

UCRL-TR-236142



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Foreign Trip Report MATGEN-IV Sep 24- Oct 26, 2007

M. Serrano de Caro

November 5, 2007

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

# Foreign Trip Report

Magdalena Serrano de Caro

Nuclear and Risk Science  
Atmospheric, Earth & Energy Division (AEED)  
Chemistry, Materials, Earth and Life Sciences Directorate  
Lawrence Livermore National Laboratory

LLNS  
Livermore, CA 94550

FTMS #200717022

Cargese, Corsica, France  
9/22-10/7/2007

Date of report: 10/25/07

Reviewed by: \_\_\_\_\_ Date: \_\_\_\_\_

Bill Halsey  
Group Leader, Nuclear and Risk Science  
Atmospheric, Earth & Energy Division  
Chemistry, Materials, Earth and Life Sciences Directorate

Submitted by: \_\_\_\_\_ Date: \_\_\_\_\_

Pat Berge  
Division Leader  
Atmospheric, Earth & Energy Division  
Chemistry, Materials, Earth and Life Sciences Directorate



Safeguards and Security Department  
Foreign Interactions Office  
7000 East Avenue, L-504  
Livermore, California 94551  
(925) 423-3583/Fax (925) 423-1032  
e-mail: fts@llnl.gov

---

## Foreign Travel Trip Report

**If trip report is classified, an active Mail Channel must exist before distribution.**

Name, Position, Org., Phone No: Magdalena Serrano de Caro, Research Scientist, Lawrence Livermore National Security, (925) 422 2169

Date of Trip Report: October 25, 2007

Dates of Travel: September 24, 2007

Name of Traveler(s): Magdalena Serrano de Caro

DOE Trip Number(s): 200717022

Funding Source\* (DOE/HQ Sponsor): NA-116 – Office of Institutional & Joint Programs

Destinations (Installation, City, and Country): Cargese, Corsica, France

Statement of Trip Purpose: Participate in MATGEN-IV school of Materials for Generation-IV Nuclear Reactors, September 24-October 6, 2007

List of Persons Contacted: V. Pontikis, D. Forse, V. Ghetta, D. Maziere, Dr. M. Inoue

List of Facilities Visited: Institut d'Etudes Scientifiques de Cargese, Cargese, Corsica, France

Abstract (i.e., major highlights, benefits of the travel, results of meetings): Gen-IV activities in France, Japan and US focus on the development of new structural materials for Gen-IV nuclear reactors. Oxide dispersion strengthened (ODS) F/M steels have raised considerable interest in nuclear applications. Promising collaborations can be established seeking fundamental knowledge of relevant Gen-IV ODS steel properties (see attached travel report on MATGEN- IV "Materials for Generation IV Nuclear Reactors"). Major highlights refer to results on future Ferritic/Martensitic steel cladding candidates (relevant to Gen-IV materials properties for LFR Materials Program) and on thermodynamic and mechanic behavior of metallic FeCr binary alloys, base matrix for future candidate steels (for the LLNL-LDRD project on Critical Issues on Materials for Gen-IV Reactors).

Statement of Activities: see attached Scientific Program



Safeguards and Security Department  
Foreign Interactions Office  
7000 East Avenue, L-504  
Livermore, California 94551  
(925) 423-3583/Fax (925) 423-1032  
e-mail: [fts@llnl.gov](mailto:fts@llnl.gov)

---

Recommendations About Follow Up Activities: At LLNL we can provide the modeling that gives fundamental understanding and predictive power for the complex behavior of the superposition of damage, H and He production when they occur simultaneously in F/M steels. We can further validate our modeling by performing ion beam irradiations at LLNL with 1 beam of both matrix 9FeCr-12FeCr and ODS samples. We contacted Dr. M. Inoue, Core and Structural Materials group leader of the FBR System Technology Development Unit in JAEA to obtain samples of their ODS steel fabricated for JAEA Sodium Cooled FBR Fuels.

We can also envisage an LLNL participation in CEA validation experiments JANNUS (Joint Accelerator for Nano Science and Numerical Simulation). Triple ion beam experiments (ions, He, and H) are starting in May 2008. These experiments will give immediate feedback in few weeks for doses up to 50 dpa (see attached document "Swelling in FeCr").

