickford(b), E.W. Holtzscheiter(b), R.W. Goles(c), D. Gombert(d), (a)SIA Radon, 7th Rostovskii per. 2/14, Moscow 119121, Russia, (b)Savannah River Technology Centre, Aiken SC 29808, USA, (c)Pacific Northwest National Laboratory, Battelle Blvd, Richland WA 99352, USA, (d)Idaho National Engineering and Environmental Laboratory, Idaho Falls ID 83415, USA

Two borosilicate glass formulations simulating vitrified INEEL sodium bearing (SBW) and Hanford high alkalinee wastes (HAW) were produced at the Radon bench-scale plant equipped with the 216 mm inside diameter cold crucible and energized from 60 kW power high frequency generator operated at frequency of 1.76 MHz. The SBW-bearing glass was predominantly amorphous and composed of borosilicate matrix with rare inclusions of unreacted quartz, baddeleyite and zircon. Infra-red (IR) spectroscopic study showed structure typical of network with high degree of connectedness formed from silicon-oxygen and boron-oxygen tetrahedra. EPR spectra of the glasses are superposition of lines due to Fe(III) and V(IV). The line with g=4.3 is due to Fe^{3+} which are located in a strong electric field when compared with Zeeman term for the determined symmetry of local electric fields. The broad g=2 line can be due to clusters of Fe^{3+} coupled by strong exchange interactions. The spectrum of V(IV) is typical of vanadia-doped borosilicate glasses and has hyperfine structure due to interaction of unpaired electron with I=7/2 nuclear spins. Fraction of V(IV) in glass is negligible and major vanadium exists as V(V). The vitrified HAW is composed of major vitreous matrix and minor aluminosilicate (nepheline, carnegieite) and spinel (high-Mn) phases and rare silver inclusions. IR spectra of these glassy products are also similar to spectra of borosilicate glasses but contain extra bands due to occurrence of crystalline phases. Both glasses demonstrate low B, Li, Na, Si, Ba, Cd, and Ag release when subjected to the PCT and TCLP leaching procedures.

10:20 **BREAK**

N-IV.6 10:35

HELIUM BEHAVIOUR IN WASTE CONDITIONING MATRICES DURING THERMAL ANNEALING

T.A.G. Wiss(a), J-P. Hiernaut(a), P.M.G. Damen(b), S. Lutique(c), R. Fromknecht(d), and W.J. Weber(e), (a)European Commission, JRC, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany, (b)Nederlands Meetinstituut, Princetonplein 5, 3584 CC Utrecht, The Netherlands, (c)CEA, DEN/DEC/SPUA/LTEC, C.E.N Cadarache,Bât. 717, 13108 Saint Paul-lez-Durance, France, (d)Institut für Festkörperphysik, Forschungszentrum Karlsruhe, Postfach 3640, 76021 Karlsruhe, Germany, (e)Pacific Northwest National Laboratory, P.O. Box 999, K8-93, Richland WA 99352, USA

Reprocessing of spent irradiated fuel produces high level waste (minor actinides, long living fission products) which might be disposed of in waste conditioning matrices. After the discovery of natural reactors, several mineral phases were proven to be able to incorporate fission products or actinides in their crystalline structure for long periods of time.

The long term behaviour of such containment matrices is, however, strongly affected by the radiogenic helium formation, as well as by self-irradiation effects due to radioactive decay of the incorporated actinides. Ascertaining whether the helium generated in these materials can be accommodated in the lattice or at trapping sites without adversely affecting the material integrity or whether helium will migrate, possibly increasing the pressure on the next confinement barrier, is of major importance on the overall waste package behaviour. In this study, synthetic compounds of zirconolite ($CaZrTi_2O_7$), apatite (Britholite, $Ca_2Nd_8(SiO_4)_6O_2$) and pyrochlores ($Gd_2Ti_2O_7$) were fabricated and doped with the short living alpha-emitter 244Cm to increase the total amount of helium and damage generated in a laboratory time scale. Helium implantations were also used to simulate the damage caused by the alpha-decay and the build-up of helium in the matrix. The samples were annealed in a Knudsen cell and the helium release profile interpreted in conjunction with radiation damage studies. Several processes like diffusion, trapping or phase changes could then be attributed to the helium behaviour depending on the material considered. Despite high damage accumulation and large amount of helium accumulated the integrity of the studied materials was preserved during storage.

N-IV.7 10:50

A NEW WAY OF PREPARATION OF THORIUM PHOSPHATE DIPHOSPHATE AND ASSOCIATED SOLID SOLUTIONS FROM CRYSTALLIZED PRECURSORS

N. Clavier(a), N. Dacheux(a), G. Wallez(b), J. Emery(c), M. Quarton(b), (a)Groupe de Radiochimie, IPN Orsay, Université Paris-Sud-11, Orsay, France, (b)Laboratoire de Cristallochimie du Solide, Université Pierre et Marie Curie, Paris, France, (b)Laboratoire de Physique de l'Etat Condensé, Université du Maine, Le Mans, France

Phosphate materials are generally considered as potential matrices for the immobilization of actinides. Among them, Thorium Phosphate Diphosphate ($Th_4(PO_4)_4P_2O_7$, TPD) exhibits several interesting properties such as high resistance to aqueous alteration, high loading capacity of tetravalent actinides (U, Np, Pu).
An original method of preparation of TPD and associated solid solutions from a low-temperature precursor, i.e. Thorium Actinide Phosphate HydrogenPhosphate Hydrate ($Th_{2-x/2}An_{x/2}(PO_4)_2(HPO_4)$, H_2O, TAnPHPH), was developped. The chemical transformations leading to TPD were especially studied through several techniques of characterization (XRD, NMR, IR, Raman) versus heating temperature. A new orthorhombic variety of TPD acting as an intermediate was evidenced. The study performed on TUPHPH solid solutions revealed that pure TUPD was obtained for $x < 2.8$ after heating at 1250°C, following the same chemical sequence. Moreover, this new way of preparation improves significantly the homogeneity of the final material as well as its sintering capability.

N-IV.8 11:05

STUDY OF THE CHEMICAL SCHEME OF DISSOLUTION OF THORIUM-URANIUM(IV) PHOSPHATE-DIPHOSPHATE SOLID SOLUTIONS

N. Clavier(a), E. du Fou de Kerdaniel(a), N. Dacheux(a), R. Drot(a), R. Podor(b), E. Simoni(a), (a)Groupe de Radiochimie, IPNO, Université Paris-Sud-11, Orsay, France, (b)LCSM, Université Henri Poincaré, Nancy I, Vandoeuvre lès Nancy, France

In the field of immobilisation of the actinides coming from an advanced reprocessing of spent nuclear fuels for an underground repository, several phosphate ceramics have been proposed. Among them, Thorium Phosphate Diphosphate (TPD) and associated solid solutions $Th_{4-x}M(IV)_x(PO_4)_4P_2O_7$ (M = U, Np, Pu) present some interesting properties (chemical durability, sintering capability).
Extensive leaching tests have been performed on TUPD solid solutions in various acidic media. Two different behaviours were observed depending on the actinide considered: uranium is preferentially released in solution while thorium quickly precipitates as a neoformed phase onto the surface of the leached pellet. The leached samples were characterised using several conventional techniques (such as SEM, TEM, μ-Raman, IR, NMR). Moreover, a multispectroscopic approach combining XPS and spectrofluorimetry, allowed to identifying the neoformed phase to the Thorium Phosphate Hydrogenphosphate Hydrate (TPHPH). On the basis of the results obtained, the scheme of TUPD solid solutions dissolution was thus proposed.

N-IV.9 11:20

HEALING OF DAMAGE IN HEAVY ION IRRADIATED FLUOROAPATITES BY X-RAY DIFFRACTION AND μRAMAN SPECTROSCOPY

F. Studer(a), S. Miro(a), D. Chateigner(1), D. Grébille(a), J.-J. Grob(b) and J-M. Costantini(c), (a)CRISMAT, ENSICAEN 6, Bd du Marechal Juin, 14050 Caen Cedex, France, (b)Laboratoire PHASE, B.P.20, 67037 Strasbourg Cedex 2, France, (c)CEA SACLAY, DMN/SRMA, 91191 Gif-sur-Yvette Cedex, France

Among the various matrices (apatite, monazite, hollandite, zirconolite, iodosodalite, titanite) investigated for nuclear waste storage purposes, the apatites were considered early since their structure allows them to incorporate many elements. The flexibility of the apatitic structure versus substitution explains why the silicate substituted apatites, also known as britholites, can be used to store iodine, cesium and minor trivalent actinides.
Most of these radionuclides transform following a complex scheme of spontaneous decays characterized by the emission of α particles. In this way, the damage is mainly due to cascades of nuclear collisions created by the corresponding nuclei recoils. α particles emission results in the creation of He gaz diffusing more or less easily inside the storage materials. Spontaneous fission, which occurs only for a few elements (Np, U, Pu), is less probable but results in the production of highly energetic ions (up to 100 MeV) with masses around 100 which can give rise to creation of latent tracks. In this work, we present a crystalline-amorphous phase analysis in heavy ion irradiated fluoroapatites by X-ray diffraction and μRaman spectroscopy. X-ray diffraction were realized on both single crystals and ceramics in grazing incidence in order to get information from the irradiated top layer of the samples (over 10 μm). Raman spectroscopy confirmed the results of X-ray diffraction and TEM experiments showed the presence of latent tracks exhibiting an amorphous core. The overall result of this damage study of fluoroapatites is that the measured amorphous fractions are the result of an equilibrium between defect creation and annealing depending on chemical compositions and electronic stopping power.

N-IV.10 11:35

PLUTONIUM INCORPORATION INTO PHOSPHATE AND TITANATE CERAMICS FOR MINOR ACTINIDE CONTAINMENT

X. Deschanels(a), V. Picot(a), J-N. Cachia(a), B. Glorieux(b), J.P. Coutures(b), (a)CEA Marcoule, DEN/DTCD/SECM/LMPA, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France, (b)PROMES-CNRS Tecnosud, Rambla de la thermodynamique, 66100 Perpignan, France

Two ceramics, zirconolite and a solid solution of monazite brabantite (ssMB) were studied for the immobilization of minor actinides: Np, Am, Cm and small quantities of unrecyclable plutonium produced by the reprocessing of the spent fuel. Zirconolite monoclinic ($CaZrTi_2O_7$) is a fluorite-derivative structure and is the primary actinide-host phase in Synroc (composite of titanates). The mineral monazite is a mixed lanthanide orthosphosphate, $LnPO_4$ (Ln=La, Ce, Nd, Gd…) that often contains significant amounts of Th and U.

