High temperature materials – The challenge for future advanced gas cooled reactors

W. Hoffelner

Department of Nuclear Energy and Safety, Paul Scherrer Institute
Wuerenlingen, Switzerland

Abstract. Advanced gas cooled reactor systems for future combined cycle applications (electricity and process heat) are planned to operate at temperatures up to or even above 1000 °C. The reliable and safe operation of such plants requires materials that are able to carry loads at these temperatures in impure helium and under neutron irradiation. The most exposed components are the pressure vessel, reactor internals, gas turbine, pipes and valves. Considering the envisaged long operating time (6 years for replaceable components) life time assessments and extrapolation methods are necessary for the determination of damage evolution and long term behaviour of the reactor components. This paper gives a summary of candidate materials and possible approaches to life-time assessment. The paper concentrates mainly on very high temperature reactors (VHTR), some material aspects of gas cooled fast reactors (GFR) are considered, too.

1. Introduction

There is an increasing interest in gas cooled reactors as a basis for future advanced energy systems. Such concepts are therefore being investigated in several arenas including the worldwide Generation IV (GIF) initiative [1], European Community projects [2] and national R&D projects. The aim of advanced reactor systems is to provide heat for direct energy conversion using a high temperature turbine and also to provide process heat (e.g. for use in hydrogen production) in a combined cycle process. Current high temperature reactor (HTR) designs operate at gas temperatures of up to 850 °C. Gas temperatures for the next generation (deployable by 2017) are expected to be higher than 950 °C and temperatures in excess of 1000 °C are expected for future advanced VHTR’s gas reactors. These temperature increases are due to the expected higher net plant efficiency (for a recuperated Brayton Cycle) as well as the expected higher efficiency of hydrogen production [3,4]. Gas temperatures for a gas-cooled fast reactor (GFR) are lower (850 °C), but fast temperature excursions (up to 1600 °C) can occur in case of loss of coolant event.

To design safe reactor plants, materials are required that are able to withstand extreme service exposures (temperatures, neutron spectra, creep) over a time period of at least 6 years (replaceable parts). The main parts of an advanced combined cycle nuclear plant based on a gas cooled reactor are: reactor pressure vessel, reactor internals (including control rods), piping, helium gas turbine, intermediate heat exchanger, high temperature process equipment (hydrogen plant). The current state of the art materials for these applications will be summarized and potential materials for the near term deployment and for gas temperatures exceeding 1000 °C will be discussed. The question regarding the choice of reactor materials remains the same regardless of whether the pebble bed or prismatic reactor design is considered.

2. Candidate materials

A summary of the materials for HTR-designs at different gas temperatures is given in Table 1. Similarities in materials for VHTR and GFR application are shown in Table 2. Aspects of the different components will be discussed in the next sections.
2.1. Pressure vessel

The pressure vessel of a HTR must be made of steel that can withstand stresses for temperatures up to 400 °C in current designs and up to 500 °C in the currently considered future designs [5]. At these temperatures the stresses upon the pressure vessel can lead to creep and/or relaxation. However, to design a pressure vessel with creep taken into account would require a lot of additional design data and curves (including creep strain data, multiaxiality and creep, creep of welds, notch sensitivity etc.) as well as procedures for surveillance under creep conditions. The avoidance of creep needs design measures and highly creep resistant materials. Currently at the laboratory for material behaviour (LWV) in PSI, steels for the reactor pressure vessel (RPV) can be used for temperatures up to 350 °C [6]. The classes of ferritic (NiCr)MoV- steels and the more creep resistant 9-12% martensitic chromium steels are very well established creep resistant materials for a temperature regime of 400 to 550 °C. They have been used in chemical plants, in boilers, in steam- and gas turbines and in jet engines. Temperature extensions to 600 °C have been tried for different applications (e.g. large steam turbine rotor forgings). A summary of these developments is given in [7]. As a result of its low activation and its high thermal conductivity this class of steels is also very interesting for fusion applications [8]. The development has now reached a stage where no significant improvements are expected by changing the chemical composition. Only a change of the matrix (from ferritic martensitic to austenitic) or reinforcements of the martensitic matrix (e.g. oxide dispersion, Fig. 1) could lead to significant improvement of creep properties. Due to the difficulties in producing large components, reliable welds and in non destructive testing it can be stated that according to current knowledge these materials cannot be used as reactor pressure vessels.