Description of Any Security Related Concern Which Occurred During Trip None  
(DO NOT INCLUDE ANYTHING CLASSIFIED):

\* Travel approved by Defense Programs (DP) and Nonproliferation (NN) no longer requires a Trip Report. However, Actual Cost report and trip summary must still be submitted through FTS within 20 days of the return date.

## MATGEN- IV “Materials for Generation IV Nuclear Reactors”

Cargese, France (Sep. 24 – Oct. 6, 2007)

M. Caro

October 10, 2007

- Coming back from a NATO School on Generation IV reactors, here is a summary of the significant effort and major interest on ODS for cladding applications.
- This document also reports on the contacts established to obtain ODS from different sources to start our own experimental program at LLNL.

### Introduction

The identification and development of the new structural materials is recognized as a technological challenge for Generation-IV nuclear reactors. Oxide dispersion strengthened ferritic-martensitic (F/M) steels (ODS) have raised considerable interest in nuclear applications. They provide irradiation swelling resistance and enhanced high-temperature strength. The high-temperature creep strength of these alloys is exceptional, i.e., at 650°C it can be three to four times larger than for the traditional F/M steel HT-9 [<http://nuclear.inl.gov/deliverables/docs/intg-matls-plan.pdf>].

This document describes specific Gen-IV activities in France, Japan and US where promising collaborations could be established seeking fundamental knowledge of relevant Gen-IV ODS steel properties.

### Gen-IV Activities in France

The French Atomic Energy Commission (CEA) is strongly involved in advancing nuclear energy technology to meet future energy needs. Jean Pierre Le-Roux, CEA Vice-Chairman, acknowledges the increasing role of Materials Science (analytical research and modeling) in predicting materials properties (metals, ceramics, and fuels). International cooperation is sought to achieve breakthroughs for the 21st century nuclear power systems. The cooperation focuses on enhancing R&D, and Gen-IV technology demonstrations. Databases of materials properties are compiled and will provide input to Multi-scale Modeling of Materials and Fuels. Also, progress is being made towards harmonized international standards (design rules, safety, non-proliferation).

R&D and technical challenges are linked to high temperature and radiation damage of core and structural material exposure for the foreseen 60-year lifetime, see table below:

Structural materials for Innovative Reactor Systems							
	SFR	GFR	LFR	VHTR	SCWR	MSR	Fusion
Coolant T (°C)	Liquid Na few bars	He, 70 bars 480-850	Lead alloys 550-800	He, 70 bars 600-1000	Water 280-550 24 MPa	Molten salt 500-720	He, 80 to 17L 300-480; Pb-480; 700
Core Structures	Wrapper F/M steels Cladding AFMA F/M ODS	Fuel & core structures SiCf-SiC composite	Target, Window Cladding F/M steels ODS	Core Graphite Control rods C/C SiC/SiC	Cladding & core structures Ni based Alloys & F/M steels	Core structure Graphite Hastelloy	First wall Blanket F/M steels ODS SiC <sub>2</sub> /SiC
Temp. °C	390-700	600-1200	350-480	600-1600	350-620	700-800	500-625
Dose	Cladding 200 dpa	60/90 dpa	Cladding ~100 dpa ADS/Target ~100 dpa	7/25 dpa			~ 100 dpa + 10 ppmHe/dpa + 45 ppmH/dpa
Other components		IHX or turbine Ni alloys		IHX or turbine Ni alloys			

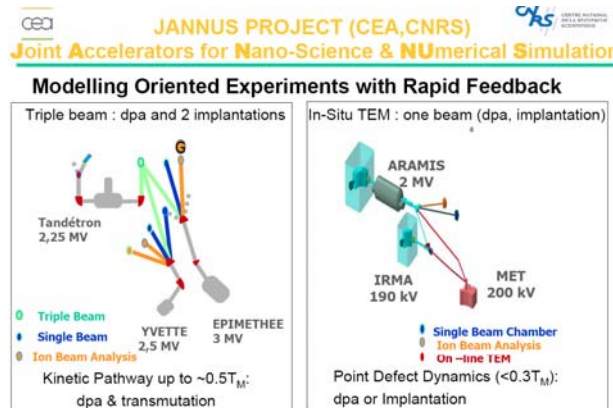
Gen-IV sodium fast reactors (SFR) have the highest priority in France. Recent progress was announced on SFR fuel cladding, i.e. a 2<sup>nd</sup> generation of ODS and ferritic-martensitic (F/M) steels with carbo/nitride precipitates that could allow increased fuel burn-up up (200 GWd/t) and higher dose rates (200 dpa).