The nominal composition of the ceramics studied in this work is $Ca_{0.87}Pu_{0.13}ZrTi_{1.73}Al_{0.3}O_7$ for zirconolite and $La_{0.73}Pu_{0.09}Ca_{0.09}Th_{0.09}PO_4$ for the solution solid monazite brabantite. These formula correspond to an incorporation of 10 wt.% PuO_2 in each materials. XANES spectroscopy shows that the plutonium is at the oxidation state +IV in zirconolite and +III in the ssMB. Thorium which is an element at the oxidation state +IV is also incorporate at 10wt.% ThO_2 into the ssMB. Aluminium balances the excess of cationic charge resulting from the incorporation of Pu(+IV) at the Ca site for zirconolite, and Ca plays the same role for thorium in the cationic site of the ssMB.

The relative density of the different pellets is higher than 90%. The samples present an homogeneous microstructure even if some minor phases representing less than 2% of the surface area were detected.

A comparison of these two ceramics in terms of actinide loading, structural and microstructural characteristics is discussed in this paper.

11:50 **DISCUSSION**

12:00 **LUNCH**

Thursday, June 2, 2005 Afternoon
Jeudi 2 juin 2005 Après-midi

13:30-14:30 POSTER SESSION

14:30 IMF Workshop
Introduction:

Session V: IMF Neutronic / Reactor
Session chairs: Vitaly Sobolev (SCK CEN), Masaki Saito (TIT)

N-V.1 15:00 -Invited-

NEUTRONIC DOUBLE HETEROGENEITY EFFECT IN PARTICLE DISPERSED TYPE INERT MATRIX FUELS

H. Akie and H. Takano, Ibaraki Univ., Hitachi-shi, Ibaraki-ken, 316-8511, Japan, Japan Atomic Energy Research Inst., Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan

As an inert matrix fuel (IMF) concept, Japan Atomic Energy Research Institute (JAERI) has studied rock-like oxide (ROX) fuel for effective Pu burning in light water reactors (LWRs). Current promising ROX concept is a particle dispersed type fuel in which Pu containing yttria stabilized zirconia (YSZ) particles are dispersed in spinel matrix. The ROX fuel is a kind of heterogeneous fuel, which is similar to that of high temperature gas cooled reactors (HTRs). This HTR is also a possible reactor type to burnup Pu by using IMF.

In the neutronics calculations of such a "double heterogeneous" system, where a heterogeneous fuel is further arranged in the heterogeneous geometry such as pellet, cladding and water moderator or fuel meat, graphite shell and coolant gas, estimation of the double heterogeneity effect is important because the neutronics calculations are often made on the homogeneous fuel model. Especially in HTRs, it is known that the double heterogeneity effect must be taken into account for the precise calculations. In this work, the double heterogeneity effect is estimated both in the ROX-LWR and YSZ-PuO_2 fuel HTR systems. In the ROX-LWR system, the heterogeneity effect is very small. When the ROX fuel specifications, such as YSZ particle diameter and the content of fuel isotopes in the particle, are based on those of actual fuel, the heterogeneity effect is negligible. While in the IMF-HTR system, the effect is notable, though smaller than in the UO_2 fuel HTR. In both LWR and HTR systems, the heterogeneity effect is strongly dependent on the fuel isotopes content in the particle. The heterogeneity effect is small in the IMF systems, presumably because the fuel isotopes in the particle are diluted with inert matrix.

N-V.2 15:20

THORIA INERT MATRIX FUEL IRRADIATION AT OECD HALDEN REACTOR

M. Streit, T. Tverberg, W. Wiesenack, Institutt for energiteknikk, OECD Halden reactor Porject, Postboks 173, 1751 Halden, Norway

A major issue in the public debate on nuclear power, is how to break down the large plutonium stockpiles. Different concepts have been developed during the last years to burn plutonium.

Two such concepts are stabilised zirconia based inert matrix (IM) and thoria (T) fuels. By using of IM fuels a larger fraction of plutonium could potentially be consumed without breeding new plutonium in comparison with today's MOX fuels. The aim of the presented study is to measure the general thermal behaviour of IM, inert matrix doped with thoria (IMT) and thoria under irradiation conditions similar to those in current LWR's. Of particular interest are the fuel thermal conductivity (and its degradation with burnup), fission gas release (FGR), fuel densification and fuel swelling. The irradiation is performed under HBWR conditions and a target burnup of ~400-450 kWd/cm3, which is equivalent to ~40-45 MWd/kg Oxide for the MOX fuel, is envisaged. Among other things considerably higher operating temperatures in the IM and IMT rods have been observed compared with those in the thoria fuel. The higher temperatures that were caused by the lower thermal conductivity of IM, result in higher FGR of the IM. This work gives the obtained results after 6 cycles of irradiation.

N-V.3 15:35

NEUTRONICS CALCULATIONS ON THE IMPACT OF BURNABLE POISONS TO SAFETY AND NON-PROLIFERATION ASPECTS OF INERT MATRIX FUELS

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Uranium-free plutonium fuels with inert matrix (IMF) may play a significant role to dispose of stockpiles of separated plutonium from military or civilian origin. For reasons of reactivity control of such fuels, burnable poisons (BP) will have to be used. The impact of different possible BP candidates (B, Eu, Er and Gd) on the achievable burnup as well as on safety and non-proliferation aspects of IMF will be analyzed. To this end, cell burnup calculations have been performed and burnup dependent reactivity coefficients (boron worth, fuel temperature and moderator void coefficient) are calculated.

All BP candidates are analyzed for one initial BP concentration and a range of different initial Pu-concentrations (0.35-1.0 g/cc) for reactor-grade Pu isotopic composition as well as for weapon-grade Pu. For the two most promising BP candidates (Er and Gd), a range of different BP concentrations is investigated to study the impact of BP concentration on fuel burnup. A set of reference fuels is identified for uranium-fuels, MOX and IMF and the spent fuel is investigated with respect to 1) the fraction of initial plutonium being burned, 2) the remaining absolute plutonium concentration in the spent fuel and 3) the shift in the isotopic composition of the remaining plutonium leading to differences in the heat and neutron rate produced. These aspects determine the attractiveness of remaining Pu in spent fuel for weapons purposes and are therefore important from a non-proliferation perspective.

15:50 **BREAK**

N-V.4 16:05

THE ROLE FOR INERT MATRIX FUEL IN THE U.S. LIGHT WATER REACTOR TRANSMUTATION FUEL DEVELOPMENT PROGRAM

W. J. Carmack(a), M. Todosow(b), M. K. Meyer(a) and K. O. Pasamehmetoglu(a), (a)Idaho National Laboratory, P.O. Box 1625, Idaho Falls ID 83415-3860, USA; (b)Brookhaven National Laboratory, 12 S. Upton Rd., Bldg. 475B, P.O. Box 5000, Upton NY 11973-5000, USA

Inert matrix and low fertile fuels have been proposed for use in light water reactors (LWR) in many forms and studied by several researchers. Currently, the U.S. Advanced Fuel Cycle Initiative (AFCI) LWR transmutation fuel development program plans to test inert matrix fuel in the LWR-2 irradiation series in the Advanced Test Reactor, located at the Idaho National Laboratory. The goal of the program is to develop fuel compositions that provide for flexibility in management of the overall LWR fuel cycle and ultimately reduce the amount of material requiring repository disposal. The most direct strategy for management of the fertile burden in a nuclear fuel cycle is to replace the U^{238} rich-depleted uranium matrix with a matrix material having a low or negligible fertile content.

A variety of MOX and IMF fuel compositions are being proposed for inclusion in the LWR-2 experiment. Combinations of varied fuel compositions will help achieve a reliable, proliferation resistant LWR fuel cycle. Each proposed fuel composition could serve a specific purpose. For example, an inert matrix fuel composition with additions of Am and Np could be used for their destruction. In practice a limited number of inert matrix fuel pins could be distributed throughout the reactor core to maintain a homogeneous power profile. Reactor grade MOX fuel compositions with or without additions of Am and Np could possibly be used as the primary heavy metal energy production composition in the core.

This paper will present the neutronic and thermal hydraulic considerations required of the low fertile matrix material compositions planned to be included in the LWR-2 irradiation test along with an explanation of the possible uses for each composition in the LWR fuel cycle.

N-V.5 16:20

THE DEEP-BURNER MODULAR HELIUM REACTOR FOR ACTINIDE INCINERATION

D. Hittner, G. B. Bruna and Ch. Trakas, FRAMATOME-ANP, Tour AREVA, 92084 Paris La Défense Cedex, France

The Deep-Burner - Modular Helium Reactor (DB-MHR), was proposed by General Atomics (GA) to fit sustainability objectives e.g. incineration of fissile plutonium and reduction of waste toxicity after one hundred year cooling-time.

When used to destroy transuranics waste, the DB-MHR three-ring active core contains two different kinds of fuels:

The Driver Fuel (DF), consisting of the plutonium and neptunium discharged from LWRs.

The Transmutation Fuel (TF), consisting of the minor actinides also discharged from LWRs, plus the transuranics left in the DF after a three-cycle irradiation. Fuels are packaged in TRISO micro particles that are assembled in ceramic (e.g. IMF) compacts which are retained in graphite fuel elements. The DB-MHR has a net thermal power outlet of 600 MW. The plutonium content of each re-loading ranges between 400 and 500 kg. The average operating temperature is 900°C. A negative temperature coefficient is granted by the graphite and a Doppler contribution from actinides. The prompt neutron lifetime is about 1 ms. After a complete irradiation, the residual mass of transuranics and the radiotoxicity of wastes depend on the Transmutation Ratio (TRU)

TRU was originally evaluated at more than 80%. In the GA's double-strata approach, the remainder of the fuel was recycled in an ADS, to achieve an almost complete incineration of the actinide charge. Analyses, conducted jointly by FRAMATOME-ANP and GA, estimated TRU more precisely at 65% ± 5%.. Recent works demonstrated that the TRU can be increased up to 70% for a critical and controlled operation.

