Effect of thermal ageing on Alloys 690 and 52 in pressurized water reactor applications

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Abstract
In modern pressurized water reactors (PWR), the substitution of nickel-base Alloy 600 and its associated filler metals Alloy 82 and 182 by Alloys 690, 52 and 152 with higher chromium content has improved the integrity of the main components in the primary circuit. However, metallurgical changes during thermal ageing of Ni-base alloys, notably intergranular (IG) carbide precipitation and short-range ordering (SRO), can affect the long-term primary water stress corrosion cracking (PWSCC) resistance of PWR components, such as the steam generator for Alloy 690 and the reactor pressure vessel (RPV) safe-end dissimilar metal weld (DMW) for Alloy 52. In addition, it is known that post-weld heat treatment (PWHT) affects narrow transition zones within Alloy 52 weld metal at the ferrite/austenite interface of DMW, but no data is available on the effect of thermal ageing.

Four conditions of Alloy 690 (solution annealed, cold-rolled and/or heat-treated) were aged between 350 and 550 °C for 10 000 h and characterized. In addition, two sets of PWR RPV narrow-gap (NG) DMW mock-ups were studied. The first weld was characterized before and after PWHT and the other after PWHT and ageing at 400 °C for 5000 and 10 000 h. No direct observation of ordering was made, but hardness and lattice parameter measurements indicated the formation SRO in Alloy 690, with a peak level at 420 °C. Heat treatment induced SRO before ageing, while stress relaxation, recrystallization and α-Cr precipitation were observed in cold-worked (CW) samples at higher temperatures. A disordering reaction was inferred in all conditions at higher temperatures. IG M23C6 carbide precipitation increased with increasing ageing temperature, as well as diffusion-induced grain boundary migration (DIGM). After comparison with recent studies, SRO was concluded to be locally as detrimental as long-range ordering (LRO) or 20% CW, but not a SCC driving force by itself. A combination of SRO and IG carbide precipitation was seen as detrimental to the SCC resistance. Results for Alloy 52 showed that PWHT increased carbon depletion in the low-alloy steel (LAS) side, and promoted a hard layer close to the fusion line inside the Alloy 52 weld metal. Thermal ageing did not affect the microstructure or hardness levels in neither LAS base metal nor Ni-base weld metal, but significantly reduced the hardness peak close the fusion line in Alloy 52 weld metal side. This strength mismatch reduction at the weld fusion line was seen as beneficial from both mechanical and SCC point of view.

Keywords Alloy 690, Alloy 52, nickel-base alloy, thermal ageing, heat treatment, dissimilar metal welding, materials, nuclear, SCC, SRO, ordering, carbide precipitation

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Preface

The doctoral thesis presents the literature review, experimental research work and results obtained for the doctoral degree at the Department of Mechanical Engineering of the Aalto University School of Engineering, between November 2012 and January 2016.

The work was financially supported by four projects involving Aalto University, VTT and Finnish and Swedish power companies. The study of Alloy 52 was carried out within the Structural Integrity of Ni-base Alloy Welds (SINI) and the Nickel-Base Alloy Welding Forum (NIWEL) research projects, funded by TEKES and the Finnish and Swedish nuclear industries. The study of Alloy 690 was done first in the “Environmental Influence on Cracking Susceptibility and Ageing on Nuclear Materials” (ENVIS) project of the Finnish Research Programme on Nuclear Power Plant Safety 2011 – 2014 (SAFIR2014), and then in the “Thermal Ageing and EAC Research for Plant Life Management” (THELMA) project of the Finnish Research Programme on Nuclear Power Plant Safety 2015 – 2018 (SAFIR2018).

Experiments were mainly carried out at Aalto University and VTT, with the exception of X-ray diffraction measurements that were obtained at the Helsinki University, Laboratory of Inorganic Chemistry.