Research is ongoing on 2 other Gen-IV systems: GFR and VHTR

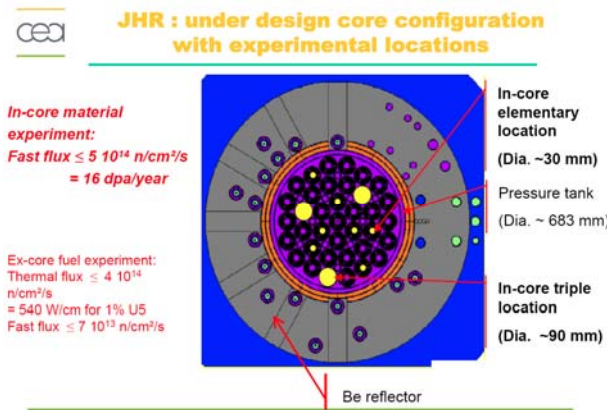
- The Gas Fast Reactor (GFR) is presented as an alternative to SFR. Candidate ceramic materials (CERMET, fiber strengthened and multi-layer materials) are manufactured and tested in Phenix. R&D areas focus on a new nanolaminate Ti<sub>3</sub>SiC<sub>2</sub> structure and in 2D SiC/SiC by NITE Process (Kyoto University) for GFR fuel pin of plate.
- Materials issues for VHTR are related to the Intermediate Heat Exchanger (IHx) materials (Ni-ODS) and technology (plate and tubular IHx concepts) and to C/C and SiCf/SiC composites (3D woven fibres, Hi-Nicalon) of the core with irradiation test performed at T~ 1050 °C and 1-6 dpa G.

### New Testing Facilities in France

We can envisage an LLNL participation in validation experiments (see FeCr model alloys A. Caro, C. C. Fu). Triple ion beam experiments (ions, He, and H) are starting in May 2008 in JANNUS (Joint Accelerator for Nano Science and Numerical Simulation). These experiments will give immediate feed-back in few weeks for doses up to 50 dpa. It is a very versatile (flux, dpa) facility oriented to modeling and parametric studies (point defects dynamics, long term kinetic pathways).



Materials Testing Reactor (MTR) experiments: The Jules Horowitz Reactor (JHR) to be built in Cadarache (France), will be dedicated to integrated experiments for fuel and materials qualification. Generation I & III: material ageing and fuel performance & safety and Generation IV: develop and qualify new materials and fuel. 5 years in typical neutron irradiations where time has to be allowed for preparation-irradiation-cooling-testing of the samples.

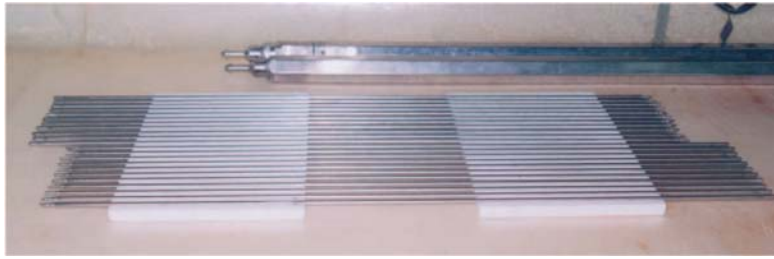


### Gen-IV Activities in Japan

We contacted the Core and Structural Materials group leader of the FBR System Technology Development Unit in JAEA, Dr. Masaki Inoue who presented the R&D progress of ODS steels fabrication for the Sodium Cooled Fast Breeder Reactor Fuels. Phase I of the Fast Reactor Cycle Development Program started in 2005 and will end in 2015 with a conceptual design of the commercial and demonstration fast reactor cycle facilities and their R&D programs.