Present results allow adopting a TRU value of 70% ± 5% as a design basis for an industrial DB-MHR. This figure indicated a significant achievement for actinide and fissile material incineration; nevertheless it remains lower than originally announced.

N-V.6 16:35

ASSESSMENT OF AMERICIUM TRANSMUTATION IN IMF OXIDE TARGETS IN DIFFERENT SPECTRAL ZONES OF ADS MYRRHA

W. Haeck, E. Malambu, V.P. Sobolev, Belgian Nuclear Research Centre SCK·CEN, Boeretang 200, 2400 Mol, Belgium

A possibility of americium transmutation in oxide inert matrix fuel (IMF) targets placed in the research ADS MYRRHA is being studied in the Belgian Nuclear Research Centre SCK•CEN in the framework of the FP5 EC project FUTURE.

The results of assessment of the transmutation performances of the MYRRHA experimental channels in the fast, resonance and epithermal neutron spectrum zones loaded with IMF targets are presented. Three types of the targets are considered with different matrices: ZrO_2, MgO and Mo. Each of them contained $(Pu_{0.5}Am_{0.5})O_{2-x}$ fuel particles. Six operation cycles were modelled; each cycle contains 90 days of irradiation and 30 days of shut-down for maintenance. The core transport calculations were performed with a more recent version of MCNPX-2.5 code. The transmutation calculations have been performed using the ALEPH burn-up code currently under development at SCK•CEN. The transmutation potentials of the considered fuels and limiting factors are estimated and compared. It was revealed that a significant part of the disappeared americium is converted into curium in all cases. Some recommendations about possible options of the more effective transmutation are discussed.

16:50 **DISCUSSION**

17:00 **IMF Future**

Friday, June 3, 2005 — Morning
Vendredi 3 juin 2005 — Matin

Session VI: IMF Materials
Session chairs: Yon-Woo Lee (KAERI), Rory Kennedy (INL)

N-VI.1 08:40 -Invited-

INERT MATRIX FUEL BEHAVIOUR IN TEST IRRADIATIONS

Ch. Hellwig(a), P. Blair(a), M. Streit(a), T. Tverberg(b), F.C. Klaassen(c), R.P.C. Schram(c), F. Vettraino(d), T. Yamashita(e), (a)Paul Scherrer Institut, 5232 Villigen-PSI, Switzerland, (b)Institutt for energiteknikk, 1751 Halden, Norway, (c)NRG, P.O. Box 25, 1755 ZG Petten, The Netherlands, (d)ENEA-Nuclear Fission Division, Via Martiri di Monte Sole 4, 40129 Bologna, Italy, (e)Japan Atomic Energy Research Institute, JAERI, Tokai-mura, Ibaraki-ken, 319-1195, Japan

Three large irradiation tests on inert matrix fuels have been initiated during the last five years: IFA-651 and IFA-652 in the OECD Halden Material Test Reactor and the OTTO irradiation in the High Flux Reactor in Petten. While the OTTO irradiation is already completed, the other two irradiations are ongoing.

The objectives of the experiments differ: For OTTO, the focus was on the comparison of different concepts of IMF, i.e. homogeneous fuel versus different types of heterogeneous fuel. In IFA-651 single phase yttria stabilized zirconia (YSZ) doped with Pu is compared with MOX. In IFA-652 the potential of calcia stabilized zirconia (CSZ) as a matrix with and without thoria additions is evaluated. The design of the three experiments is explained and the current status is reviewed. The OTTO experiment showed that the homogeneous, single phase YSZ-based fuel and the macro-dispersed heterogeneous spinel-based fuel show good irradiation behaviour. The single phase YSZ-based fuel is also irradiated in IFA-651 where the stable irradiation behaviour was confirmed. The fuel showed a strong densification in the beginning (but with constant fuel temperature) and later in life a strong gaseous swelling in the hot pellet centre. IFA-652 shows that the addition of thoria increases the thermal conductivity of the fuel. In general it can be said that homogeneous fuel of CSZ or YSZ is the most promising concept. Nevertheless the fuel temperatures were relatively high due to the low thermal conductivity leading to high fission gas release. This disadvantage of this type of IMF must be taken into account in the fuel design.

N-VI.2 09:00

MODELLING HEAT CAPACITY, THERMAL EXPANSION AND THERMAL CONDUCTIVITY OF OXIDE IMF

V.P. Sobolev, S.E. Lemehov, Belgian Nuclear Research Centre SCK·CEN, Boeretang 200, 2400 Mol, Belgium

Prognosis of the in-pile behaviour of the inert matrix fuels (IMF) and targets is still difficult because of very limited or often missing information on their thermal and mechanical properties. In this situation, the basic physical modelling and similarity principle can be very useful.

In this presentation, a combination of the macroscopic and microscopic approaches is proposed to use for the development of the sound physical models of heat capacity, thermal expansion and thermal conductivity of oxide nuclear fuels and matrices. Based on a simplified model of the phonon spectrum, on the extended Debye-Grüneisen model of thermal expansion, on the Klemens model of thermal conductivity of solids, some useful relationships bounding the properties of the materials of interest are deduced in quasi-harmonic approximation. The developed model was first applied to UO_2, ThO_2, NpO_2, ZrO_2 and MgO, and the obtained results showed rather good agreement with the available experimental data in the temperature range of 30 to about 2000 K. Then the extension of the model to IMF, presenting some mixtures of the considered oxides is proposed.

N-VI.3 09:15

EVALUATION OF THERMAL PROPERTIES OF ZIRCONIA-BASED INERT MATRIX FUEL BY MOLECULAR DYNAMICS SIMULATION

T. Arima, Sh. Yamasaki, K. Yamahira, Y. Inagaki, K. Idemitsu, Institute of Environmental Systems, Faculty of Engineering, Kyushu University, Japan

Zirconia-based oxides doped with plutonium are likely to be an attractive candidate of an inert matrix fuel (IMF) for burning excess plutonium from spent fuels of light water reactors and dismantlement of nuclear weapons. Stabilized zirconia has good properties, e.g. high melting point, chemical stability, small neutron capture cross-section and so on. In the present study, using the molecular dynamics (MD) simulation, the lattice structure and thermal properties of zirconia-based IMF were investigated from 300 K to 1500 K.

The MD program MXDORTO was used to simulate the zriconia-based IMF, which was doped with Er, Y and Pu, as well as Ce-doped zirconia since Ce was an analogous of Pu. In this simulation, the Born-Mayer-Huggins interatomic potential was applied with fully or partially ionic model. The potential parameters of Pu ion were determined to reproduce the thermal expansion of PuO_2 and compressibility of CeO_2, and those of other ions were obtained from the literature. The lattice parameter of stabilized zirconia was increased with Pu or Ce content, and thermal expansion of Ce-doped zirconia was comparable with our experimental data. The constant-pressure heat capacity was discussed in terms of the phonon contribution, which was calculated from the velocity auto-correlation function, and the dilation contribution. The MD simulation showed that thermal conductivity of such a zirconia was rather insensitive to temperature compared with that of UO_2.

N-VI.4 09:30

DUAL PHASE MAGNESIA-ZIRCONIA CERAMICS FOR LIGHT WATER REACTOR INERT MATRIX FUEL

P.G. Medvedev, S.M. Frank, M.J. Lambregts, A.P. Maddison, T.P. O'Holleran, M.K. Meyer, Argonne National Laboratory West, Idaho Falls ID 83404-2528, USA

To address the low thermal conductivity of the ZrO_2-based IMF and the instability in water of the MgO-based IMF, the dual phase MgO-ZrO_2 ceramics are proposed as a matrix for LWR fuel for actinide transmutation and Pu burning. It is envisioned that in a dual-phase system MgO will act as efficient heat conductor while ZrO_2 will provide protection from the coolant attack. This paper describes results of fabrication, characterization, hydration testing and thermal analysis of MgO-ZrO_2 ceramics containing 30-70 wt. % of MgO.

Ceramics were fabricated from the oxide mixture using conventional pressing and sintering techniques. Some compositions were doped with 7 wt. % of Er2O3 to simulate addition of burnable neutron poison. The final product was found to consist of two phases: cubic ZrO2-based solid solution and pure cubic MgO. The amount of MgO dissolved in the ZrO_2 was 13-17 mol. %. Er_2O_3 dopant preferentially dissolved in the ZrO_2 phase. Limited degradation of the ceramics in static deionized water at 300oC and 1246 psi occurred due to the hydration of the MgO phase. Normalized mass loss rate was found to decrease exponentially with ZrO_2 content in the ceramics. Presence of boron in the water had a dramatic positive effect on the hydration resistance. The final product exhibited thermal conductivity values of 5.5-9.5 W/(m-K) at 500°C, and 4-6 W/(m·K) at 1200°C depending on the composition. Thermal conductivity was derived from thermal diffusivity measured by laser flash method in the 200-1200°C temperature range, measured density, and heat capacity calculated using the rule of mixtures. Attempts to dissolve MgO-ZrO_2 ceramics in HNO_3 to simulate reprocessing resulted in selective dissolution of the MgO phase leaving behind a ZrO_2 skeleton.

N-VI.5 09:45

NEW PROCESSING METHODS TO PRODUCE SiC AND BeO MATRIX FUEL

A.A. Solomon, S. Kuchibhotla, J. Fourcade, R. Latta, S.G. Lee and Michael King, School of Nuclear Engineering, Purdue University, W. Lafayette IN 47907, USA

SiC and BeO represent two possible matrix phases that exhibit low neutron absorption, high chemical and radiation stability and high thermal conductivity. However, both represent significant processing challenges. We have developed the Polymer Impregnation and Pyrolysis, or *PIP*, method to consolidate both particulate fuels like TRISO fuels, actinide particles and waste forms, and to impregnate UO_2 fuels with pure SiC to improve their thermal conductivity. For the latter, a new “slug/bisque” method of fabricating the fuel granules was necessary, but almost complete impregnation was obtained.

For BeO, a second approach was developed that involves just a “co-sintering” route to produce high density fuels with co-continuous BeO and UO_2 phases. The advantages of the PIP process is that it represents a non-damaging consolidation process for particulates, and forms a continuous pure SiC phase. But several impregnation cycles are necessary to obtain high density SiC. The BeO “co-sintering” process requires special powder and granule mixing techniques, but only one normal sintering cycle. The handling of BeO needs to be controlled, but the requirements are similar to those for UO_2 powders. The neutronic, thermal and thermomechanical properties of these new fuel forms are presented.