TABLE 1. SUMMARY OF POSSIBLE MATERIALS FOR (V)HTRS. THE TEMPERATURES INDICATE THE REACTOR GAS OUTLET TEMPERATURE (DS DIRECTIONALLY SOLIDIFIED, SC SINGLE CRYSTAL, ODS OXIDE DISPERSION STRENGTHENED, TBC THERMAL BARRIER COATING, IHX INTERMEDIATE HEAT EXCHANGER, LWR LIGHT WATER REACTOR, RPV REACTOR PRESSURE VESSEL

<table>
<thead>
<tr>
<th>Component</th>
<th>T&lt;850 °C</th>
<th>850 °C &lt;T&lt; 950 °C</th>
<th>T&gt; 950 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Pressure Vessel</td>
<td>LWR-RPV</td>
<td>2 1/4 Cr 1 Mo (ferritic)</td>
<td>9-12 % Cr steel (martensitic)</td>
</tr>
<tr>
<td>Control Rod</td>
<td>Ni-base superalloy</td>
<td>Ni base superalloy, SiC/C, SiC/SiC</td>
<td>SiC/C, SiC/SiC</td>
</tr>
<tr>
<td>Graphite, ceramic internals</td>
<td>Graphite</td>
<td>Graphite (new grades), SiC/C or SiC/SiC structural parts</td>
<td>Graphite (new grades), SiC/SiC structures, (superplastic) ceramics</td>
</tr>
<tr>
<td>Metallic internals</td>
<td>Steels</td>
<td>Steels, Ni-base superalloys, ODS</td>
<td>Steels, Ni-base superalloys, intermetallics, ODS</td>
</tr>
<tr>
<td>Piping/IHX/valves</td>
<td>Ni-base superalloys</td>
<td>Advanced Ni-base superalloys (eventually with TBC-coatings)</td>
<td>Advanced Ni-base superalloys with TBC-coatings, cooled designs, ceramics, intermetallics, composite structures</td>
</tr>
<tr>
<td>He-Gas Turbine: Blades/Vanes</td>
<td>Ni-base superalloys (gamma-prime γ’ hardening)</td>
<td>Ni-base superalloys (DS, SC)</td>
<td>Ni-base superalloys (DS, SC), cooled designs, ODS, intermetallics, refractory alloys, composites</td>
</tr>
<tr>
<td>Rotor</td>
<td>Ferritic-martensitic steels (cooled designs)</td>
<td>Ferritic-martensitic steels (cooled designs), Ni-base superalloys (γ’ -hardening)</td>
<td>Ni-base superalloys (γ’-hardening),advanced production technology, (cooled) composites</td>
</tr>
</tbody>
</table>
TABLE 2. COMPARISON OF MATERIAL SIMILARITIES BETWEEN VHTR AND GFR

<table>
<thead>
<tr>
<th>CONDITIONS</th>
<th>VHTR</th>
<th>GFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutrons</td>
<td>Thermal</td>
<td>fast</td>
</tr>
<tr>
<td>Max. temperature</td>
<td>&gt; 900 °C</td>
<td>Max. 850 °C</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>&lt; 490 °C</td>
<td>490 °C</td>
</tr>
<tr>
<td>Loss of coolant</td>
<td>Up to 1200 °C</td>
<td>Up to 1600 °C in 100 sec</td>
</tr>
</tbody>
</table>

COMPONENTS:

<table>
<thead>
<tr>
<th>Reactor pressure</th>
<th>VHTR</th>
<th>GFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel</td>
<td>9-12% Cr</td>
<td>2 1/4 Cr 1Mo, 9-12 % Cr</td>
</tr>
</tbody>
</table>

Internals:

<table>
<thead>
<tr>
<th></th>
<th>VHTR</th>
<th>GFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflector</td>
<td>-</td>
<td>ZrₓSiy (Intermetallic)</td>
</tr>
<tr>
<td>Claddings</td>
<td>-</td>
<td>ODS, SiC/SiC, MMC</td>
</tr>
<tr>
<td>Internals (structural)</td>
<td>C, SiC/SiC</td>
<td>Ceramics, Composites, Refractory alloys</td>
</tr>
</tbody>
</table>

Turbine:

<table>
<thead>
<tr>
<th></th>
<th>VHTR</th>
<th>GFR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blades</td>
<td>DS, SX</td>
<td>Equiaxed cast (IN-738, IN-792)</td>
</tr>
<tr>
<td></td>
<td>Intermetallics, Ceramics</td>
<td></td>
</tr>
<tr>
<td>Rotor</td>
<td>Ni-base</td>
<td>Ni-base</td>
</tr>
<tr>
<td>Pipings etc.</td>
<td>IN-617, HA-230</td>
<td>IN-800H</td>
</tr>
</tbody>
</table>

The choice of material for a VHTR depends on the design of the vessel and the design rules. There are claims that a 2 1/4 Cr 1 Mo-steel would be sufficient but the majority of researchers propose an advanced steel of the 9-12 % Cr-class. It should however be noted that use of 9-12% martensitic chromium steels for RPVs represent a significant challenge for complete through-section heat treatment, fabrication, welding and post weld heat treatment. It should also be noted that 9-12% martensitic chromium steels are not currently included in the ASME Boiler and Pressure Vessel Code but there are plans to include 9Cr-1Mo (T91) steel in future revisions.

2.2. Reactor internals

The reactor internals of a current HTR mainly consist of a graphite core, control rods (superalloy Hastelloy XR) and steel support structures.

A fundamental problem of graphite in nuclear reactor cores is the deterioration of mechanical and other properties as a result of the neutron irradiation. The primary source of degradation is the stresses that develop during irradiation [9]. Graphite will remain the core part of VHTR’s and therefore the irradiation behaviour of different graphite properties is to be investigated in different international research projects, e.g. [10]. It also might be worth considering designs in which bricks or core parts are replaced by composite structures filled with graphite for use as a moderator. The advantage of composite structures is that their structural integrity is maintained even when locally cracked. This is the reason why black composite ceramics (C/C, SiC/C and SiC/SiC) are currently being investigated as future materials for smaller structural parts and liners. A possible near term application for black ceramic compounds is as components of the control rod [1,6]. Different properties of C- and SiC-type materials are therefore currently being investigated (e.g. Fig. 2).
FIG. 1. Microstructure of a ferritic ODS alloy (TEM micrograph) ODS = oxide dispersion strengthened alloys.

SiC/C ceramic matrix composite for VHTR application

FIG. 2. Microstructure and results of punch test in different orientation of a SiC/C fibre reinforced ceramic.
In case of higher gas outlet temperatures, the gas inlet temperatures will go up and so the temperature level in the reactor will also increase. As well as the core, possible materials for support structures, boltings and fixtures must also be able to accommodate higher temperatures. Oxide dispersion strengthened (ODS) materials, intermetallic phases and (superplastic) ceramics are considered as possible candidates. Intermetallic phases are ordered structures (e.g. TiAl, NiAl, Fe₃Al, MoSi₂, Si₃N₄, etc.). A level of high energy is needed for the movement of dislocations in ordered structures, which leads to a high yield strength (and low toughness) up to high temperatures. Titanium aluminides and nickel aluminides are already in use today for conventional structural applications [11]. Other intermetallics are still in the development phase. Research for the reinforcement of intermetallics in terms of fibers or dispersoids to improve their very high temperature properties is currently being investigated worldwide, e.g. [12,13]. The influence of point defects created by the irradiation of the ordered intermetallic structure [14,15] will be a main topic to be investigated for future VHTR applications. Another scientific question to be clarified concerns the effect of impurities in the reactor helium on the long-term behaviour of these materials. For temperatures in the range of 1000 °C and higher ceramic materials could be used, however complex shaped parts are difficult to machine out of solid ceramics. ZrO₂-based fine grained superplastic ceramics can be shaped into complex structures much easier. Feasibility studies are currently underway to demonstrate the capability of this class of materials for core internal applications in future VHTR’s [16].

2.3. Pipings and valves

Solid solution strengthened nickel base superalloys like IN 800, IN 800 H or similar have already been investigated thoroughly for piping and other balance of plant applications for today’s HTR-technology [17]. In Section IIC, Pipings and Valves, it is indicated that Alloy 800H can be used for temperatures up to 950 °C. However, no guidance for use of this material at 950 °C is currently included in the ASME Boiler and Pressure Vessel Code, Section III, Division 1- Subsection NH, Class I Components in Elevated Temperature Service. Also, future revisions of Subsection NH to include design information that would include this service temperature for Alloy 800H are not planned. Temperatures of up to 950 °C can be probably better reached with higher creep resistant, advanced nickel base superalloys like Haynes 230 or IN 617. A further temperature increase (up to 1000 °C) also pushes these materials towards their temperature limits where strength and creep properties drop very quickly. For heavily stressed parts subjected to very high temperatures, reinforcement like dispersoids (ODS) or intermetallics could be alternatives. Double walled piping with cool gas moving through the outer section can help to cool the hot gas ducts. Thermal barrier coatings can further reduce the material temperature. For piping sections this concept would allow operating temperatures in excess of 1000 °C. However, as soon as no possibility for the removal of heat exists thermal barrier layers will not help and then ceramic concepts (reinforced) have to be considered.