ODS samples can be obtained using the appropriate license linked to the commercial patent. ODS manufacturing process is mastered. Anisotropy issues have been solved. These were due to grain boundary sliding at high temperature, which degraded the ODS creep rupture strength and loss of ductility in cladding tubes. ODS morphology control at the microstructure level is used to prevent  $\alpha/\gamma$  phase formation in 9Cr ODS and re-crystallization in 12Cr-ODS. Strength and ductility levels of ODS steel cladding tubes are adequately maintained under neutron irradiation up to 15 dpa at 800K.

A full scale demonstration of ODS fuel pins performance is carried-out in the 60 MW<sub>th</sub> fast reactor BOR-60 (Russia) for 2 kinds of clad fuel pins: 1) Vibro-packed fuel with 9Cr-ODS cladding material and MOX fuel with 12Cr-ODS cladding. The goal is to reach up to 15 GWd/t burn-up. Irradiations started in June 2003 with retrieval and analysis due after 5, 10 and 15 GWd/t. Note: Specifications of the fuel pin: 6.9 mm OD, 1050 mm length, 15 wt% Pu/(Pu+U) and 9 g/cm<sup>3</sup> smear density.



View of ODS cladding fuel pins irradiated in BOR-60 within the Japan Nuclear Cycle Development Institute (JNC)-State Scientific Center of the Russian Federation, Research Institute of Atomic Reactors (RIAR) collaboration.

#### **Gen-IV Activities in USA**

Oak Ridge could provide samples for LLNL ion beam irradiations. Collaboration with S. Zinkle could accelerate the definition of a local program for the development of materials for high fuel burn-up.

We contacted D. Kaoumi, a student of Arthur Motta, in the Department of Mechanical and Nuclear Engineering, Pennsylvania State University. Kaoumi performed ion beam irradiations (Fe+ 200 keV) of ODS steel samples. TEM microstructure after 12 dpa irradiation at 25 °C and 500 °C was investigated. Five ODS steels were tested: ODS-MA956 and ODS-MA957 samples provided by PNNL, ODS-DY and ODS-MA957 from CEA, and ODS M16 from JNC. Preliminary XRD analysis shows carbides and oxides precipitation for the latter and stability of oxides for all the ODS-MA. ODS-MA steels are known for their low swelling and embrittlement with exposure to high-energy neutrons ( $> 0.1$  MeV) up to  $10^{23}$  n/cm<sup>2</sup>. MA956 has best high-temperature strength and oxidation resistance. MA957 has similar properties, and although not produced commercially, could be fabricated on a special order.



## Swelling in FeCr

M. Caro

October 10, 2007

This document reports on two recent publications that show the complex behavior of the superposition of damage, H and He production when they occur simultaneously. Since the relation between dpa/H/He production depends on the neutron spectrum, these papers are relevant for the study of materials for LIFE and may help define an eventual experimental plan in house and in collaboration with JANNUS (France).

### Introduction

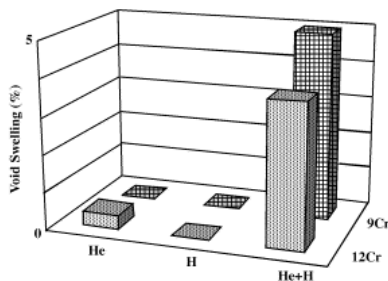
Two recent papers [1,2] investigate the synergistic effect of displacement damage, helium and hydrogen production on swelling of ferritic/martensitic steels.

### Ion Beam Irradiation of FeCr Model Alloys

In the first one, single, dual and triple ion-beams consisting of  $\text{Fe}^{3+}$ ,  $\text{He}^+$  and  $\text{H}^+$  were used for irradiation of Fe-9Cr and Fe-12Cr alloys to 50 dpa at 510 °C. The ion beam irradiations were carried out using TIARA facility in JAERI Takasaki. The accelerating voltages for  $\text{Fe}^{3+}$ ,  $\text{He}^+$  and  $\text{H}^+$  were 10.5, 1.05 MeV and 380 keV, respectively.