N-VI.6 10:00

FABRICATION AND THERMOPHYSICAL PROPERTY CHARACTERIZATION OF ACTINIDE ALLOYS AS NUCLEAR TRANSMUTATION FUELS

J. R. Kennedy, A. P. Maddison, D. D. Keiser, St. M. Frank, Idaho National Laboratory, Idaho Falls, Id 83403, USA

INL has produced and characterized a series of non-fertile and low-fertile metal alloy test nuclear fuels for the transmutation of actinide isotopes in either fast spectrum reactors or accelerator driven systems under the United States Department of Energy (US-DOE) Advanced Fuel Cycle Initiative (AFCI). The uranium free alloys are currently under irradiation testing in the Advanced Test Reactor (ATR) in the United States and two of the fuel compositions will begin irradiation testing in the Phénix reactor in France under the FUTURIX program in 2006.

There are a good number of challenges associated with the fuel development program and many of them are a direct result of the deficiency in the database of the fundamental properties and reactivities of the actinides and their alloys.

Characterization efforts on the as-cast products include phase identification (XRD), microstructure analyses (SEM), fuel-cladding-chemical-interaction (fcci) diffusion couple studies, thermal expansion (TMA), heat capacities and enthalpies of transition (DSC) and thermal conductivities (LFD). The fabrication of nuclear fuels containing americium, whether metal alloy or other, is problematic due to the high volatility (vapour pressure) of americium and consequential loss during extended high temperature heating processes. Quantitative analysis of Am retention from the arc-casting fabrication process used to produce these fuels has been performed and shows very low losses as well as good distribution of the elements throughout the fuel samples. These issues will be discussed during the presentation together with pertinent experimental results.

10:15 **BREAK**

N-VI.7 10:30

PRODUCTION OF ZIRCONIA-BASED TRANSMUTATION TARGETS

A. Fernandez, D. Haas, J. Somers, European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany

Yttria stabilised zirconia (YSZ) is one of the favoured inert matrix materials to be used in fuels and targets for the transmutation of plutonium and minor actinides. Production methods based on combinations of the sol gel and infiltration routes have been developed, both to minimise waste, and reduce potential radiation exposure to the operating personnel. High quality products meeting reactor specifications have been obtained. To overcome the inherent low thermal conductivity of YSZ based materials, recourse to CERCER or CERMET pellet type fuels can be made. The first results on the production and property determination of $(Zr,Pu)O_2$ and $(Zr,Pu,Am)O_2$ homogeneous materials are presented, along with first tests on the production of composite materials in which the actinide containing ceramic is diluted in a Mo matrix.

N-VI.8 10:45

USE OF ZrC FOR THE INERT MATRIX MATERIAL IN MINOR ACTINIDES TRANSMUTATION

Young-Woo Lee, Si-Hyung Kim, Dong-Koo Kim, Ho-Jin Ryu, Dong-Seong Sohn, Korea Atomic Energy Research Institute, PO Box 105 Yuseong, Daejeon 305-600, Korea

There have been a number of studies worldwide on the inert matrix materials for minor actinide (MA) transmutation in the different forms of targets and fuel materials. Among others, stabilized zirconium oxide, aluminium magnesium spinel and other non-oxide materials such as SiC and TiN. Zirconium carbide, ZrC, is known as a high performance structure material owing to its high melting point, stability against radiation and good mechanical property and it is one of the candidate coating materials for Very High Temperature Reactor (VHTR) coated particle fuel.

In this work, it is attempted to see the feasibility to use ZrC as a inert matrix material for the MA transmutation. ZrC powder was mixed with UO_2 or CeO_2 as a surrogate for PuO_2 and/or AmO_2 and sintered in Ar gas in the temperature range between 1773 K and 1973 K. There was no reaction between ZrC and UO_2 while a reaction was observed between ZrC and CeO_2 to form mixed Ce-Zr oxdes. Physico-mechanical properties such as hardness, toughness and high temperature fracture strength were analysed and compared with other similar materials to evaluate the feasibility of inert matrix material for MA transmutation. Also discussed was the possible reaction mechanism of the formation of the mixed Ce-Zr oxide phases.

N-VI.9 11:00

IMF IN DISPERSION TYPE FUEL ELEMENTS

A.M. Savchenko, A.V. Vatulin, A.V. Morozov, V.L. Sirotin, I.V. Dobrikova, G.V. Kulakov, S.A. Ershov, V.P. Kostomarov, Y.I. Stelyuk, A.A. Bochvar Institute of Inorganic Materials (VNIINM), Rogova St 5A, PO Box 369, 123060 Moscow, Russia

Consideration is given to the advantages of using IMF as dispersion fuel in aluminium alloy matrix. They are low temperatures in fuel centre, achievable high burn ups, serviceability in transients, environmentally friendly process of fuel rod fabrication. At A.A. Bochvar Institute two main versions of IMF are under development, viz., having heterogeneous and isolated distribution of plutonium. The results are presented on out of pile investigations of IMF having dioxide uranium simulator. Fuel elements with dioxide uranium composition fabricated at A.A. Bochvar Institute are currently under MIR tests (RIAR, Dimitrovgrad). The fuel elements reached the burn up of 88 MW d/kg U (equivalent to the burn up of the standard dioxide uranium pelletized fuel) without less of tightness by cladding. The feasibility is considered of fabricating IMF of the particular type with plutonium dioxide to be in-pile irradiated.

N-VI.10 11:15

POST IRRADIATION EXAMINATION OF THE OTTO IRRADIATION EXPERIMENT FOR PLUTONIUM INCINERATION

F.C. Klaassen(a), R.P.C. Schram(a), K. Bakker(a), Ch. Hellwig(b), T. Yamashita(c), (a)Nuclear Research and consultancy Group, P.O. Box 25, 1755 ZG Petten, The Netherlands, (b)Paul Scherrer Institut, 5232 Villigen-PSI, Switzerland, (c)Japan Atomic Energy Research Institute, JAERI, Tokai-mura, Ibaraki-ken, 319-1195, Japan

The OTTO irradiation experiment has been performed to test Inert Matrix Fuels (IMF) for the incineration of plutonium in a Once Through, Then Out (OTTO) mode. The test matrix of the OTTO irradiation consisted of seven capsules, six of which had a $(Zr,Y,Pu,U/Er)O_{2-x}$ fissile phase in inert matrices of either yttria-stabilised zirconia or spinel. Capsule 7 contained MOX-fuel for reference purposes. The fissile plutonium content in the capsules was in the range of 0.35-0.4 g/cm^3.

Irradiation was performed in the High Flux Reactor in Petten for 548 full power days. During irradiation only limited swelling or even shrinkage of the inert matrix pellets was observed, except for one spinel inert matrix target, which showed a cladding failure due to swelling of spinel. The total plutonium depletion at the end of irradiation was around 35% in the inert matrix fuels, whereas in the MOX reference capsule, which experienced a similar burn-up, it was only 15%.

The results of both non-destructive and destructive post-irradiation examination are presented, as well as the neutronics modelling after irradiation by means of MCNP. The results confirm the absence of large swelling observed during irradiation. The crack formation, observed in the zirconia-based targets, is comparable to that of UO_2 fuel. The fission gas release is around 10% for the zirconia-based targets, whereas for the heterogeneous spinel-based targets, which experienced a much lower irradiation temperature, it is around 5%. The homogeneous targets show very low fission gas release.

N-VI.11 11:30

YTTRIUM STABILISED ZIRCONIA INERT MATRIX FUEL IRRADIATION AT OECD HALDEN REACTOR

M. Streit(a), W. Wiesenack(a), T. Tverberg(a), B. Oberländer(b), C. Hellwig(c), (a)Institutt for energiteknikk, OECD Halden Reactor Project, Postboks 173, 1751 Halden, Norway, (b)Institutt for energiteknikk, 2027 Kjeller, Norway, (c)Paul Scherre Institut, 5232 Villigen PSI, Switzerland

Different concepts have been developed during the last years to transmute transuranium elements (TRU) using an uranium free inert matrix fuels (IMF) in a once-through-cycle to reduce the amount of TRU in the nuclear waste. For today's LWR's yttrium stabilised zirconia (YSZ), and other oxides like for example alumina, spinel or ceria have been proposed as materials to be inert matrices. By using of IMF a larger fraction of plutonium could potentially be consumed without breeding new plutonium in comparison with MOX fuels.

The aim of the presented study is to measure the general thermal behaviour of YSZ IMF under irradiation conditions similar to those in current LWR's in direct comparison to standard MOX fuel. Of particular interest are the fuel thermal conductivity (and its degradation with burnup), fission gas release (FGR), fuel densification and fuel swelling. A secondary aim is the direct comparison of the fuel performance between YSZ IMF and MOX fuels. The irradiation is performed under HBWR conditions and a target burnup of ~500 kWd/cm3, which is equivalent to ~50 Mwd/kgOxide for the MOX fuel, is envisaged. Among other things considerably higher operating temperatures in the IMF rods have been observed compared with those in the MOX fuel. The higher temperatures , that were caused by the lower thermal conductivity of IMF, result also in higher FGR of the IMF rods. This work gives the obtained results after 6 cycles of irradiation.

N-VI.12 11:45

THORIA, INERT MATRIX FOR THE IMMOBILIZATION OF PLUTONIUM

D. Barrier, A.A. Bukaemskiy, G. Modolo, Institut für Sicherheitsforschung und Reaktortechnik, Forschungszentrum Juelich GmbH, 52425 Juelich, Germany

The reduction of the long term radiotoxicity of nuclear waste has been foreseen by the Partitioning & Transmutation of minor actinides (MA), which requires the development of inert ceramic support materials. Moreover, after separation, the actinides can be conditioned into stable dedicated solid matrices (Partitioning & Conditioning strategy). Thorium oxide is very attractive matrix from the waste minimisation point of view. In fact by using thoria as support for burning of Plutonium in PWR, the actinide production is very low and so the consumption rates of plutonium are very high. Moreover, thoria is also a stable matrix, very resistant to leaching and so can be used as inert matrix for a final disposal. The aims of the present work are twice. The possibility of synthesising Thoria based ceramic for Plutonium burning and storage, by using simple and mild method of production, was investigated. The impact of the addition of ceria, employed as simulate for tetravalent actinide, on the properties of matrix was evaluated. Thus, several oxides material composed of thoria and ceria have been synthesised by co-precipitation method and the products have been characterised by Thermogravimetry coupled by Differential Scanning Calorimetry (TG-DSC) and X-Ray line diffraction. This $(Th,Ce)O_2$ system crystallise in CFC structure, fluorite type for all ceria content and the system follows the Vegard's law. The microstructure was investigated by SEM coupled with EDX. For all ceria content, pellets present well formed grains and homogeneous distributed pores. The mechanical properties of pellets were investigated. The microhardness increases with ceria content from 8.8 to 10.3 GPa. On contrary the fracture toughness decreases with ceria content from 1.06 to 0.96 $MPa.m^{-1/2}$. Thermal conductivity investigations are in progress.