2.4. Helium turbine

The key components of concern are: blades, vanes and the rotor (Fig. 3). Gas temperatures exceeding 1000 °C are common in conventional gas turbines. The high temperatures are accommodated by an appropriate choice of materials and the use of advanced cooling systems, bringing the metal temperature down to ~900 °C.
Advanced nickel base super-alloys produced either with columnar grains (directionally solidified DS) or even as single crystals (SC) are currently employed. These materials are based on an austenitic, solid solution strengthened NiCr matrix reinforced with coherent γ'-particles, which are intermetallic compounds of type Ni₃Al. At a material temperature of 1000 °C these superalloys operate at more than 80% of their intrinsic melting temperature, which means that their temperature capability has been reached. Such material temperatures can be avoided by appropriate cooling concepts. In this case not only cooling is achieved but the surface of the blades can additionally be coated with a thermal barrier layer (usually ZrO₂) providing a further increase in gas temperature of ~150 °C [18]. The application of such a technology to a helium turbine should be quite straightforward as only the impurities in the He-atmosphere needs further consideration. If material temperatures in excess of 1000 °C are envisaged, super alloys will be at their limits and new blade/vane materials must be considered. Austenitic ODS, refractory materials (Mo, W, Nb-based), intermetallic silicides (fibre reinforced or bulky) or SiC/SiC ceramics would then be a solution.

Another critical component is the turbine rotor which has to carry the centrifugal forces from the blades. The situation for the helium turbine is the same as for conventional large land based turbines. Either a cooled concept is used which allows a 9-12% martensitic steel solution or an uncooled concept with a high temperature resistant material. In this case the ferritic martensitic steels are at their temperature limits, as already discussed in the pressure vessel section. Large ODS forgings are currently impossible to produce, so γ'-strengthened austenitic super alloy rotors (Udimet 720) are currently in discussion. The problem is that superalloys are designed to resist high temperature deformations which in turn makes them difficult to be properly forged. Unsatisfactory inhomogeneous microstructures with partly inferior mechanical properties are the result as shown in conventional gas turbines. Advanced powder metallurgy techniques could possibly help to overcome these problems, which would also help to accommodate gas temperatures of more than 1000 °C [19].

3. Damage and life time assessments

For components that are supposed to remain in operation for at least 6 years in severe environments (e.g. in a VHTR), extrapolation of laboratory data and damage assessments are necessary. Degradation of the mechanical properties by irradiation and corrosion must be considered. Creep strength and creep strain are of importance as well as the stress/strain response and impact properties.

A thorough understanding of the correlations between mechanical properties and the microstructure forms the basis for appropriate life-time assessments. Several scales of damage formation must be
considered. An overview of such a multiscale approach is given in Fig. 4. Particularly advanced X-ray and neutron analyses which are coupled to beamlines allow novel techniques of microstructural to be used in investigations. Other important techniques are the instrumented micro- and nano-mechanical tests that allow direct correlations between the local microstructure and the local mechanical properties.

3.1. Extrapolation of data

Tests in the laboratory are often confined to relatively short exposure times (several thousand hours maximum) whereas components can operate for 60,000 hours and more. This means that the appropriate level of damage can rarely be satisfactorily achieved in the laboratory. In many cases the first signs of damage become obvious during the first 10% of the lifetime (e.g. formation of grain boundary voids under creep loading, or microcracks at stress raisers during low cycle fatigue [20,21]). This allows conclusions after short times, however, this can only be done if the microstructural response is known. Therefore methods must be found for the acceleration of damage evolution. Another difficulty is that during service several damage mechanisms act simultaneously, a situation that cannot easily be simulated in the laboratory.