During the course of the doctoral degree, numerous papers were presented at international conferences and several journal articles were published that include work presented in this thesis.
Acknowledgements

I would like to express my special thanks to my supervisor Professor Hannu Hänninen, who supported me throughout my Master’s thesis and doctoral studies. I would like to thank you for the opportunity to work at Aalto University, the never-ending financial support and the great help in writing both the thesis and all my other papers. Your advice on research and the opening of your network will be the base of my career. I would also like to thank principal scientist Ulla Ehrnštén for her advices, her kind words and very positive support, and for her amazing ability to connect the right persons for the right task. A special thank you to Teemu Sarikka, friend and colleague, and best support in the laboratory, to Matias Ahonen for easing greatly my trips abroad, to Mykola Ivanchenko for monitoring my naps in the TEM room, to Yuriy Yagodzinskyy for his time and support and finally to Kim Widell and Laura Tiainen who always helped me when I needed in the laboratory. All of you have been there to support me during my Ph.D. thesis, and I am very grateful to you.

A special thanks to my family, which extended quite a lot during the past few years. I cannot express how grateful I am to my daughters Minea and Mimosa, who certainly made the completion of the thesis more challenging but are bringing me joy every day. I would like to thank my parents for their unaltering support and their dedication to their three boys. Thank you to my brothers for coping with me then and now. I would also like to thank all of my friends who supported me in times of need and celebrated with me in times of joy, Sergei, Eva, Gauthier, Teppo and so many more and so far away. Finally, I would like to express my love for Leena, who spent countless sleepless nights with me, supported me and reminds me always to smile a little bit more.

Espoo, January 2017
Roman Mouginot
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>BWR</td>
<td>boiling water reactor</td>
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<td>CEFM</td>
<td>coupled environment fracture model</td>
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<tr>
<td>CW</td>
<td>cold work</td>
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<tr>
<td>DMW</td>
<td>dissimilar metal weld</td>
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<tr>
<td>EAC</td>
<td>environmentally-assisted cracking</td>
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<tr>
<td>EBSD</td>
<td>electron backscatter diffraction</td>
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<tr>
<td>EDS</td>
<td>energy-dispersive spectroscopy</td>
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<td>FEG-SEM</td>
<td>field emission gun scanning electron microscopy</td>
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<tr>
<td>FL</td>
<td>fusion line</td>
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<tr>
<td>GB</td>
<td>grain boundary</td>
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<tr>
<td>HAC</td>
<td>hydrogen-assisted cracking</td>
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<tr>
<td>HAZ</td>
<td>heat-affected zone</td>
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<tr>
<td>HEAC</td>
<td>hydrogen environmentally-assisted cracking</td>
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<tr>
<td>HIC</td>
<td>hydrogen-induced cracking</td>
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<tr>
<td>HR EBSD</td>
<td>high-resolution electron backscatter diffraction</td>
</tr>
<tr>
<td>IASCC</td>
<td>irradiation-assisted stress corrosion cracking</td>
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<tr>
<td>IG</td>
<td>intergranular</td>
</tr>
<tr>
<td>IGSCC</td>
<td>intergranular stress corrosion cracking</td>
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<tr>
<td>IHAC</td>
<td>internal hydrogen-induced cracking</td>
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<td>LAS</td>
<td>low-alloy steel</td>
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<tr>
<td>LRO</td>
<td>long-range ordering</td>
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<tr>
<td>NPP</td>
<td>nuclear power plant</td>
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<td>PMZ</td>
<td>partially melted zone</td>
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<td>PWHT</td>
<td>post-weld heat treatment</td>
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<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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</tr>
<tr>
<td>PWR</td>
<td>pressurized water reactor</td>
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<tr>
<td>PWSCC</td>
<td>primary water stress corrosion cracking</td>
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<tr>
<td>RPV</td>
<td>reactor pressure vessel</td>
</tr>
<tr>
<td>SCC</td>
<td>stress corrosion cracking</td>
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<tr>
<td>SRO</td>
<td>short-range ordering</td>
</tr>
<tr>
<td>SS</td>
<td>stainless steel</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TT</td>
<td>thermal treatment</td>
</tr>
<tr>
<td>UMZ</td>
<td>unmixed zone</td>
</tr>
<tr>
<td>VVER</td>
<td>veda-vodyanoi energetichesky reactor</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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The work carried out during the doctoral studies presents a number of original features. First of all, it is among the few recent comprehensive studies on the short-range ordering of a commercial melt of Alloy 690, with other studies carried out either in the 80’s or on model alloys. The quality of characterization equipment has greatly improved in 30 years and the use of model alloys, while making it easier to characterize ordering, overlooks the influence of the complex chemical composition of a commercial alloy. The results presented in this thesis are therefore very valuable to build detailed understanding of the long-term behaviour of Alloy 690, and therefore for the safe operation of PWRs. The study characterizes precisely the transition from ordering to disordering in a narrow temperature range between 420 and 475°C. It is the first time that nanoindentation is used to characterize the hardness variations associated with the formation of ordering, with good results. Concerning the Alloy 690 weld consumable, Alloy 52, it is the first time that the thermal ageing of Ni-base alloy weld metals and its effect on the weld metal and the weld interfaces are studied. The results are of great importance for the operation of modern PWRs, including in Finland. The work carried out during the doctoral thesis is therefore at the forefront of the global research effort to characterize the long-term behavior of Alloys 690 and 52, which aims at setting proper inspection intervals for ageing of the future power plants.
During the course of the doctoral studies, the author conducted the literature review on pressurized water reactor components and materials selection, primary water chemistry, stress-corrosion cracking, Ni-base alloys, effects of thermal ageing and ordering reactions, presented in the beginning of the doctoral thesis.