- 1) single ion ( $\text{Fe}^{3+}$ ) irradiation: good swelling resistance (0.5%) for both ferritic alloys.
- 2) dual ion ( $\text{Fe}^{3+} + \text{He}^+$ ) irradiation of the 12Cr alloy: swelling of about 0.4%.
- 3) dual ion ( $\text{Fe}^{3+} + \text{H}^+$ ) irradiation: No effect of the presence of  $\text{H}^+$
- 4) triple ion ( $\text{Fe}^{3+} + \text{He}^+ + \text{H}^+$ ) irradiation

The synergistic effect of He and H was shown clearly in the triple ion ( $\text{Fe}^{3+} + \text{He}^+ + \text{H}^+$ ) irradiation. The swelling was enhanced to almost 4% for the 12Cr alloy. The swelling was much higher in 9Cr than in 12Cr alloy.

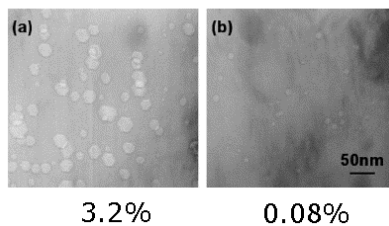


The authors conclude that this synergistic effect is a general phenomenon in ferritic steels, affecting Cr concentrations.

### Ion Beam Irradiations of F82H Ferritic/Martensitic Steel

This confirms a previous study carried out in 2002 [2], where the swelling of IEA-heat F82H (Fe-8Cr-2W-0.2V-0.04Ta-0.1C) steel irradiated with triple ( $\text{Fe}^{3+} + \text{He}^+ + \text{H}^+$ ) and dual ion ( $\text{Fe}^{3+} + \text{He}^+$ ) beams to a dose of 50 dpa at 470 °C was about 3.2% and 0.08%, respectively. Irradiations were performed in the same TIARA facility in JAERI Takasaki.

#### Swelling



The average swelling in F82H steel was significantly enhanced by the triple ion irradiation. Cavities formed in F82H steel irradiated at 470 °C to 50 dpa at the depth of around 1  $\mu\text{m}$  under (a) triple beams of  $\text{Fe}^{3+}$ ,  $\text{He}^+$  and  $\text{H}^+$  ions and (b) dual beams of  $\text{Fe}^{3+}$  and  $\text{He}^+$  ions.

### References

- [1] T. Tanaka, K. Oka, S. Ohnuki, S. Yamashita, T. Suda, S. Watanabe and E. Wakai, "Synergistic effect of helium and hydrogen for defect evolution under multi-ion irradiation of Fe-Cr ferritic alloys", JNM 329-333 (2004) 294-298.
- [2] E. Wakai, T. Sawai, K. Furuya, A. Naito, T. Aruga, K. Kikuchi, S. Yamashita, S. Ohnuki, S. Yamamoto, H. Naramoto and S. Jistukawa, "Effect of triple ion beams in ferritic/martensitic steel on swelling behavior", JNM 307-311(2002) 278-282.

## Scientific Program

"Materials for Gen-IV Nuclear Reactors"

September 24 - October 6, 2007

Cargese, Corsica, France

September 25

- The energy issue and the possible contribution of the various nuclear energy production scenarios (Prof. H. Nifenecker)
- Introduction to thermodynamics (Prof. G. Inden)
- Outlook on Generation IV Nuclear Systems and related materials R&D challenges (F. Carre)
- Introduction to neutronics (Dr. J-M. Cavedon)
- Neutrons and radiation damage in structural materials (Prof. J. Wallenius)

September 26

- Energy production scenarios: emphasis on safety, non-proliferation aspects and consequences on materials selection (Pr. H. Nifenecker)
- Kinetics of phase transformations in multi-component systems (Pr. G. Inden)
- Fundamentals of neutronics: reactivity coefficients of nuclear reactors (Dr. P. Reuss)
- A First-Principles Approach to Designing Materials (Dr. A. Pasturel)
- RT-1: Safe, reliable, robust and non-proliferant generation IV systems