N-VI.13 12:00

POST IRRADIATION EXAMINATION ON PARTICLE DISPERSED ROCK-LIKE OXIDE FUEL

N. Nitani, K. Kuramoto, T. Yamashita, K. Ichise, K. Ono and Y. Nihei, Japan Atomic Energy Research Institute, Tokai, Ibaraki, 319-1195, Japan

To evaluate irradiation behaviour of the ROX fuel, irradiation experiment was carried out using 20% enriched U instead of Pu. Three fuels were prepared; a single phase fuel of YSZ containing UO2 (U-YSZ), two particle-dispersed fuels of U-YSZ particle in spinel or corundum matrix. The U-YSZ particles were prepared by crashing presintered U-YSZ pellets and by sieving them. U-YSZ particle sizes were about 100-200 µm. These fuels were irradiated in Japan Research Reactor No.3 for 13 cycles, about 300 days. The estimated fuel centre temperatures were 1300-1500K.

Non-destructive and destructive post-irradiation examinations were carried out. No significant appearance changes were observed for all fuel pins. Any change in axial pellet stack length was not recognized. Though many cracks were observed in the pellets by X-ray photographs, the gaps between pellets existed and significant pellet fragmentation was not observed. Distribution of typical FPs was analyzed by the γ scanning over the fuel pin. Non-volatile nuclide remained in the fuel pellet. On the other hand, a part of Cs moved to the gaps between the pellets and to the insulators. Cs-134 and Cs-137 showed different distributions at the plenum for all type fuels. Fuel pellets were taken out from fuel pins without bonding. Spinel decomposition and subsequent restructuring were not observed probably due to low irradiation temperature.

12:15 **CONCLUSIONS**

12:30 **LUNCH**

13:30-14:30 **POSTER SESSION END**

14:30-15:30 **DRAFT SESSION**

POSTER SESSIONS

Tuesday, May 31 and Thursday, June 2, 2005

13:30 – 14:30

N/P.01 MICROSTRUCTURAL STUDIES OF NUCLEAR MATERIALS BY SYNCHROTRON RADIATION : A NEW CHALLENGE FOR THE NEAR FUTURE

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Understanding and modelling of physico-chemical and/or mechanical properties of nuclear materials are highly dependent on experimental results. During the last decades, use of synchrotron facilities which provide intense X-ray photons fluxes over large energy ranges, has emerged as an indispensable tool for characterizing properties of matter. The construction of SOLEIL, the new third generation French synchrotron radiation facility, will be the opportunity to erect the MARS (MAtière Radioactive à SOLEIL) beam-line fully dedicated to research on radioactive matter. The aim is clearly an extension of research towards the use of synchrotron radiation for multidisciplinary fields with multi technique equipment. With respect to national and European safety regulations, this dedicated station will offer a unique possibility to investigate radioactive samples with an activity up to 18.5 GBq (500 mCi), value never offered yet. Although MARS beam-line will be located on a bending magnet port, the X-ray optics will be designed for performing high resolution diffraction, fluorescence and absorption spectroscopy with an extension of time resolved analyses. When necessary, very high energy photon experiments will be carried out on the high energy beam-line located on an insertion device port downstream MARS beam-line one. Equipment will mainly be housed by two lead shielded hutches equipped with airlocks and under ventilation. Sample preparation will be possible in glove boxes. The MARS beam-line shall be operational beginning of 2007 and so to the international scientific community.

N/P.02 OPTIMISATION AND CHARACTERISATION OF THICK W COATINGS ON Cu-Cr-Zr ALLOY FLAT SUBSTRATES

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W is a promising armour material for plasma facing components (PFC) of nuclear fusion reactors because of its low sputter rate and favourable thermo-mechanical properties. Among all the techniques able to realise W armours, plasma spray looks attractive because of its straightforwardness, its suitability to cover extended surfaces and the possibility of in situ repair. The present work concerns the optimisation of spraying parameters aimed at realising flat 5 mm thick coating mock ups to be used for thermal fatigue tests before and after neutron irradiation. The manufacturing of flat coatings is an arduous task because the stress field in the edge regions induces detachments at the W-Cu alloy interface. For this reason, a big effort was spent for the optimisation of the coatings and particular care was paid to the characteristics of bond coat and interlayer also to avoid the degradation of the mechanical properties of the CuCrZr substrate.

The coating microstructure was characterised by means of scanning electron microscopy (SEM) and scanning tunnelling microscopy (STM). Residual strain measurements were performed using the hole drilling technique. FIMEC indentation tests were employed to compare the coatings cohesion with that of monolithic tungsten. The adhesion of the bonding interlayer was assessed according to modified ASTM standards.

N/P.03 SANS ANALYSIS OF NANO-SIZED IRRADIATION-INDUCED DEFECTS IN THE EUROFER 97 RAFM STEEL

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The reduced activation ferritic/martensitic (RAFM) steel EUROFER 97 is presently considered as a promising structural material for first wall and breeding blanket applications in fusion reactors. Series of specimens of the EUROFER 97 have been irradiated with 590 MeV protons in the Proton Irradiation Experiment (PIREX) facility, at the Paul Scherrer Institute, at various temperatures ranging between 50 and 350°C and to various doses ranging between 0.3 and 2 dpa. Small angle neutron scattering (SANS) measurements were performed on unirradiated and irradiated specimens of the EUROFER 97, at room temperature and with a saturating magnetic field applied to the specimens. It was found that the scattering associated to the irradiation-induced defects is consistent with a distribution of nano-spheres (voids and/or helium bubbles) whose size peaks at about 0.6 nm. The number density of these features clearly increases with the irradiation dose and decreases with increasing the irradiation temperature. The size of the defects does not increase with dose in the investigated dose range.

N/P.04 HE CLUSTER IN TITANIUM ALLOYS

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This work presents first results on the growth of He-bubbles in titanium sheets measured by means of small angle X-ray scattering (SAXS). 200 keV He ions were implanted at room temperature at FZ Rossendorf into 15 µm thick titanium sheets up to fluence of 3x1017/cm2. This resulted in thin layer of He with peak concentration of about 20 %. SAXS measurements have been performed at the KMC-2 beam-line at BESSY using a 2-dimensional detector and an X-ray energy of 8 kV. The measurements have been performed ex-situ at RT after annealing the specimen at 300°C, 400°C, 500°C, 600°C, 650°C and 700°C for 1800 sec.

Small changes in the spectra were already observed after annealing at 300°C. Appreciable changes in the spectra occurred after annealing at 500°C and 600°C while heat treatment above 600°C caused only minor changes in the SAXS spectra. The changes in the spectra are ascribed to the formation of He bubbles in titanium. The results of these measurements show that SAXS is a promising tool for the study of He-agglomeration in fusion materials. The possibilities of in-situ experiments at high temperature with appreciably higher photon flux at the new SAXS facility of HMI at the 7T Wiggler at BESSY are discussed.

N/P.05 SLIDING WEAR BEHAVIOUR OF STEAM GENERATOR TUBE MATERIALS IN PRESSURIZED WATER AT 300°C

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Wear damage of steam generator tubes of nuclear power plants can cause the leakage of radioactive substances. So the evaluation of tubes integrity is very important in the view point nuclear ecocide. In the present study, sliding wear behaviours of Inconel 600 and 690 steam generator tube materials mated with 409 stainless steel commonly used as support plate were investigated in pressurized water at 300°C. For more precise prediction of wear behaviours of steam generator tubes, Archard equation was modified and the modified wear coefficients were estimated as a function of the sliding distance. When using the modified Archard equation, the reliabilities for prediction of wear behaviour of Inconel 600 and 690 mates with 409 stainless steel increased from 20.5% to 65.5% and from 38% to 60.4%, respectively.

N/P.06 EFFECT OF MN ON THE CAVITATION EROSION RESISTANCE OD FE-CR-C-SI ALLOYS FOR REPLACING CO-BASE STELLITE 6

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Co-base Stellite alloys have been used as hardfacing materials for nuclear power plant valves. However, Co is known to be a main contributor to the occupational radiation exposure. Thus, Stellite has been needed to be replaced by Co-free hardfacing alloys having equivalent properties. Resistance to cavitation erosion is one of the important properties needed in the new alloy. Mn is known to decrease stacking fault energy and enhance the formation of martensite. In this study, the effect of Mn on the strain-induced martensitic phase transformation and its effect on the cavitation erosion behaviour of the alloy were investigated using a 20kHz vibratory cavitation erosion test equipment. The cavitation erosion resistance was measured by the cumulative weight loss of the Mn added Fe-base alloy and compare to that of Stellite 6. The phase transformation was examined by X-ray diffraction before and after cavitation erosion tested specimens and the surface damage of the present specimens was investigated by SEM and OM.

N/P.07 SLIDING WEAR BEHAVIOUR OF HARDFACING ALLOYS FOR NUCLEAR POWER PLANT VALVES IN A PRESSURIZED WATER ENVIRONMENT

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Co-base Stellite alloys have been used as hardfacing materials for nuclear power plant valves. Stellite, main contributor to the occupational radiation exposure, has been needed to be replaced by cobalt-free hardfacing alloys having equivalent properties. Among the properties, wear resistance is one of the most important properties. In this study, sliding wear behaviour of newly developed Fe-base Co-free hardfacing alloy (Fe-Cr-C-Si) was investigated and compared to that of Stellite 6 and Fe-base NOREM 02 in the temperatures ranging from 25°C to 300°C under a contact stress of 15 ksi in pressurized water. The weight loss of Fe-Cr-C-Si was equivalent to that of Stellite 6 over all temperature in 100 cycle wear test. The weight loss of NOREM 02 was nearly equivalent to that of Stellite 6 below 200°C, however, galling occurred above 200°C in 100 cycle wear test. The weight loss of Fe-Cr-C-Si increased with temperature up to 300°C but was less than that of Stellite 6 in 1000 cycle wear test.