Upon reception of the Alloy 690 materials, the author planned, alone or in collaboration with the thesis supervisor Hannu Hänninen, principal scientist Ulla Ehrnstén or project specialist Teemu Sarikka, the experiments needed for the study. Upon reception of the NG-DMW mock-ups, a matrix of experiments was planned by the research teams in Aalto University and VTT and approved by the steering groups of the SINI and NIWEL projects.

The author prepared all samples for the study of Alloy 690 and the NG-DMW mock-ups, with the help of Mykola Ivanchenko from VTT for the preparation of TEM samples. The author conducted alone most of the experiments related to the study of Alloy 690, including SEM, EDS, EBSD, microhardness measurements and nanoindentation, with the exception of XRD, AFM and TEM. HR EBSD was performed with the help of Teemu Sarikka at Aalto University School of Engineering.

- XRD was performed at the University of Helsinki, Department of Inorganic Chemistry by Mikko Heikkilä, on samples selected and prepared by the author.
- AFM was performed at Aalto University School of Science, Department of Applied Physics by Nikolay Houbenov on samples selected and prepared by the author.
- TEM was performed at VTT by Unto Tapper and Mykola Ivanchenko on samples selected by the author and prepared with the help of Mykola Ivanchenko.

The details of the experimental methods, the presentation of the results, the discussion and conclusions of the doctoral thesis were all written by the author, and sometimes modified according to the thesis supervisor Hannu Hänninen’s advice.
1. Introduction

In the context of an ever-growing need for energy, nuclear fission energy has rapidly expanded worldwide from the 1960’s to 80’s to become a reliable base-load source of electrical energy. The International Atomic Energy Agency (IAEA) counted, as of February 2016, 442 nuclear reactors operating worldwide and 66 under construction, for a total of 508 units and 448 GWe of electrical capacity. The predominant reactor design is by far the pressurized water reactor (PWR), followed by the boiling water reactor (BWR), representing respectively 63% and 18% of units in 2015 (IAEA 2016). Nuclear power is used to provide over 10% of the world’s electricity, while 13 countries rely on it to supply more than 25% and up to 75% of their total electricity. After being considered a dying energy source during the 80’s and 90’s, it is now re-envisaged as a future source of energy with the 66 new reactors under construction, mostly due to global warming and volatile fossil fuel prices. However, public concern is high on the issues of nuclear safety, disposal of radioactive wastes, transportation of nuclear materials and security of nuclear facilities.