**FIG. 4.** Scheme of a multiscale approach for damage analysis. The line separates conventional (right) and advanced (left) techniques, modified after [6]. (finite element (FM), (high resolution) transmission electron microscope (HR)TEM, atomic force microscope (AFM), scanning electron microscope (SEM), electron probe micro analysis (EPMA), secondary ion mass spectroscopy (SIMS).
Well known methods for acceleration include the use of more aggressive environments or, in case of creep, testing at operation temperatures but at higher stresses or vice-versa. Assuming that there is a unique parametric relationship between stresses, temperature and creep rupture life, long term behaviour can be predicted from short term behaviour. Examples of typical approaches include the Iso-Stress-Method (see Fig. 5 replotted from [23]), the Larson-Miller parameter or the Manson-Haferd parameter. Very often the validity of a potential law between secondary creep rate and creep rupture life is assumed (Monkman-Grant rule) [24]. Although these parameters were originally developed for metallic materials only, they are also applied to almost all materials including ODS, intermetallics [25] and even SiC/SiC [26] and other ceramics. The danger of such an approach lies in the fact that deformation mechanisms can be stress dependent and/or temperature dependent and this can give misleading predictions. For the application of proper extrapolation methods an understanding of the damage mechanisms is necessary. The presence of irradiation complicates the situation even more because the neutrons create a high density of point defects which can interact in-situ with dislocations and/or diffusion controlled creep mechanisms (see Fig. 6 replotted from [27]). Short term creep tests under irradiation at high temperatures can help to clarify the picture.

3.2. Life-time assessments

The linking of mechanical properties with microstructural damage for high temperature applications (interaction creep-fatigue-environment) has attracted material scientists concerned with life assessments of components since the 1970’s e.g. [28,29].

FIG. 5. Iso-Stress plot for different Ni-base superalloys showing a linear relationship between log stress rupture time and temperature.\textsuperscript{23}
For automotive, aerospace and energy applications different attempts were tried in huge joint research projects and the following difficulties were encountered:

- Exposure conditions (state of stress, temperature changes, exposure time, and environment) were different for the component and for the sample;
- The interaction of different damage mechanisms is difficult to be described quantitatively, e.g. it makes a difference whether a stochastically occurring load/temperature cycle occurs with fresh material, with creep pre-damaged material or with locally corroded material;
- Scatter in the material data (production related) cannot be avoided;
- Traditionally, mechanical tests are performed with large samples whereas microstructural investigations concern small volumes only, making linking difficult; and
- Accelerated methods for characterization of long term behaviour might give misleading results.

These difficulties will persist for life-time models of VHTRs to. It can, however, be expected that the improved investigation methods with the possibilities for linking local damage with local mechanical properties as well as advanced in-situ investigations (e.g. in-situ creep in synchrotron X-ray devices) will lead to a more quantitative understanding of damage development. Increases in computer performance allow relatively straightforward applications of numerical simulations such as molecular dynamics and/or kinetic Monte Carlo [31] as well as complex finite element analyses (e.g. modelling of time dependent fibre pull out in SiC/SiC [30]). The life-time predictions will therefore be combinations of constitutive damage rate equations based on mechanical properties and physical models based upon local damage development.

4. Conclusions

The future challenges for materials and material mechanics challenges in very high temperature reactors were briefly summarized. It can be assumed that for the coming generation of VHTR combined cycle demonstration plants with maximum gas temperatures of up to 1000 °C material solutions exist although many candidate materials are at the very end of their temperature capabilities.
The main emphasis has to be put on the establishment of design data bases (9-12% Cr-steel, nickel-base super alloys, graphite) and on design concepts that are in accordance with the envisaged materials. Development of composite materials (C/C, SiC/SiC, ODS) is necessary for some core internal applications (e.g. control rod, fixing and supporting elements). Coatings and thermal barrier layers should be considered as a design requirement. The fact that the materials currently under discussion are at their temperature limits highlights the need for a quantitative understanding of damage formation and damage evolution as a basis for proper life-time assessments. For future commercial systems with even higher gas temperatures new materials like advanced ceramic, metallic and intermetallic materials, and reinforced materials with dispersoids or fibres must be further explored and developed to a stage at which components can be produced.

ACKNOWLEDGEMENTS

The author would like to thank PSI for supporting the work on high temperature materials for VHTR applications. Helpful discussions with members of the GIF-VHTR steering committee and with the European HTR group are very much acknowledged.

REFERENCES


