Ten years of high temperature materials research at PSI
- an overview paper

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Abstract – At the Paul Scherrer Institute high temperature materials research for advanced nuclear systems is performed since a decade, formerly by the HT-Mat group and today the advanced nuclear materials (ANM) group. In this paper the activities being conducted in this time are summarized. This includes the study of three major materials classes, intermetallics with a titanium aluminide, nanostructured steel with different ODS candidates, and ceramics with silicon carbide composites. The studies being performed include experimental work, studying the mechanical behavior as function of irradiation exposure and temperature, including also in situ studies such as the creep under ion beam irradiation plus miniaturized samples such as pillars. The microstructure changes as function of these exposures, using electron microscopy on one hand and advanced beamline techniques on the other hand. Part of the finding lead to the development of new damage mechanism models. Complementary to the experimental approach, modelling activities were conducted to understand the basics of the damage mechanisms. The research lead to a consolidation of the candidate materials to the most promising ones, namely the oxide dispersion strengthened steels (ODS) and the silicon carbide based composite materials. The research lead to new, relevant data such as the creep behavior of material under extreme reactor conditions, the embitterment mechanism in advanced materials, and much more. A sketch of the research philosophy and an outline of the main results will be given.

I. INTRODUCTION

The HT-Mat project at the Paul Scherrer Institute concentrated on the research of high temperature materials for Generation IV reactors, mainly the gas cooled (very) high temperature reactor (V)HTR and also the other gas cooled concept the gas cooled fast reactor (GFR). Today the HT-Mat has become the ANM which stands for advanced nuclear materials, indicating the more general scope for all GenIV systems and also for subcritical reactors (ADS) and materials for spallation sources. The original philosophy of the HTMat project is the development of lifetime assessment methods and to identify materials candidates for long term, high temperature applications under irradiation. The three materials classes being selected as good candidates for this purpose and to develop the lifetime assessment are the oxide dispersion strengthened (ODS) steels, the intermetallic titanium aluminides (TiAl) and ceramic materials. The motivation for the ODS and TiAl materials is their very high creep resistance for metallic materials, see for this the Larson Miller plot in Fig. 1. As ceramic material SiC was selected because of its excellent high temperature properties and the known tolerance to radiation. As new materials should be qualified for application in nuclear system, on one hand under extreme condition such as temperature, radiation exposure, corrosion, and on the other hand for very long times such as 60 years, the development of an advanced lifetime assessment was regarded as essential. For this purpose it was decided to build up a modelling team addressing the different levels in a multi scale...
approach, and on the other hand a team tackling advanced analytical methods to address essential material degradation effects and partially to validate modelling results. For this purpose a further material class was selected for experimental research, so called model alloys, simple enough to meet the limited complexity of modelling, and to address some irradiation effects in well defined systems. As basis for ferritic ODS steels highly pure Fe-Cr systems are taken as model alloys. A good overview of nuclear materials in general, also presenting many approaches and findings of the HT-mat group, can be found in a book of the former project leader, Wolfgang Hoffelner [1].

II. BASICS OF ADVANCED LIFETIME ASSESMENT

The GenIV systems are very demanding for structures, requesting an outreach to advanced materials. New promising candidates exist, as for example dispersion strengthened steels. It is however challenging to proof the long term performance, as data is missing and cannot be created in appropriate time. Therefore lifetime assessment methods must be developed to qualify the materials for their application. Accelerated aging methods bear the risk that some degradation processes could possibly not develop in the short time and become effective in the real aging. Therefore classical lifetime prediction methods must be extended by advanced analysis and computational approaches leading to an early identification of degradation kernels and basic understanding of such potential life limiting degradation processes. The HT-Mat project addressed this challenge by experimental techniques such as Beamline analysis, mechanical testing in-situ under irradiation and temperature exposure, miniaturized testing of pristine and pre-irradiated material. On the modelling and model validation side a multi scale approach was taken, ranging from ab initio to the continuum (see Fig. 2). During this time ab initio to dislocation dynamics was implemented modelling wise. Experimentally all scales were addressed. Fig. 3 shows examples of effects which can be addressed by the different scales of modelling, and which are covered by different experimental techniques.
different experimental methods being addressed, and the right column shows the correspondence in the modelling scale. According to [3].

III. EXAMPLES OF IMPLEMENTATIONS

This sections presents some examples of implementations of advanced analysis techniques and of modelling and validation.