After the Three Mile Island, Chernobyl and Fukushima accidents, there is a strong emphasis to improve plant operations and maintenance. Especially, the structural integrity of components is crucial for the safe operation of nuclear systems, as in-service failures may result in widespread damage and fatalities and maintenance is tedious and expensive. Components are designed to resist failure under every condition and operation (start-up, normal operation, loss of coolant and shut-down), but material degradation due to irradiation, corrosion and thermal ageing is inevitable and will change the properties of materials and alter the original properties of components. The question is then whether or not the properties of the components can reach critical levels during the service life of the power plant. Mostly, the risk of delayed catastrophic brittle fracture due to embrittlement of materials or stress-corrosion cracking is the main issue being addressed when considering structural core materials, especially in the case of plants exceeding their planned service life. To that end, the nuclear power industry has been developing and improving designs, technologies and materi-
als selection for over 50 years, notably with the use of nickel-base alloys in critical applications. This thesis is focused on the effect of thermal ageing on some of the most critical nickel-base alloys used in modern PWRs, with regard to their embrittlement and susceptibility to stress-corrosion cracking, therefore addressing the key issues in the safe operation of the nuclear power systems.
2. Context: materials challenges for nuclear power systems

2.1 Pressurized water reactors (PWR)

2.1.1 Design and history

The pressurized water reactor (PWR) is a generation II nuclear power reactor that uses pressurized water as coolant and neutron moderator. They were first designed by Bettis Atomic Power Laboratory, USA, for submarine propulsion. The first nuclear submarine of this type was the Nautilus, launched in 1945. After that date, the world’s first nuclear power plant started operation in USSR in 1954 (Obninsk, 5 MWe), in England in 1956 (Calder Hall, 50 MWe) and in the US in 1957 (Shippingport, 90 MWe). The first full-scale commercial PWR (250 MWe, Yankee Rowe) was designed by Westinghouse in the USA and operated from 1960 to 1992. The first BWR (250 MWe, Dresden-1), developed by the Argonne National Laboratory and General Electric, started in 1960. The Soviet Union commissioned from the early 60’s its first PWR known as water-cooled power reactor (veda-vodyanoi energetichesky reactor, VVER). By the end of the 70’s, PWRs and BWRs of more than 1000 MWe were commissioned. (Fischer 1997)

After a decrease in the commissioning of NPPs around the world from the early 80’s to 2000’s, a new generation III+ of PWRs is under construction in Finland, France and China (European PWR or EPR, 1600 MWe). The revived interest in nuclear power comes as a result of volatile fossil fuel prices, concerns about the security of energy supplies, and global climate change (Adamantiades & Kessides 2009).

As seen in Figure 2.1, a PWR consists of a primary circuit and a secondary circuit. In the primary loop, pressurized water (155 bar) at 275°C is pumped to the pressure vessel containing the fuel assemblies (nuclear reactor core) to be heated by the energy generated during the nuclear fission reaction. Modern reactors use uranium dioxide (UO2) enriched to 3.2% as fuel, which is contained in Zircaloy (zirconium alloy) tubes. The pressurized water exits the reactor at about 325°C and is then circulated to the steam generator where its heat is
transferred through U-tubes to a lower pressure, lower temperature secondary coolant loop. In the primary circuit, a pressurizer maintains the water at a high pressure to prevent boiling. In the secondary circuit with lower pressure, the water evaporates to pressurized steam (62 to 73 bar), which powers the turbines to activate an electric generator. The steam is then condensed and recirculated. The high pressure primary circuit including the reactor pressure vessel, the pressurizer, the steam generator and the coolant pumps, has a relatively high level of radioactivity and is located in a containment vessel. The design prevents the steam generated in the steam generator from becoming radioactive, and the secondary circuit including the turbine and the rest of the system is located outside of the containment, much alike a conventional power plant (Young 1989).

