RG5 Structural Integrity: THELMA (Thermal Ageing of Materials) – one topic in the project:

Thermal ageing of nickel-base Alloy 690 TT

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³ VTT Technical Research Centre of Finland LTD
⁴ Korea Atomic Energy Research Institute
Background: Why study thermal ageing?

**Nuclear power safety:**
- Strong emphasis for long design time (60 years) and to improve plant operation and maintenance.
- Critical when extending the planned service life of nuclear power plants.
- Wide range of potential materials ageing issues to consider in the license renewal.

**Structural integrity of components:**
- Components are designed to resist failure under every condition of operation, but material degradation from thermal ageing/irradiation/corrosion is unavoidable.
- The risk of catastrophic brittle fracture due to embrittlement of materials or stress-corrosion cracking (SCC) is the main issue when considering structural materials.

**Thermal ageing** (the degradation of a material over time caused by changes at the atomic level due to temperature).
- Reduction of mechanical properties such as ductility.
- Increase the susceptibility to SCC and other failure mechanisms.
- Testing with accelerated ageing (higher temperature ± longer time) until materials from NPPs are available.
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- 40 years ➔ 60 years
- High temperature (325 °C)
- Embrittlement
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Embrittlement

Simulation and characterization of long-term behavior of materials.
**Background: Why Alloy 690 TT?**

**Primary structural materials used in PWRs:**
- Low-alloy steels (LAS): Pressure vessels
- Stainless steels (SS): Piping, cladding
- Ni-base alloys (Ni-Cr-Fe): Penetrations, steam generator, welds

**Ni-base alloys:**
- High performance materials to replace stainless steels for critical applications.
- Good corrosion resistance and toughness at high temperatures.
- Suffer from a special form of intergranular stress corrosion cracking in the primary circuit: primary water stress corrosion cracking (PWSCC).

**Alloy 690 TT (Ni-30Cr-10Fe):**
- Extremely high PWSCC resistance.
- Used in modern PWR designs.
- Not totally immune to PWSCC.
- Concern for long-term operation (>60 years) at temperatures higher than 300 °C.
Alloy 690 TT (Ni-30Cr-10Fe):
- Replaced Alloy 600 since the 90’s.
- Thermally treated (TT) condition with intergranular (IG) carbides.
- Used in RPV head penetrations and steam generator tubing.
- PWSCC resistance is critical.

Factors affecting the PWSCC resistance:
- High levels of cold work (20 % CW).
- Inhomogeneous microstructure.
- Carbide precipitation.

Thermal ageing of Alloy 690 TT:
- Increase of PWSCC, but the mechanisms are unclear.
- Promotion of IG carbide precipitation.
- Trigger an atomic ordering.
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*Strain localization
Protective film rupture
Hydrogen embrittlement*
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Ordering reactions:
- Stronger attraction between non-similar atoms (Ni and Cr).
- Re-arrangement where neighbouring atoms are different.
- Formation of the Ni$_2$Cr phase.
- Stronger attraction = smaller distance between atoms.

Short-range or long-range ordering:
- Short-range order (SRO), when only nuclei of Ni$_2$Cr phase.
- Long-range order (LRO), when the phase extends over large domains.
- The reaction occurs below a critical temperature, depending mostly on the Fe content in the Ni-Cr-Fe system.

Consequences in Alloy 690:
- Lattice contraction.
- Hardness increase.
- Reduction of mechanical properties.

**Graph**

- Alloy is Disordered
- Alloy Can Develop Short Range Order
- Alloy Can Develop Long Range Order

- Tc = 550 °C at 0 wt.% Fe
- Tc ± 420 °C at 9.5 wt.% Fe

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**Chart**

- **Y-axis**: Temperature (°C)
- **X-axis**: Iron Content (at.%) in Approximately Ni$_2$Cr Alloy Can Develop Short Range Order
- **Legend**: Alloy is Disordered, Alloy Can Develop Short Range Order, Alloy Can Develop Long Range Order
- **Note**: Times > 10,000 hours required to show LRO below ~350°C
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Issue
SRO is difficult to identify
Lattice contraction in the range of 0.03 %
Limited hardness variations
## Materials and experimental methods

### Alloy 690

#### Chemical composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
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<td>wt. %</td>
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### 6 conditions

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SA: solution anneal at 1100 °C for 1 h  
WQ: water quench  
TT: thermal treatment at 700 °C for 17 h

### Methods

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### Additional notes:

- **Microhardness (9.8 N)**
- **Nanoindentation (1.5 mN)**
- **X-ray diffraction (XRD)**
- **High resolution EBSD**
Alloy 690 TT microstructure

- Austenitic (fcc) matrix
- IG carbides
- Golden TiN particles
- Twin boundaries

Optical microscopy

SEM with Argus™ FSE/BSE detector
Evolution of grain size and IG carbide precipitation
Nature of IG carbide precipitation

- Identification with TEM: **Cr-rich M$_{23}$C$_6$ carbides**
- Distribution with EBSD: GBs, migrated GBs, twin boundaries
- Twin boundaries: carbide plates
Study of the SRO levels

Microhardness (9.8 N load)
- No influence of ordering.
- Clear influence of grain size and IG precipitation
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**Nanoindentation:**
- Hardness increase upon thermal ageing.
- **Highest hardness at 420 °C.**
- Disordering reaction at higher temperatures.

**XRD:**
- Lattice contraction upon thermal ageing.
- Contraction in the range of 0.03-0.05 % (SRO).
- **Strongest contraction at 420 °C.**
- No lattice contraction at 550 °C (disordering).
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Highest hardness/lattice contraction at 420 °C (9.8 wt.% Fe).
Levels similar to that of 20 % CW.
Effect of SRO on strain localization

- No effect of SRO on strain levels.
- No effect of SRO on strain localization.
- Effect of IG carbide precipitation on strain localization.

AFM:
- No effect of SRO on GB hardness.
Conclusions

- Thermal ageing of Alloy 690 TT was studied, with a special focus on the formation of SRO and IG carbide precipitation and their link with strain localization and effect on PWSCC resistance.

- IG carbide precipitation of Cr-rich IG $M_{23}C_6$ carbides increased during thermal ageing with the ageing temperature.

- The formation of SRO was suggested upon ageing at 350 °C and more clearly upon ageing at 420 °C, while the effects of a disordering reaction were seen at 475 and 550 °C.

- Thermal ageing at 420 °C increased the hardness of Alloy 690 TT to levels higher than that of Alloy 690 TT with 20% CW.

- Heat treatment of Alloy 690 after solution annealing promoted ordering in relation to a lower carbon content after IG carbide precipitation, favoring the nucleation of SRO.

- No link found between SRO and strain buildup or IG strain localization.

- IG carbide precipitation increased IG strain localization.

The combination of IG strain localization and SRO is deemed detrimental to the PWSCC resistance over longer ageing times.

All results are extracted from R. Mouginot’s doctoral thesis, including more Alloy 690 conditions and the study of welds.
Thank you for your attention!

Further work in THELMA

- Study of the link between thermal ageing and hydrogen embrittlement of Alloy 690.
- Atome probe tomography (APT) at Chalmers University, Sweden, to observe SRO nucleation directly.

List of publications