III.A. Micro-Pillar testing

Irradiation effects on advanced nuclear materials are the main topic being researched in the HT-Mat project. The radiation can be induced in different ways; the most obvious one is the reality near irradiation in nuclear test reactors. This approach has however the disadvantage that the radiation exposure is very expensive and the samples are activated and need special precautions in order to be tested, furthermore systematic studies are difficult, as the sample extraction is not always difficult, and might be bound to operation cycles. Another very common approach is the simulation of neutron exposure by using ion irradiations. Here different approaches exist. Either one can introduce high displacement damage (displacement per atom, dpa) by using heavy ions, or one can additionally introduce He and/or H, which would normally form due to nuclear reactions, by irradiating with He ions and/or protons. In order to reach the most appropriate ratio of all effects, one can also do dual or triple irradiation, using heavy ions, He ions and protons. Recommendations of simulating neutron damage by using ions can be found under [4]. When it comes to mechanical properties of irradiated material, the major challenge is the very limited irradiated volume, being typically a few micrometers thick surface layer. If the change in hardness is of interest, a good approach is nano-indentation, as shallow penetrations depths can easily be analyzed. For yield strength nano-indentation is a less effective method, however, one possible technique for extracting a stress-strain curve using nano-indentation is described in [5]. An uniaxial test is much more suitable for yield strength information. A possible way to do uniaxial testing on such a shallow layer is to compress nano/micro pillars. These are prepared by a focused ion beam (FIB) and the compression is performed with a flat punch on a nano indenter. Typical pillar diameters are around 1 µm, with this dimensions size effects can appear. To clarify this point, numerous tests were performed on ODS steels. For these it was found that size effects could be neglected. A possible explanation is the dispersoids, being present in a very high density, with typical distances being much lower than the pillar dimensions. Figure 4 shows a comparison between dog-bone and pillar testing for PM2000 [6], a former commercial ODS from Plansee. In Fig. 5 the same material is tested before and after irradiation. The pillar height corresponds to the Implantation depth, which was 2.7 µm being irradiated with He ions at energies from 750 keV to 1.5 MeV.

Fig. 4: Dog bone and pillar testing of PM2000, a former commercial. Stress-strain curved in the upper part and pillars before and after compression.

Fig. 5: Dog bone testing of pristine PM2000 and after irradiation [7]. Because of the ease of ion beam irradiations and the possibility to very well control the exposure
parameters, the pillar technique allows doing systematic studies on the mechanical properties changes. Furthermore the pillars can be dimensioned and places in a way that only single grains are addressed, excluding the influence of grain boundaries. Both allow the identification of basic effects and to directly compare with the microstructure characterized by electron microscopy. The fact that single grains can be extracted and also the grain orientation can be determined. This allows finding the critical resolved shear stress (CRSS), a basic matrix property which can directly validate results from dislocation dynamics. Figure 6 shows a DD simulation in a field of dispersoids representing the one of PM 2000. The resulting shear stress with different probabilities according to the size probability is represented in the blue bars. Figure 7 shows an experimental example of pillars being characterized for their CRSS being directly used as input for DD.

Miniaturized sample testing therefore presents a good way of bridging mechanical testing with microstructure and with modelling. It is possible to extract and isolate features, allowing special studies. This is on one hand the single grain in a normally polycrystalline material, but can also be special locations in welds, corroded regions or any other location being of interest. A further aspect of miniaturized samples and/or testing could be condition based monitoring. Here the idea is to minimize the tested volume in such a way, that even being attached to an operational component, its extraction or testing would be negligible and not compromise its functionality [8].

Creep is an important degradation mechanism of structural materials in general, and especially of structures in nuclear reactors. Normally creep is a temperature driven process, however in nuclear reactors it can also be driven by radiation. A major argument for all classes of materials investigated in this project is their creep resistance at high temperatures, opening new operational temperatures. How do the features, as the dispersoids in ODS steel, or the second phase structure in intermetallics behave under irradiation. Even the high temperature creep resistance of ceramics must be revisited for irradiation creep. To answer all these questions, in-situ creep experiments are essential. In the HT mat group such a creep device, where the sample is exposed to an ion beam, is operational (see Fig. 8). Fig. 10 shows the irradiation creep compliance as a function of the inverse temperature. The two ODS classes show very similar behavior, even thought the ODS 19 Cr from Kyoto university has dispersoid sizes in the range of 2-4 nm, and the commercial PM 2000 has dispersoids which are about 20 nm. The smaller dispersoid size of the first one promise much better creep behavior at high temperatures, the higher density of oxide particles offers more pinning points for dislocations. This effect is confirmed experimentally; however, when it comes to irradiation creep, the higher density seems not to be effective anymore. This is an important finding, which could only be identified by in-situ experiments. Together with electron microscopy a deeper understanding of the irradiation creep can be
developed. This way another feature of the dispersoids was found, their acting as sinks for helium. And here the finer oxide particle distribution of the advanced ODS becomes advantageous. As the mean free path to the next matrix-oxide interface is much smaller, than in the commercial ODS, and the interface surface is more important, more helium can diffuse to the dispersoids, mitigating helium embrittlement in the matrix.