Both PWR and BWR designs are light-water reactors (LWR), which means that they use ordinary water as coolant and neutron moderator. The main difference between PWRs and BWRs is that the latter consists of a single water circuit designed to boil the water in the core of the reactor with steam flowing directly to the turbine, which eliminates the steam generator and pressurizer found in the PWR. In contrast, high pressure in the primary loop of PWR prevents the water from boiling inside the reactor. Water turning to steam would slow down the fission reaction (this phenomenon is called the negative void coefficient, and is one of the main inbuilt safety features of PWRs, the other being the dissolution of boron in the water).
Even with the use of a neutron moderator, however, the reaction needed to produce heat in the nuclear reactor still generates energetic neutrons and gamma radiation that can damage the surrounding materials. In addition to these radiation fluxes, the combination of high stresses, high vibrations, high temperatures and chemically aggressive water creates a difficult environment for materials (Zinkle & Was 2013). This is addressed both by controlling the water chemistry and by the proper selection of materials.

2.1.2. Material selection

With the exception of the materials used for fuel cladding (zirconium alloys) and condenser tubes in the secondary circuit (titanium alloys), and although the requirements can differ, the primary materials used in PWRs are low-alloy steels (LAS), stainless steels (SS) and Ni-base alloys from the Ni-Cr-Fe system (Féron 2012). Major structural components (reactor pressure vessel, pressurizer, steam generator, steam lines) are made of low-carbon or low-alloy steel such as SA 508 or SA 533 Gr.B, which are selected as they favor a leak-before-break type of failure that maximizes safety (Ashby 2005). Low-carbon steels (<0.3 wt.% C) have a good weldability and enough ductility and are commonly used in the steam lines. Low-alloys steels (LAS) alloyed with low percentages of Cr, Ni, Mo and V, among others, can reach strength levels up to 830 MPa with a bainitic microstructure and have higher corrosion properties than low-carbon steels (MacDonald & Cragnolino 1989). Austenitic stainless steels are used for core structural materials (Types 304, 304L, 316, 316L) and corrosion-resistant cladding of the reactor pressure vessel and pressurizer (Types 308 and 309). Nickel-base alloys are used for high-strength components (springs, fasteners and bolts), critical applications (reactor pressure vessel head penetrations and heat exchangers in steam generator) and welds.

Nickel-base alloys are the focus of this doctoral thesis, in particular the alloys from the Ni-Cr-Fe system. Indeed, the selection of Ni-base alloys and austenitic stainless steels for core materials and critical applications is essential due to the necessity for good corrosion resistance at high temperatures. These alloys have low corrosion rates due to the formation of adherent, high-density, chromium-rich protective surface layers that grow very slowly at operating temperatures (Zinkle & Was 2013). They have a high resistance to general corrosion in caustic solution, increased resistance to chloride stress corrosion cracking and a good thermal conductivity (MacDonald & Cragnolino 1989). Tremendous work in the understanding of materials behavior and constant materials development have been ongoing since the early failures of NPPs in the 60’s and 70’s, and most
PWRs have been operating so far without major incidents. New challenges are emerging for materials, however, as the plants and their core components age and start to reach the end of their planned service life.

Fig. 2.2. Ternary Fe-Ni-Cr diagram at 400 °C, with the approximate locations of commercial alloys of nuclear power plant components (MacDonald & Cragnolino 1989).

2.1.3. Primary water chemistry

The primary water is the coolant used in the primary circuit of PWRs, which goes from the nuclear reactor to the steam generator. The reactor coolant in PWR uses pure water. The main role of the primary water is to act as neutron moderator and coolant. However, the interaction of an aqueous environment with metallic alloys leads to corrosion issues. Mostly, the pH of the solution and the electrochemical corrosion potential (ECP) of the metal are the most important parameters in determining the corrosivity of an aqueous environment. The ECP controls the intensity of the reactions (amount of transferred electrons), while the pH influences the reactivity of the material surfaces with the coolant. A lower potential is beneficial for both general corrosion and stress corrosion cracking resistance of materials in the primary circuit. For example, ECP is the main factor determining the susceptibility of SS and Alloy 600 to pitting corrosion and stress corrosion cracking, while the pH more generally determines the severity of general corrosion (MacDonald & Cragnolino 1989).
The most common factors in the steam cycle are temperature, flow velocity, pressure and solute species and concentrations. An increase in temperature increases the rate of corrosion reactions (Arrhenius equation) and the ECP, while increasing the fluid flow greatly increases the corrosion rate of alloys in steam cycles (MacDonald & Cragnolino 1989). The chemistry of the coolant is also critical, mostly to control the pH. The optimization of the primary water chemistry aims at limiting the transport of radioactive species out of the reactor core, controlling material degradation and preserving fuel performance (Wood 2012).

