Materials for Gen III reactors

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Generations of nuclear reactors

**EARLY PROTOTYPES**
- Magnox (1956)
- Shippingport (1957)
- Dresden (1959)
- RBMK (1963)
- FBR (1963)
- HTR (1966)

**COMMERCIAL POWER REACTORS**
- LWR: PWR and BWR
- CANDU, AGR

**NEW GENERATION**
- LWR-PLANTS + HTR
- VVER-1000, ABWR
- EPR
- SWR-1000, AP-1000
- ESBWR-1500

**GENERATION IV**
- Very competitive
- New application, such as process heat
- Enhanced/inherent safety features
- Reduced waste generation
- Improved proliferation resistance

- Economically more competitive evolution types
- High efficiency
- Long life time
- Passive safety

**Timeline**
- Generation I
- Generation II
- Generation III
- III+ — Generation IV

- 1950
- 1960
- 1970
- 1980
- 1990
- 2000
- 2010
- 2020
- 2030

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# Comparison of Structural Materials Requirements

<table>
<thead>
<tr>
<th></th>
<th>Fission (Gen. I, II, III)</th>
<th>Fission (Gen. IV)</th>
<th>Fusion (DEMO/PROTO)</th>
<th>Spallation (ADS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural alloy $T_{\text{max}}$</td>
<td>$&lt;300^\circ\text{C}$</td>
<td>500-1000$^\circ\text{C}$</td>
<td>550-1000$^\circ\text{C}$</td>
<td>400-600$^\circ\text{C}$</td>
</tr>
<tr>
<td>Max dose for core internal structures</td>
<td>$\sim 1$ dpa</td>
<td>$\sim 30-100$ dpa</td>
<td>$\sim 150$ dpa</td>
<td>$\leq 60$ dpa</td>
</tr>
<tr>
<td>Max transmutation helium concentration</td>
<td>$\sim 0.1$ appm</td>
<td>$\sim 3-10$ appm</td>
<td>$\sim 1500$ appm (~10000 appm for SiC)</td>
<td>$\sim 2000$ appm</td>
</tr>
<tr>
<td>Coolants</td>
<td>$\text{H}_2\text{O}$</td>
<td>He, $\text{H}_2\text{O}$, Pb-Bi, Na</td>
<td>He, PbLi, Li</td>
<td>PbLi, PbBi</td>
</tr>
<tr>
<td>Structural Materials</td>
<td>Zircaloy, stainless steel</td>
<td>Ferritic steel, ODS steels, Superalloys, C-composite</td>
<td>Ferritic/martensitic steel, V alloy, SiC composite</td>
<td>Ferritic/martensitic steel</td>
</tr>
</tbody>
</table>

*Generation III reactors are from treatment point of view closed to Gen II*

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Material ageing
Material ageing due to:

- Thermo-mechanical strain – temperature, overpressure,
- Cyclis strain
- Influence of corrosive environment (N, H, He, C, S)
- Radiation strain
Material ageing due to:

- Thermo-mechanical strain – temperature, overpressure,
- Cyclic strain
- Influence of corrosive environment (N, H, He, C, S)
- Radiation strain

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Material ageing due to:

- Thermo-mechanical strain – temperature, overpressure,
- Cyclis strain
- Influence of corrosive environment (N, H, He, C, S)
- Radiation strain

Fig. Three different types of hot corrosion: layers type (a), transient type (b) and non-layer type (c).
Material ageing due to:

- Thermo-mechanical strain – temperature, overpressure,
- Cyclis strain
- Influence of corrosive environment (N, H, He, C, S)
- Radiation strain

<table>
<thead>
<tr>
<th>Particle type (E_{kin} = 1 MeV)</th>
<th>Typical recoil (or PKA) feature</th>
<th>Typical recoil energy T</th>
<th>Dominant defect type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td></td>
<td>25 eV</td>
<td>Frenkel pairs (Vacancy-Interstitial pair)</td>
</tr>
<tr>
<td>Proton</td>
<td></td>
<td>500 eV</td>
<td></td>
</tr>
<tr>
<td>Fe-ion</td>
<td></td>
<td>24 000 eV</td>
<td>Cascades &amp; sub-cascades</td>
</tr>
<tr>
<td>Neutron</td>
<td></td>
<td>45 000 eV</td>
<td>Transmutation</td>
</tr>
</tbody>
</table>
Changes of mechanical properties due to irradiation

Charpy test

Tensile test
Requirements for new materials

Problems of GEN II:

- Corrosion,
- Embrittlement of RPV (DBTT shift),
- Material erosion due to coolant flow,
- Ageing and thermal shock,
- Tube/pipe or Weldment leakage.

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Problems of GEN II:
- Corrosion,
- Embrittlement of RPV (DBTT shift),
- Material erosion due to coolant flow,
- Ageing and thermal shock,
- Tube/pipe or Weldment leakage.