N/P.08 THE EFFECTS OF B ON SLIDING WEAR BEHAVIOUR OF FE-BASED HARDFACING ALLOYS FOR NUCLEAR POWER PLANTS VALVES

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The present research is aiming at the improvement of new Fe-base wear resistance alloy, which has been expected to be substituted for Stellite 6 in nuclear power industry. Sliding wear tests of Fe-Cr-C-Si-xB alloys with x varing from 0 to 3wt% were performed in air at the temperature range of 25-450°C under a contact stress of 103MPa. As increasing B content, the friction coefficient has been lowered and the hardness and wear resistance have been increased. Especially the weight loss of B added Fe base alloy was less than those of Stellite 6 and B free Fe base alloy. It is thought to be caused by promotion of strain-induced martensitic transformation in the B added Fe base alloy.

N/P.09 X-RAY ABSORPTION SPECTROSCOPY STUDY OF ZIRCONIUM ALLOY CORROSION LAYERS

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ZrO2 corrosion layers have been studied by X-ray Absorption Fine Spectroscopy (XAFS) in order to investigate their crystallographic phase, and oxygen deficiencies.

In this study, we have carried-out Zr L-edges X-ray absorption experiments at variable incident angle (VIA-XAFS) at the SLS-LUCIA beam-line for various zirconia films obtained by zirconium alloy (Zry) corrosion. Film samples were obtained by Zirconium Alloy corrosion: a 10 µm film Zry/ZrO_2 produced by corrosion in liquid water at 320°C under 15 MPa (A360), and Zry/ZrO_2 20 and 100 µm samples produced by corrosion of Zry at 415°C in water steam. XAFS was recorded in fluorescence mode for the samples and for the powder monoclinic ZrO_2 and sputtered Zr thin film references for the oxide and the metallic phases. After the self-absorption correction, data are discussed to obtain information for different depths.

N/P.10 RADIATION-INDUCED CHANGES IN THE ELECTRICAL PROPERTIES OF CARBON FILLED PVDF THICK FILMS

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Radiation interacts with polymers in two ways: chain scission, which results in reduced tensile strength and elongation; and cross-linking, which increases tensile strength but reduces elongation. Both reactions occur simultaneously, but one is usually predominant, depending upon the specific polymer and additives involved. Poly(vinylidene fluoride) (PVDF) is widely used polymer for technical/engineering applications. PVDF is a high-molecular-weight polymer with the predominant repeating unit established as ($–CH_2–CF_2–$). It is a semi-crystalline material with a melting point of 338°C. PVDF is quite resistant to radiation dose and no irreversible changes occur below 1000 kSv.

This work investigates the electrical properties of PVDF thick films under gamma radiation. These films were filled with 6 wt.% of Carbon to increase their conductivity. DEK RS 1202 screen printer was used for thick film fabrication. All films were exposed to a disk-type 137Cs source with an activity of 370 kBq. Changes in the current-voltage characteristics were measured after each exposure dose. A tenfold increase in the values of current was recorded after a dose of 228 microSv. A higher dose of 342 microSv resulted a decrease in the values of current. Therefore, PVDF+Carbon system has potential application in low-dose radiation dosimetry. It was noticed that as-printed films trend to electroform at about 12V, whereas films irradiated with 171 microSv showed strong electroforming effect already at 5V. Radiation-induced high current caused heating and shorting the devise, due to the metal inclusions from the Ag contact material. For that reason, a proper design of dosimetry system is essential to eliminate such effects.

N/P.11 CHARACTERIZATION OF HYDROGEN IN ZIRCALOY

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Zircaloy takes up hydrogen during corrosion in water. Hydrogen is dissolved in the metal and forms hydrides when the solution limit is exceeded. The amount of hydrogen is characterized by various analytical techniques such as metallography, neutron radiography and hot extraction approach. Metallography in combination with scanning electron microscopy allows determining the local distribution and orientation of hydrides in the Zircaloy. However the neutron radiography delivers relative information on the total hydrogen distribution in metal on a macroscopic scale, while the hot extraction permits determination of the total hydrogen content on a macroscopic piece of metal. Therefore solid nuclear magnetic resonance (^1H NMR) measurements have been performed to determine the type of the hydrogen species in the Zircaloy. This technique will be applied to a series of Zircaloy samples loaded with various amounts of H at different temperatures.

N/P.12 EVALUATION OF THERMAL PROPERTIES OF UO2 AND PUO2 BY MOLECULAR DYNAMICS SIMULATION FROM 300 K TO 2000 K

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Thermal properties of UO_2 and PuO_2 have been investigated by the molecular dynamics (MD) simulation from 300 to 2000 K. For development of nuclear reactor system and its safety operation, deeply understanding of physico-chemical properties of such nuclear materials is needed as well as that of the nuclear characteristics.

In the present MD calculation (MXDORTO program), the Born-Mayer-Huggins interatomic potential was applied with the fully (FIM) or partially ionic model (PIM). The potential parameters of U and Pu ions were determined to reproduce the thermal expansion and compressibility of UO_2 and PuO_2, respectively. Thermal expansion behaviours of UO_2 and PuO_2 are well reproduced by assuming the effective ion valence of 67.5% for PIM. The constant-pressure heat capacity can be generally defined as the constant-volume heat capacity and the dilation term. These heat capacities obtained by the MD simulation are a little smaller than experimental data. This result indicates that the electronic contribution is not negligible for the heat capacity of the actinide oxide including 5f-electrons, e.g. Schottky or small polaron contribution. The thermal conductivity can be evaluated by time auto-correlation function of energy current expressed by the Green-Kubo formula in the equilibrium MD calculation. The thermal conductivities thus obtained for both UO_2 and PuO_2 decreased with increase of temperature and were comparable with experimental data at temperatures greater than 500 K.

N/P.13 AB INITIO MODELLING OF THE BEHAVIOUR OF XENON AND HELIUM IN OXYDE NUCLEAR FUELS

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We study the stability of point defects and the behaviour of xenon and helium in UO_2, PuO_2 and AmO_2. We use a plane-wave pseudopotential approach in the Generalized Gradient Approximation of the Density Functional Theory (DFT). We show that this approach can satisfactorily describe the cohesive properties of the actinide dioxides considered. As a first step, we calculate the formation energies of extrinsic (vacancies and interstitials) as well as intrinsic (Frenkel pairs and Schottky defects) point defects. We find that UO_2 is unstable towards oxygen incorporation at an octahedral interstitial site, in contrast to PuO_2 and AmO_2, confirming the easier oxidation of UO_2. The stability and the solubility of the rare gases Xe and He in the dioxide crystals are discussed in terms of incorporation energies and solution energies. The solution energies are determined taking into account the concentration of the trap sites and the oxide stoichiometry. Xenon is found to induce a large swelling of the UO_2 crystal in which it is however highly non soluble. As to helium, small solution energies (around 1 eV at the most) are obtained in UO_2, AmO_2, and PuO_2. Helium is thus found at the edge of solubility in all oxides considered.

N/P.14 FABRICATION PROCESS AND MATERIALS PROPERTIES OF FISSION PRODUCTS CONTAINING URANIUM NITRIDE FROM SIMULATED SPENT LWR FUEL

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The effects of fission product element in spent LWR fuel on the fabrication process of the nitride fuel by carbothermic reduction process were investigated in order to analyze the feasibility of dry re-fabrication process of spent nitride fuel. Simulated spent light water reactor fuel (SIMFUEL) was fabricated by adding various oxide surrogates such as Nd_2O_3, CeO_2, and ZrO_2 whose amounts are calculated by ORIGEN-2 code into balance uranium oxide powder. After sintering the mixture of oxides at temperature of 1700°C for 4 hr in a hydrogen gas stream, the sintered pellets of uranium oxide containing fission product elements as solute atoms and precipitates were pulverized by a thermochemical method through repeated oxidation and reduction processes. SIMFUEL powders were mixed with graphite powders and were compacted for a carbothermic reduction in a flowing nitrogen atmosphere. Thermogravimetric(TG) analysis showed that the conversion into nitride was retarded in the SIMFUEL powder compared with natural UO_2 powder. Under 1400°C each nitride shows similar weight gain due to phase transformation from a mononitride to a sesquinitride. X-ray diffraction exhibit a mononitride phase was formed when the atmosphere changed to Ar gas under 1400°C. Sintering of nitride powder from SIMFUEL at temperature of 1700°C for 10 hr in an Ar atmosphere resulted in a relative density of 80%. For the dry process re-fabrication of spent nitride fuel, various powdering methods including oxidation, nitriding and milling of sintered nitride pellet were compared with one another.

N/P.15 IMF WITH LOW MELTING POINT ZIRCONIUM BRAZING ALLOYS

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Various versions are suggested to improve IMF using low melting point zirconium brazing alloys. Alloys are incorporated into a fuel component. Upon heating they melt down and due to capillary properties they penetrate fuel particle joints and ensure metallurgical contact between both cladding and fuel component and between fuel components themselves. The brazing alloys developed at A.A. Bochvar Institute have melting temperatures of 690 to 860°C and are produced in the form of both granules and amorphous (metglass) strips. Zirconium brazing alloys used in IMF increase thermal conductivity and allow a high-quality bond to fuel cladding which will result in higher serviceability of fuels under transient conditions. Various versions are reviewed as applied to the feasibility of low melting point zirconium brazing alloys in IMF.