**Radiation field control**

In the primary circuit, the dissolution of boric acid ($\text{H}_3\text{BO}_3$) is used to control the neutron activity, with a decreasing concentration throughout the fuel cycle (starting from 1200 ppm at the beginning of the cycle). It is a very weak and stable acid at higher temperatures, but is a challenge for the control of pH and ECP. The addition of lithium as LiOH is usually used for pH control. It forms a coordinated boron and lithium concept, with concentration of LiOH gradually reduced in line with the boric acid concentration to maintain a constant pH. In addition to boric acid, radiolytic oxygen formation during the radiolysis of water in the nuclear reactor is another source of lower pH and higher ECP. It is countered by the addition of hydrogen (with a minimum of 25 ml/kg) to keep oxygen levels below 5 ppb and reduce the ECP while raising pH levels (Aaltonen & Hänninen 1997; MacDonald & Cragnolino 1989; Wood 2012).

The main goal of the coordinated B/Li concept is to control plant dose rates (radiation fields out of the reactor core). Radiation fields are an indirect result of corrosion reaction in the primary circuit. Corrosion products are released (mostly from the steam generator tubing), circulated to the reactor core where they build up on fuel cladding and are activated. They are then re-circulated out of the reactor, where insoluble species tend to deposit (crud build-up) and cause high radiation fields. Radiation field build-up can be controlled at the source by minimizing corrosion product transport and activation. It is done by adjusting the pH level. Studies showed that nickel ferrite is a prime constituent of the crud build-up, against which a pH of 7.4 is optimum. However, original concerns for fuel cladding (corrosion of zircalloy) set a conventional limit to the LiOH concentration at 2.2 ppm, corresponding to a pH of 6.9. Most plants were slow to increase the LiOH concentration, although crud formation at low pH proved to be more detrimental to the cladding (fuel performance) than at higher Li levels. Higher pH levels became the norm in the 90’s, and a pH of 7.3 is now the stand-
ard (Wood 2012). Lastly, the injection of zinc was used in BWRs to control radiation fields and it was also implemented in PWRs, although mostly for reasons related to materials degradation.

**Materials degradation**

Concerning materials degradation, an important matter was originally the transgranular chloride stress corrosion cracking of materials in environments typical of LWRs. Nickel-base alloys were then selected as they have an extremely good resistance to both general corrosion and transgranular chloride stress corrosion cracking. However, they are susceptible to intergranular stress corrosion cracking in the environments of the primary circuit of PWR (MacDonald & Cragnolino 1989). This particular case of stress corrosion cracking is called primary water stress corrosion cracking (PWSCC). It resulted in extensive work on the thermodynamics of nickel-water systems at service temperatures of power plants. It was found that the maximum in PWSCC crack growth rates (CGR) occurs close to the ECP corresponding to the Ni/NiO equilibrium condition. Increasing temperature renders Ni more active, which is seen by a shift of the Ni/NiO equilibrium to more negative values (MacDonald & Cragnolino 1989). On the contrary, studies showed that the effect of Li, B and pH on the PWSCC of nickel-base alloys are minimal in comparison, especially concerning the crack propagation. There is therefore flexibility to optimize the B/Li/pH chemistry to minimize radiation field build-up without concerns for the PWSCC of Ni-base alloys.