Material improvements GEN III (60+ years):
- Higher ultimate tensile stress,
- Higher melting point,
- Optimal hardness and toughness,
- Better corrosion resistance,
- Smaller DBTT shift and upper shelf energy decrease,
- Better resistance to defects accumulation and Helium formation during irradiation.

Optimization:
- Chemical composition,
- Deformation treatment,
- Heat treatment,
- Microstructure.

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Chemical composition

Reduced elements:
As, Sn, Sb, P, S - Diffusion to grain boundaries, segregation, embrittlement, S, P - radiation and thermal embrittlement and cracking, max. content 0,08% - 0,008% max,
C - hardening, radio-activation,
Cu – corrosion resistance, radiation embrittlement,
Ni ,Co - Graphitizing elements – free graphite formation (brittle structure),
Co, Ni - Long-term radioactivity.

Optimization content of:
V – limits grain size (-), creep and impact resistance (+),
Mo – increase strength (+), long-term radioactive (-),
Si – elasticity increase (+), free graphite formation (-), oxide jointer (+), larger grains (-), content 0,05-0,35% wt.,
Nb – corrosion (-), long-term radioactivity (-), strength increasing (+),
B – helium formation and embrittlement (-), precipitation hardening (+/-), strength increase (+),

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Chemical composition

Fig. 2. The hardening (change of yield strength of the irradiated measurement compared to the unirradiated measurement) for all materials is illustrated in function of the neutron fluence. Some results found in literature are added. The empty symbols symbolize the low-Cu steels, while the full symbols are results of high-Cu steels. For both type of steels a trend line is given, and for the high-Cu steels a region with an error of 30% is added.

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# REQUIREMENTS FOR BELTLINE RPV MATERIALS

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>As</th>
<th>Sb</th>
<th>Sn</th>
<th>P+Sb+Sn</th>
<th>Co</th>
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<tbody>
<tr>
<td><strong>GENERATION II</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15Kh2MFAA</td>
<td>0.012</td>
<td>0.015</td>
<td>0.08</td>
<td>0.010</td>
<td>0.005</td>
<td>0.005</td>
<td>0.015</td>
<td>0.020</td>
</tr>
<tr>
<td>15Kh2NMFAA</td>
<td>0.010</td>
<td>0.012</td>
<td>0.08</td>
<td>0.010</td>
<td>0.005</td>
<td>0.005</td>
<td>0.015</td>
<td>0.020</td>
</tr>
<tr>
<td>A 533-B, Class 1</td>
<td>0.012</td>
<td>0.015</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 MnD 5</td>
<td>0.008</td>
<td>0.008</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>20 MnMoNi 55</td>
<td>0.012</td>
<td>0.012</td>
<td>0.10</td>
<td>0.036</td>
<td></td>
<td></td>
<td>0.011</td>
<td></td>
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<tr>
<td><strong>GENERATION III</strong></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>SA-508 Grade 3</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Class 1</td>
<td></td>
<td></td>
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<tr>
<td>SA 533-B</td>
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</tr>
<tr>
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<td>0.008</td>
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<td>0.08</td>
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</tr>
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<td>15Kh2NMFAA</td>
<td>0.010</td>
<td>0.012</td>
<td>0.08</td>
<td>0.010</td>
<td>0.005</td>
<td>0.005</td>
<td>0.015</td>
<td></td>
</tr>
</tbody>
</table>

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**Chemical composition**

Addition of elements:

- **Al, Ti, Y** - increasing corrosion resistance and oxide jointer,

- **V, Ti, Nb, Ta, Zr** - carbides and nitrides former - less amount of unstable Fe$_3$C,

- **W** – refine grains, thermal resistance, strength increase,

- **Mn** – sulfur immobilization (0,5-1 %wt.),

- **Cr** – heat resistance, corrosion resistance, strength increase, influence on DBTT shift together with grain size.
Chemical composition

**Structural materials:**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>308</th>
<th>309</th>
<th>800</th>
<th>304</th>
<th>316</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0,043</td>
<td>0,08</td>
<td>0,1</td>
<td>0,08</td>
<td>0,03</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>2</td>
<td>1,5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Si</td>
<td>0,62</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>P</td>
<td>0,011</td>
<td>0,045</td>
<td>0,45</td>
<td>0,045</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0,015</td>
<td>0,03</td>
<td>0,015</td>
<td>0,03</td>
<td>0,03</td>
</tr>
<tr>
<td>Ni</td>
<td>9,98</td>
<td>12-15</td>
<td>30-35</td>
<td>8-11</td>
<td>10-14</td>
</tr>
<tr>
<td>Cr</td>
<td>19,96</td>
<td>22-24</td>
<td>19-23</td>
<td>17,5-20</td>
<td>16-18,5</td>
</tr>
<tr>
<td>Mo</td>
<td>0,01</td>
<td>2-3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0,04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0,57</td>
<td>0,15-0,6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0,002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0,03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0,011</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Priority for GEN III: Low activation capability

- „Low level waste“ already after ~100 years
- No „high level“ waste disposal
- The impurities Nb and Mo are dominating the hatched area
- Huge Progress in the development of RAFM
Heat treatment and Time-temperature metallurgical changes

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Heat treatment and Time-temperature metallurgical changes

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Heat treatment and Time-temperature metallurgical changes
New perspective materials

Ferritic/martensitic steels

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New perspective materials

Figure 5. Ti₃Al-TiC composite fabricated through MA and HIPing: a) etched, shows the TiC particles; b) shows the formation of fine oxides.