September 27

- Fracture mechanisms (Prof. R. Odette)
- Fracture mechanisms and scaling properties of fracture surfaces (Dr. E. Bouchaud)
- Particle/matter interaction in the keV-MeV range (Dr. E. Balanzat)
- Multiscale computer simulations for the study of radiation effects in materials (Dr. P. Geysersmans)
- Correlation between electronic structure, magnetism and physical properties of Fe-Cr alloys: ab-initio modelling (Prof. I. Abrikosov)
- Equilibrium phase diagrams (Prof. G. Inden, Dr. M.-N. de Noirefontaine)

September 28

- Crystal plasticity from Dislocation Dynamics (Dr. V. Bulatov)
- Microstructural and mechanical properties of irradiated structural materials (Dr. S.J. Zinkle)
- Radiation-induced solute segregation and precipitation in alloys (Dr. A. Ardell)
- Parametric dislocation dynamics and boundary element modeling of elastic interaction between dislocations and precipitates (Dr. A. Takahashi)

Poster Session I

September 29

- Multiscale computer simulations and predictive modeling of RPV embrittlement (Dr. N. Soneda)
- Kinetic Monte Carlo simulations of radiation damage in structural materials (Dr. P. Olsson)
- The Computational Modeling of Alloys at the Atomic Scale: From Ab Initio and Thermodynamics to Radiation-Induced Heterogeneous Precipitation (Dr. A. Caro)
- Presentation of the toughness module from the Perfect project (Dr. S. Bugat)
- Electronic structure calculations in iron with defects and/or gases (Dr. C.C. Fu, Dr. G. Lucas)

October 01

- Particle/matter interaction in the keV-MeV range (Dr. E. Balanzat)
- SiC as a material for application in generation IV systems: electronic, structural and mechanical properties. (Prof. P. Pirouz)
- Oxidation of SiC/SiC composites in low oxidising and high temperature environment (Dr. C. Cabet)
- Neutron damage in structural ceramics (Dr. L. Snead)
- Ab-initio calculation of defect properties in SiC
- October 02
- Fundamentals of liquids, part I (Prof. JP. Hansen)
- Fundamentals of Interfaces (Pr. P. Wynblatt)
- Wetting (Dr. D. Chatain, Dr. V. Ghetta)
- Accurate measurements of thermal conductivity, surface tension and structural properties of liquid metals (Pr. G. Pottlacher)

October 03

- Fundamentals of liquids, part II (Prof. J. P. Hansen)
- Wetting (Dr. D. Chatain & Dr. V. Ghetta)
- Liquid sensors: principles and measurements (Prof. J. Fouletier, Dr. V. Ghetta)
- Influence of Liquid Sodium on mechanical properties of steels, refractory alloys and ceramics: Corrosion and Reactions with Impurities Dissolved in Sodium (Dr. H.U. Borgstedt)
- Chemistry control in large installations: feedback from Phenix, Superphenix and other Liquid Metal Fast Breeder Reactors at the experimental or "approaching industrial" levels in the world. (Dr. C. Latge)
- Liquid metal embrittlement (Dr. Ghetta, Dr. D. Gorse, Dr. V. Pontikis)

Poster Session II

October 04

- Influence of Liquid Sodium on mechanical properties of steels, refractory alloys and ceramics: Creep Rupture and Low Cycle Fatigue of Reactor Materials in Liquid Sodium (Dr. H.U. Borgstedt)
- Research and Development of Oxide Dispersion Strengthened Ferritic Steels for Sodium Cooled Fast Breeder Reactor Fuels (Dr. M. Inoue)
- Structural Materials for Fusion Power Plants (Dr. J.L. Boutard)
- RT-2: Materials issues for generation IV systems.

October 05

- Introduction to the physics of molten salt reactors (Dr. E. Merle)
- Physical and chemical properties of molten salts (Prof. J.C. Poignet)
- Combined effect of molten fluoride salt and irradiation on Ni-based alloys (Prof. A.S. Bakai)
- Specific features of particule/matter interaction for accelerator-driven subcritical reactors, part I (Dr. S. Leray)
- Liquid sensors: application to heavy liquid metals. (Prof. J. Fouletier)

October 06

- Specific features of particule/matter interaction for accelerator-driven subcritical reactors, part II (Dr. S. Leray)
- Operation of high power liquid metal spallation targets: a challenge for the structural materials (Dr. J. Henry)