However, the effect of dissolved hydrogen on PWSCC became the focus of a new research effort. Indeed, the concentration of dissolved hydrogen affects significantly the ECP corresponding to the Ni/NiO equilibrium condition, and therefore PWSCC CGRs. The lower limit of dissolved hydrogen (25 ml/kg) was set to provide adequate margin over the level of hydrogen needed to suppress water radiolysis and heavy crud formation. Studies showed that increasing hydrogen levels reduce PWSCC CGRs, while reducing hydrogen delays PWSCC initiation. As a result, some countries consider raising the levels of dissolved H2 up to 60 ml/kg to reduce PWSCC CGR, while others consider lowering it to reduce PWSCC initiation.

The injection of Zn to levels of 10-30 ppb in the primary water was also showed to delay significantly the initiation of PWSCC by producing thinner and more protective oxides on SS and nickel-base alloys, without negative impact on plant components and operations. More work is needed, however, on the effect of Zn on fuel performance.
**Fuel performance**

For fuel performance, water chemistry is used to limit issues such as fuel cladding corrosion, crud deposition and axial offset (AO) in which an inhomogeneous crud deposition leads to trapping of boron and a reduction in the neutron flux. The use of higher pH levels has limited to influence of crud build-up, but the move to greater fuel duty, with operation of fuel at higher temperatures, can increase crud related problem. In addition, changes in water chemistry, such as Zn injection, are always a concern for fuel performance (Wood 2012).

### 2.2. Structural materials challenges in PWR

Given the large share of PWRs among the NPPs worldwide, materials issues encountered in this type of reactor are of great interest. Among these, the issues experienced in the primary circuit and the core materials are crucial for the plant integrity as they are facing the most extreme conditions of stress, corrosion and radiation. In addition to the microstructure of the materials, it is necessary to understand the nature of the cracking mechanisms. Indeed, failure cannot ultimately be avoided but it can be delayed or controlled by design, material selection and control of the service environment. It requires, however, the understanding of cracking mechanisms and of the role of both environment and materials in order to take further preventive measures.

#### 2.2.1. Main challenges: stress, corrosion and radiation

The reactor pressure vessel, dissimilar metal welds, Ni-base alloy components and steam generators are among the first entries on the IAEA list of critical items for a PWR NPP. The reason for this is that the materials in these components are exposed to the harshest conditions in the plant: primary water chemistry (boric acid, radiolytic oxygen), radiation and flux (neutron flux producing vacancies and interstitials, gamma flux producing local heating and release of activated species by corrosion reactions), vibrations due to high velocity flow, high temperature water and solid depositions of corrosion products. One of the major degradation mechanisms in the RPV is the irradiation embrittlement of the ferritic LAS, in which damage caused by neutron bombardment increases the ductile-to-brittle transition temperature, effectively increasing the risk of brittle fracture in the material. In addition, despite careful materials selection and water chemistry control, corrosion remains the significant concern in all the major systems exposed to a water environment and it can affect any material
used in the plant, carbon and low-alloy steels, stainless steels and nickel-base alloys (Guerin et al. 2009).

The combination of corrosion and the above-mentioned factors (stress, vibration and radiation) give birth to many different degradation mechanisms, such as stress corrosion cracking (SCC), corrosion fatigue (CF) and irradiation-assisted stress corrosion cracking (IASCC). Notably, SCC has emerged as one of the main form of material degradation in the reactor pressure vessel penetrations, steam lines and steam generator tubes. Weld structures with high residual stresses and cold-worked components are also affected as both residual stresses and cold work are well known to accelerate SCC. They have been related to a number of incidents involving intergranular cracking of austenitic stainless steel pipes. (Aaltonen & Hänninen 1997; MacDonald & Cragnolino 1989; Ehrnstén 2012; Fyfitch 2012).