ODS steels

Figure 4. Dispersed oxide particles in the ODS coatings observed by TEM, showing nano-sized, spherical balls of Y₂O₃ dispersed inside Fe-Cr-Ni-Al-Y-O coating.

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Microscopic methods - overview

**Techniques**
- TEM Transmission electron microscopy
- SEM Scanning electron microscopy
- OM Optical Microscopy
- SANS Small Angle Neutron Scattering
- PAS Positron annihilation spectroscopy
- XRD X-Ray Diffraction
- MS Mössbauer spectroscopy

**Defects**
- Grain boundary
- Dislocations
- Dislocation loops, precipitations
- Frenkel Defects, Small Vacancy clusters

**Dimensions**
- ~10 µm
- ~100 nm
- ~10 nm
- ~1 nm
- ~10⁻⁵ m
- ~10⁻⁷ m
- ~10⁻⁸ m
- ~10⁻⁹ m
- ~10⁰ Å
- ~10⁻⁵ Å
- ~10⁻⁶ Å
- ~10⁻⁷ Å
Reasons for application of PAS

- Mechanical tests give not enough information about changes in material microstructure. Therefore, additional methods should be applied.

- PAS technique is a well-established method for studying open-volume type atomic defects and defect’s interactions in metals.

- Ability of PAS to detect very small defects as well as very low defects concentration.

- PAS can give additional information about:
  - radiation induced defects,
  - thermal annealing of these defects.
Thermalization → Diffusion → \( m_e = 0.511 \text{[MeV/c}^2\text{]} = 9.1 \times 10^{-31} \text{[kg]} \) → Annihilation

\( \gamma \text{511 keV} \)

Open volume defects (vacancies, vacancy clusters, dislocations, small grain boundaries, surface)

\( \text{511 keV} \)

Trapping due to local reduction of the electron density resulting into the increasing of the positron lifetime

Non-open volume defects (precipitation’s, negatively charged impurities)

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### Possible positron lifetimes in real Fe-Cr microstructure

**Positron annihilation Lifetime spectroscopy**

<table>
<thead>
<tr>
<th>Positron lifetime [ps]</th>
<th>&lt; 115</th>
<th>120 – 140</th>
<th>150 - 160</th>
<th>170 - 180</th>
<th>190 - 200</th>
<th>&gt; 200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Possible defects</td>
<td>bulk</td>
<td>Dislocations</td>
<td>dislocations, 1(2)V+2He(H)</td>
<td>dislocations, 1V+1He(H)</td>
<td>1(2)V, 6V+6He, etc.</td>
<td>various combination of vacancies and He (H) atoms</td>
</tr>
<tr>
<td>(component interpretation)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MLT interpretation</td>
<td>pure, well annealed material</td>
<td>bulk + low dislocation density</td>
<td>bulk + high dislocation density</td>
<td>dislocations + vacancies</td>
<td>significant presence of vacancy type defects</td>
<td>significant presence of vacancy clusters</td>
</tr>
</tbody>
</table>

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Possible positron lifetimes in real Fe-Cr microstructure

Doppler broadening spectroscopy

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Observation of different chemical composition and radiation damage

(Krsjak, V., Non-destructive examination of helium implanted Fe-Cr model alloys.)

Optimization of chemical composition on the ground of open-volume defects presence. Results shows importance role of chromium content in chromium steels.

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PAS results from annealing of WWER-steels at 475 °C.

The 3D presentation of PLEPS results (Tau1) of irradiated (1.25x10^24 m^-2) and annealed Sv-10KhMFT steel (WWER-440 weld).

The effectiveness of the annealing process to removing of small defects (mono/di-vacancies or Frenkel pairs) can be followed via significant decrease of parameter tau1. This figure also shows rapid increase of mentioned small defects in WWER type of RPV steels after about 480 °C.

Correlation between PAS and TEM

Annealing behaviour of irradiated CuCrZr-sample.

*Slugen, V. et al.* In: Fusion Engineering and Design, 70/2, 2004, 141
Correlation between PAS and TEM

PAS parameters in comparison to results from other techniques (HV10).

- Stress-strain experiments on Fe
- Distinct positron trapping after 80% Hooks range (fully elastic region)
- Early stage of fatigue

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Thank you!

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