N/P.16 ZIRCONIA AND ZIRCONIA - SPINEL BASED CERAMIC COMPOSITES AS INERT MATRIX FUEL FOR LWRS

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Development of uranium free inert matrix incorporating plutonium for its rapid burning, without any further breeding, is being tried in many countries of the world. Zirconia and Zirconia-spinel ($MgAl_2O_4$) based ceramic – ceramic composites along with ThO_2 are considered as suitable candidate inert matrices. In our present study, two types of inert matrix fuel pellets of compositions, 85%ZrO_2 - 10%ThO_2 - 5%CeO_2 and 60%ZrO_2 - 10%ThO_2 - 5% CeO_2 25%$MgAl_2O_4$ were fabricated by conventional powder metallurgical route comprising of milling, compaction and sintering at 1923K in air. Ceria was used as simulator for plutonia. Sintered pellets were characterized by XRD for different phases. It was found that ZrO_2 forms fluorite type solid solution with ThO_2 and CeO_2 in case of pellets made from stabilized zirconia. Solid solution compositions were determined from lattice parameter measurements. Leaching tests of these pellets were carried out in water at 353K for seven days and it was observed that the leach rates of the elements in the pellets are much less than those of borosilicate glass (PNL 76-68). The present paper also highlights the results of thermal conductivities of the pellets from 800 to 1800K calculated from thermal diffusivity values measured by laser flash method.

N/P.17 SINTERING BEHAVIOUR AND PROPERTIES OF CARBIDES AND NITRIDES FOR THE INERT MATRIX BY SPARK PLASMA SINTERING

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Zirconium Carbide, titanium carbide, zirconium nitride and titanium nitride which is candidates for the matrix ceramic of IMF(inert matrix fuel) to transmute long-lived actinides were sintered using spark plasma sintering(SPS) technique. Pellets were fabricated by pressing of mechanically milled commercial powders of ZrC, TiC, ZrN and TiN. Sintering temperature, holding time and sintering pressure were optimized to obtain denser pellets in a short time at lower sintering temperature. Mechanical properties such as hardness and Young's modulus and thermal properties such as thermal conductivity were measured as a function of porosity and compared with those of conventionally sintered pellets.

N/P.18 STATUS OF ISTC PROJECT "MATINE -STUDY OF MINOR ACTINIDE TRANSMUTATION IN NITRIDES: MODELING AND MEASUREMENTS OF OUT-OF-PILE PROPERTIES

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Uranium free nitride fuels have been proposed to use for transmutation of Am and Cm in ADS with fast neutron spectrum. Presently several fuel types of this kind (IMF) are under investigation in the world. The programs cover study of different fabrication techniques, out-of-pile properties, modelling, irradiation tests and post-irradiation examinations. Today there are few data on properties and irradiation behaviour of uranium free nitride fuel. MA's bring additional problems (poor thermal properties, high volatility, helium production, chemical interaction, actinide migration). Hence the international collaboration in this field is very important.Beginning on May, 1 2004 the ISTC Project has started. The participating institutions are:IPPE, VNIINM, RIAR, KTH and CEA. The objective of the Project is to carry out comprehensive modeling of the performance of (Pu,Am,Cm,Zr)N (with ZrN=60%, Pu/Am/Cm=40/50/10) fuel under irradiation in fast neutron spectrum of ADS up to high burn-up in order to compare relative performance of helium, sodium and lead-bismuth bonded pins. Two different fuel forms (pellet and vibropacked) should be compared also. Compilation of data from existing nitride fuel investigations in- and outside of Russia and measurements of thermo-physical properties of (Pu,Zr)N laboratory samples, such as creep rates, thermal conductivity and high temperature stability, will be done in order to perform data file on (Pu,Am,Cm,Zr)N properties. Besides, assessment of the feasibility of fabricating nitride fuels containing up to 10 atomic percent of curium at RIAR site will be carried out, in order to define the possibility of future collaborative work. The main result of the project is identification of uranium-free nitride fuel types that would perform well under irradiation to high burn-up in a fast neutron spectrum of ADS.

N/P.19 EFFECT OF TEMPERATURE AND REDOX CONDITIONS ON PHASE COMPOSITION OF Gd-Mn-Ti OXIDE CERAMICS

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Ceramic samples based on (in molar %) gadolinium (8-20%), manganese (10-21%), and titanium oxides (60-72%) were synthesized by both cold pressing and sintering and melting in a resistive furnace at temperatures of 1400-1500°C under oxidizing and reducing conditions and examined by XRD, SEM/EDS, and TEM. In the most of the samples a fluorite-related cubic phase with seven-fold elementary fluorite unit cell whose structure is built from pyrochlore and murataite modules was found as major phase. Other phases with fluorite-derived structure found in the ceramics were pyrochlore (in the most of the samples) and phase with five-fold fluorite unit cell. The structure of the phase with seven-fold fluorite cell (7C) may be represented as a combination of two pyrochlore (two-fold fluorite unit cell - 2C) and one murataite (three-fold fluorite unit cell - 3C) modules (2C+3C+2C) and the phase with five-fold fluorite unit cell is formed by one pyrochlore and one murataite modules (2C+3C). Some samples also contained perovskite type phase. Increase of synthesis temperature results as a rule in pyrochlore phase stabilization. Oxidizing potential reduction increases filling up of six- and five-coordinated sites in the structure of the 7C-phase with Ti ions whereas Gd and Mn ions occupy eight-coordinated positions. The phases of the pyrochlore-murataite polysomatic series are capable to accommodate both actinides/rare earths and corrosion products (iron group elements) of HLW that makes them promising matrices for waste immobilization.

N/P.20 APPLIATION OF POLYSILOXANES IN NUCLEAR INDUSTRY

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The German policy prefers interim storage of all radioactive waste till a final repository will be found. The common procedure of radioactive waste treatment is the solidification by concrete. The most important problem of long-term storage is the corrosion of storage containers. The presence of concrete water significantly accelerates the container corrosion. Moreover, the handling and transport can lead to damaging of container walls and facilitate the metal corrosion. Most of the existing containers showing significant corrosion damages after some years. Therefore a need of advanced protective coatings for the storage containers exists.
Polysiloxan has good physical and chemical properties and seems to be adequate for storage of radioactive wastes. The aim of the present work is the application of Polysiloxan for the storage container. It can be used as an outer or inner coating for the purpose of mechanical and corrosion protection. Investigations were carried out at different polysiloxane types and supplied the results with regard to corrosion protection, mechanical properties, water vapour diffusion, radiation resistant and application techniques. The investigations showed that the simple spray techniques can be used for polysiloxane application, providing good protection against mechanical impacts. Due to its chemical structure, this material is hydrophobic and waterproof. But the water vapour diffusion was investigated and it is much higher than in other elastomer materials. It was confirmed in first experiments on basic materials showing unsufficient protection against corrosion. Investigations for improvement of rust protection by using different polysiloxan systems with pigment coatings are in progress

N/P.21 INFLUENCE OF OXIDATIVE AND RADIOLYTIC SPECIES ON LEACHING STABILITY OF (Th,U)O2 FUEL KERNELS

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Two HTR reactors operated in Germany have produced about 1 million spent fuel pebbles. The direct disposal of spent fuel in deep geological formations is considered as one of the most attractive methods to utilise the spent HTR fuel. In the accident scenario of water ingress intro repository the leaching stability of the ceramic fuel kernels will play an important role for long-term radionuclide retention. The radiolysis of aqueous phases, induced by high spent fuel activity, changes the nominally anoxic conditions in the final disposal vault and affects the stability of both the engineered barriers and the spent fuel.
In the present work the influence of external gamma-source and oxidative NO_3- and HNO_2 species on fuel kernels leaching behaviour was investigated. The experiments were performed with unirradiated reactor-grade UO_2 and mixed oxide $(Th_{0.906},U_{0.094})O_2$ and $(Th_{0.834},U_{0.166})O_2$ fuel kernels at 90°C under inert atmosphere. It was observed that the oxidative species have a baneful influence on the leaching stability of UO_2 fuel kernels. Changing the leachate from 5M HCl to 5M HNO_3 solution leads to about 4 orders of magnitude increase of UO_2 dissolution rate. Under the same conditions mixed oxide fuel kernels show no visible influence of medium change on their dissolution rate. The leaching experiments in deionised water under gamma-irradiation also testify the high leaching stability of $(Th,U)O_2$ solid solutions. Despite the acceleration of UO_2 dissolution of about two orders of magnitude the mixed oxide fuel kernels seem to be insensitive to the presence of radiolytic species in solution.

N/P.22 EFFECTS OF IRRADIATION ON THORIUM PHOSPHATE DIPHOSPHATE CERAMICS AND CONSEQUENCES ON THE DISSOLUTION.

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In the field of immobilization of actinides, the Thorium Phosphate Diphosphate must present a high resistance to self-irradiation. This phenomenon, which can modify the chemical and physical properties of this material (particularly its resistance to aqueous alteration), was simulated by external irradiations with several ion beams. Leaching tests were performed consecutively.

The amorphization of TPD was obtained under ion beams of several hundred MeV in energy which energy loss is mainly due to electronic interactions. Depending on the energy loss, the samples were either partly or fully amorphized which allowed the estimation of the threshold in dE/dx for total amorphization. For several MeV ion beams which nuclear contribution is not negligeable, complete amorphization was observed. The dissolution tests on irradiated material revealed a significant increase of the element release in the leachate for the fully amorphized solid, probably due to the increase of the specific area of irradiated materials.

N/P.23 MASS TRANSPORT IN THE PBI2 - I2 SYSTEM AND EFFECT OF GROWTH CONDITIONS ON THE STRUCTURAL PERFECTION OF PBI2 CRYSTALS

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PbI_2 single crystals have considerable potential for use in optical information recording systems, nonlinear optical devices, and X-ray and gamma detectors. The fabrication of devices from large melt-grown crystals in-volves mechanical and chemical treatments of the crystal surface, which may have a significant effect on the properties of the crystals and the engineering performance of the devices. For this reason, detailed studies of PbI_2 crystal growth from the vapour phase attract intense interest. Based on earlier results on the equilibrium vapour composition in the Pb-I_2 system, we analyze the vapour-phase growth of PbI_2 crystals in a closed system in the presence of excess iodine using a model of mass transport in a non-isothermal one-dimensional system of constant volume containing one or two vapour species. The model describes the main kinetic and equilibrium parameters of vapour-phase growth, with no allowance for gravity-driven convection. The derived equations provide a self-consistent solution to the problem of mass transport and pressure distribution in the system. Experimental results confirm that the rate of mass transport is governed by the source and deposition temperatures and iodine vapour pressure. The optimal conditions of PbI_2 crystal growth from the vapour phase are established. Data are presented on the morphology and structural perfection of PbI_2 crystals grown from the vapour phase in a closed system. By varying growth conditions, plate-like, ribbon, needle, twinned, and dendritic crystals were prepared, as well as combinations and intergrowths of these habits.