Irradiation creep results for other candidate materials, such as TiAl can be found in [11]. Generally in can be said, that the irradiation creep experiments are very successful. They will lead to an important input for the lifetime assessment, especially of components which are exposed to high irradiation doses.

III.C. Modelling and model validation

A good example how multiscale modeling was employed in the HT Mat group is given in [14]. As already mentioned in the last section, helium plays an important role in the modification of mechanical behavior due to irradiation. Similar to the dispersoids in the ODS steels, helium bubbles can act as pinning points for dislocations, leading to an important hardening and embitterment of the material. The reference [15] shows a concrete implementation how experimental work could act as input for modeling. In this case bubble size densities as input for dislocation dynamics. Figure 9 shows a concrete determination of helium bubble size distribution in PM 2000, based on a TEM micrograph. Based on this data DD simulation was performed, calculating the pinning force of the helium bubble field, resulting in an increased CRSS. In the lower part of Fig. 9 the bubble density depending CRSS is expressed, starting from the matrix value at zero density.

![Fig. 8: In-situ creep station, with a degrader wheel, allowing an even ion beam irradiation throughout the sample.](image)

![Fig. 10: Irradiation creep compliance as a function of the inverse temperature for PM 2000 [6] and ODS 19 Cr [12] according to [13].](image)

![Fig. 9: Helium bubble distribution being experimentally derived. TEM micrograph in the upper part with the corresponding distribution. In the lower part a dislocation being trapped by a helium bubble according to DD simulation with the CRSS being calculated due to the bubble size distribution. According to [15] and [14].](image)
Iron-chromium is the base alloy of many ODS materials being of interest in the project. Therefore many physical properties of these simplified alloys were identified, characterized and analyzed towards their influence in damage creation and evolution. The iron-chromium system shows an interesting magnetic behavior up to 10 at% Cr. The reason is a frustration of the ferromagnetic behavior of pure iron, and the antiferromagnetic behavior of chromium. As a consequence the mixing enthalpy in this regime is not completely known, which enters directly as parameter into modeling. As a contribution to the clarification of this incertitude, it was decided to study the magnetic structure as a function of the iron content. On way of directly depicting the magnetic domains is photo emission electron microscopy (PEEM) coupled with X-ray magnetic circular dichroism (XMCD). Figure 11 shows the magnetic domains at the sample surface of two Fe-Cr alloys with 6.2 and 12.7 at% Cr.

![Figure 11: XMCD-PEEM micrographs of Fe-Cr alloys with 6.2 at% Cr on the left, and 12.7% Cr on the right. The lateral dimensions are in µm. Taken from [16].](image)

IV. CONCLUSIONS

The HT-mat project showed in an impressive way that advanced testing and analysis techniques, coupled with modeling and validation, can help to importantly improve the understanding of mechanisms in materials degradation. The initial materials selection turned out to be well tuned. With the three very different materials classes, the advanced steels, the intermetallics and the ceramics, many of the effects could be studied in all the systems, and by choosing only one representative from each class, ODS, TiAl and SiC, without loosing the focus. After the initial phase, and with accomplishing a thesis on TiAl [17], it was decided to further concentrate in the two other candidates. The concrete version of TiAl, which was ABB2, turned out to suffer important irradiation embrittlement. The reason for that was the laminar, needle like structure of the second phase, which leads to important helium embrittlement. One of the conclusions drawn from these studies was that with a globular structure a much better embrittlement resistance could be achieved. Here the argument was the same as for the ODS steels, where fine dispersoids offer a large interface surface, acting as helium sink. ODS and ceramics have been conducted to be still very valuable candidates, and studies are continuing, aiming for a deep understanding of selected processes, possibly contributing to a lifetime prediction for the application in Gen IV reactors.

V. ACRONYMS

CRSS: Critical resolves shear stress acronyms
DD: Dislocation dynamics
FIB: Focused ion beam
MD: Molecular dynamics
ODS: Oxide dispersion strengthened
PEEM: Photo emission electron microscopy
XMCD: X-ray magnetic circular dichroism

REFERENCES