N/P.24 KINETICS OF IRON OXIDATION IN SILICATE GLASSES : IMPLICATION FOR NUCLEAR WASTE STORAGE

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The most adapted material for nuclear waste storage is borosilicate glass. The presence of multivalent elements, as iron, within the glass compositions can significantly affect physical properties of glasses. The redox reactions must be understood to control vitrification processes.

Many studies have been undertaken to characterize redox reactions in iron-rich silicates, especially for thermodynamic purposes. The few studies carried out on redox kinetics have exhibited two diffusion mechanisms: oxygen or divalent cations diffusion (Schreiber et al, 1986 ; Cook and Cooper, 2000). So a kinetic study is required in order to identify limiting mechanisms and to improve vitrification processes. Because XANES spectroscopy allows to derive redox state and structural information about iron (Galoisy et al, 2001), our goal was to follow the evolution of redox with time and temperature through XANES experiments. Many compositions (various alkaline rates) were studied at Fe-K edge on several temperature stages around Tg. Our results are in good agreement with previous studies (Wilke et al, 2001) or results from other methods. Significant redox changes around Tg suggest that rate-limiting factor is not oxygen diffusion (coupled to network relaxation) but diffusion of network modifying cations (Magnien et al, 2004). Alkalinee elements make redox reactions faster, especially in the case of lithium. To complete those conclusions, new experiments should be performed to show the effect of the rates of alumina or iron on redox kinetics.

N/P.25 RADIONUCLIDE RETENTION IN COMPACTED BENTONITE CONTACTING HIGH BURNUP SPENT FUEL

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Aim of this work is to study the processes, if spent fuel, which is effectively encapsulated by compacted bentonite comes in contact with groundwater. Special attention is directed on the retention behaviour of radionuclides within the compacted bentonite and the associated consequences due to groundwater interaction. In related experiments, both, the fuel slice and the compacted bentonite pellets were sealed in a reaction cell allowing groundwater access. Granite/bentonite groundwater was used for the immersion with reaction times up to 4.5 years. The results from radiochemical analysis of the groundwater have shown that the radionuclides were mobilized from the fuel interface, but retained at various extent. Thus, at final pH 8.6, Cs, Sr and U were encountered in solution at levels of $5x10^{-7}$, $3x10^{-8}$ and $4x10^{-8}$ M. However, concentrations of Am, Eu, Pu, Np, Tc below the detection limit indicate their strong retention within the compacted bentonite. These findings will be discussed in the context with preliminary results from the analysis of the solids.

N/P.26 IMMOBILIZATION OF TETRAVALENT ACTINIDES IN PHOSPHATE CERAMICS

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Three phosphate based ceramics were extensively studied for the immobilization of tri- and tetravalent actinides: britholite $Ca_9Nd_{1-x}An^{IV}_x(PO_4)_{5-x}(SiO_4)_{1+x}F_2$, monazite/brabantite $Ln^{III}_{1-2x}Ca_xAn^{IV}_xPO_4$ and Thorium Phosphate Diphosphate (□-TPD) $Th_{4-x}An^{IV}_x(PO_4)_4P_2O_7$. For each material, the incorporation of thorium or uranium (IV) was studied. This work was the early beginning of the incorporation of ^{239}Pu and/or ^{238}Pu in order to evaluate the effects of α-decay on the three crystallographic structures. In order to simulate the plutonium dioxide, we performed the incorporation of tetravalent cations from dioxides. Thus, the syntheses were carried out by dry chemistry methods, using mechanical grinding in order to improve the homogeneity (then the reactivity) of the initial mixture. The powders were heated at high temperature (1100 - 1400°C) then extensively characterized using several techniques (XRD, SEM, EPMA, XPS). For britholites, we showed that the thorium incorporation is complete for weight loading up to 20 wt%. The linear increase of the unit cell volume versus the thorium amount in the solid led to conclude to the preparation of solid solutions. The coupled substitution (Nd^{3+}, PO_4^{3-}) $\Leftrightarrow$ (Th^{4+}, SiO_4^{4-}) was necessary to prepare homogeneous and single phase samples. Due to redox problems, the incorporation of uranium is limited to 5 to 8 wt.% and always leads to a two-phase mixture of U-britholite and CaU_2O_{5+y}. Two ways of syntheses are now studied to minimise the presence of this secondary phase. For □-TPD and brabantite compounds, the syntheses involving the incorporation of thorium and uranium were improved by dry chemistry method using three cycles of mechanical grinding – calcinations. For both compounds, homogeneous solid solutions of □-TUPD and monazites/brabantites were obtained. For each matrix, dense pellets were prepared prior to the study of their chemical durability during leaching tests in closed an open system reactors. The leaching rates of brabantites and □-TUPD were found to be close to data reported in literature for natural monazite samples or □-TUPD (prepared by other way of syntheses). We also evidenced the formation of neoformed phases onto the surface of Th-britholite or U-britholite samples.

N/P.27 URANIUM DIOXIDE INTERACTION WITH GROUNDWATER – LEACHING BEHAVIOUR AND SORPTION TESTS

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The study of uranium dioxide behaviour in contact with groundwater is essential for assessment of long-term storage of spent nuclear fuel as well as for possibility of using of depleted uranium dioxide as engineered barrier in repository systems. In this study the leaching behaviour, solution/surface speciation and sorption of Np(IV) and Np(V) by different UO_2 samples were studied.

Samples of UO_2 used in the study were prepared at different temperatures in reductive media, e.g. 600, 700 and 800°C and were different in U(IV)/U(VI) ratio in surface oxidized layer as determined by XRD and XPS.

The leaching behaviour of samples was studied in 0.01 M $NaClO_4$ solutions and synthetic Yucca Mountain groundwater (J-13). It was established that solubility was governed by the presence of U(VI) in surface oxidized layer and was in the range of 10^{-7} – 10^{-5} M (pH= 4.5 – 7.5). For the same type of solution solubility increase corresponding to increasing of U(VI) concentration. Successive micro- and ultrafiltrations demonstrated that major part of uranium was found in true-soluble fraction while small fraction was found in colloidal fraction. The possible secondary phase formation was studied by XPS, TEM and SIMS.

The sorption of Np(IV) and Np(V) by these samples was studied as a function of pH in 0.01 M $NaClO_4$ solutions. It was established that sorption of Np(V) was proportional to the presence of U(VI). According to the redox speciation slow reduction of Np(V) to Np(IV) was observed upon interaction with the samples.

The dependence of Np(IV) sorption upon pH for all studied samples had a minimum at pH=5.5. According to the redox speciation this corresponds to the partial oxidation of Np(IV) to Np(V).

N/P.28 EUROPEAN LABORATORIES FOR ACTINIDE RESEARCH: THE ACTINET POOLED FACILITIES

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The aim of the European Network on Excellence ACTINET is to promote excellence in Actinide research within the European Community. In order to enhance the potentialities for research on radioactive material, European Actinide laboratories are networked and access for scientists is promoted and supported. Laboratories operated by CEA (France), ITU (Joint Research Centre, EU), INE-FZK (Germany), SCK-CEN (Belgium), IRC-FZR (Germany) and PSI (Switzerland) are coordinated within the ACTINET 'pooled facilities'. A broad variety of standard analytical and radioanalytical instrumentation, hot cell and glove box equipment thus becomes accessible for researchers in universities and national institutions interested in actinide research. Numerous state-of-the-art speciation and characterization techniques are offered for actinide research in the fields of (1) Chemistry and Physics of Actinides in solution and solid phases, (2) Chemistry of Actinides in the geological environment and (3) Chemistry and Physics of Actinide materials under/after irradiation. The ACTINET 'pooled facilities' are introduced in the present contribution and possible research activities are outlined.

N/P.29 MAJOR OUTCOMES OF THE FRENCH RESEARCH ON THE SPENT FUEL LONG-TERM EVOLUTION IN INTERIM DRY STORAGE AND DEEP GEOLOGICAL DISPOSAL

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The 1991 Nuclear Waste Management Act gave 15 years to the French research to study the various potential options for managing long-lived radioactive waste. Within this context, the Commissariat à l'Energie Atomique initiated the PRECCI research project in 1999 to investigate the long-term behaviour of spent nuclear fuel. This project is jointly supported by the French electricity utility EDF. Its primary objective was to produce the scientific and technical elements in order to address the operational questions of interim dry storage and deep geological disposal of spent fuel. Therefore, the studies focused on the behaviour of the spent nuclear fuel under the following boundary conditions:

*in a closed system which corresponds to the nominal scenario in storage and to the first confinement phase in disposal; it consisted in evaluating the effects of the residual temperature and high radioactivity on the chemical and physical properties of the spent fuel;

*in air which corresponds to an incidental loss of confinement during storage or to a rupture of the canister before the site re-saturation in geological disposal; oxidation kinetics of UO_2 and spent fuel were studied by coupling a microscopic approach with the macroscopic classical method;

*in water which corresponds to the nominal scenario after the breaching of the canister in repository; in this case, the effect of water α-radiolysis on the spent fuel matrix dissolution was particularly investigated. Some studies were also dedicated to the evolution of the irradiated cladding during interim long-term dry storage, due to creep and hydrides re-orientation during cooling under internal pressure.

This paper will give an overview of the major outcomes of the PRECCI project on these topics in view of the end of the 15 years research defined by the French law.

N/P.30 USE OF NON METALLIC MATERIALS IN A HIGH TEMPERATURE REACTOR

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High Temperature gas cooled Reactors (HTR) materials provide a high temperature heat source for electricity production and industrial applications (including hydrogen production). They have to be operated in a severe environment: materials are exposed to neutron irradiation, very high temperatures (up to 1000°C) in a potentially oxidizing medium. In some parts, a long operating period without maintenance and a long lifetime (several decades) is required. There are also drastic requirements on the level of some impurities in order to minimize the waste activation. Therefore there are large needs for material development.

Graphite and C-based composites are good candidates for such an application, particularly for components of the reactor core and internal structures. Nevertheless the use of non ductile materials and advanced materials with very little or no experience in nuclear reactors is a challenge and requires a precise and long selection and qualification process supported by a large testing program.

The specificities and problematic linked to the use of such materials in an HTR are described. The criteria for selection are defined together with the required experimental program.