In particular, weldments involving two or more materials, called dissimilar metal welds (DMW), are especially susceptible as they present transition zones in terms of chemical composition and differential thermal expansion. As an example, intergranular stress corrosion cracking (IGSCC) in the weld heat-affected zones (HAZ) of DMWs in the RPV safe-ends and piping has occurred due to low temperature sensitization (LTS). In addition, cracking incidents concerning Ni-base alloys Inconel 600 and Inconel 182 used in the pressure vessel head penetrations have been observed in many plants, while SCC issues in U-bend tubes of steam generators made of Ni-base alloys Inconel 600 and 182 have been so widespread that they obtained their own name: primary water stress corrosion cracking (PWSCC) (Aaltonen & Hänninen 1997; MacDonald & Cragnolino 1989; Fyfitch 2012). More recently, irradiation has emerged to play an increasingly important role in irradiation-assisted stress corrosion cracking (IASCC) (Scott 1994; Was & Bruemmer 1994).

2.2.2. Stress-corrosion cracking mechanisms

Introduction

As presented shortly in the previous chapter, the study of materials degradation is complex as it involves many different and often overlapping mechanisms. Since one of the main interest of the work presented in this thesis concerns the SCC resistance of materials, various forms of SCC, such as IGSCC, PWSCC and IASCC will be dealt within this chapter. They are considered to be major issues for Ni-base alloy components in PWRs. These mechanisms can be seen as particular cases of environmentally-assisted cracking (EAC), one of the most pre-
dominant forms of degradation of metallic structures, leading each year to numerous failures and costly maintenance. EAC is the key ageing degradation mechanism for a number of major components throughout the primary and secondary side of nuclear reactors (Couvant et al. 2005). EAC is defined as a form of corrosion that produces a brittle fracture in alloys with minimal uniform corrosion (Turnbull 1993). Three major forms of EAC are found, classified according to the nature of the stress and the chemical species involved in the reactions. These are i) stress-corrosion cracking (SCC), ii) hydrogen-assisted or -induced cracking (HAC or HIC) and iii) corrosion fatigue (CF). The borders between these mechanisms can be blurred, and EAC requires an interdisciplinary approach to be understood, including mechanics, materials science, electrochemistry, surface science and physics. The parameters influencing EAC are environmental (temperature, pressure, solute species, solute concentration, pH level, electrochemical potential), mechanistic (stress level, stress state, strain rate, loading mode and crack geometry) and metallurgical (alloy composition, cold work, intermetallic phases, GB segregation and residual stresses). Dynamic strain ageing (DSA) has been showed to enhance EAC, as it can enhance the localization of plastic deformation by favoring planar deformation, therefore favoring brittle cracking of oxide films. The main difference between SCC, HAC and CF is that SCC involves static tensile stress, CF involves a cyclic stress and that HAC, while it involves also tensile stress, is more related to the penetration of hydrogen into the metal. It is most often difficult to differentiate between SCC and HAC mechanisms (Rhodes 2001; Scott 1996).

![Diagram](image)

**Fig. 2.3.** Factors affecting EAC: a combination of material, environment and stress (Speidel 1984).
Overview of SCC

Stress corrosion cracking (SCC) is defined as the delayed failure of alloys by crack propagation resulting from the combined interaction of a specific corrosive environment and a static tensile stress. It is delayed as crack growth rates are usually very low, until catastrophic failure occurs (Lynch 2011a). Both the corrosive media and the tensile stress must act simultaneously to produce SCC. SCC mechanisms are specific to each alloy-environment combination, as they are frequently the result of the action of a specific chemical species from the environment on the material, and an environment causing SCC of a given alloy may not cause SCC in another alloy (Raja & Shoji 2011). Virtually all alloys are subject to SCC in a suitable environment, even alloys forming a protective surface film that are generally immune to uniform corrosion (Jones 1987). SCC occurs within the material, as cracks propagate through the internal structure, and leaves the outer surface unharmed. It makes SCC a dangerous form of corrosion, occurring at low stress levels and difficult to detect since it often occurs without any visible deformation of the material (Chatterjee et al. 2001; Kovač et al. 2012; Hänninen 2003).

The tensile stress can be an applied mechanical stress, a thermal stress or a residual stress due to cold work or welding. It has to exceed a threshold stress to produce SCC, which is usually below the yield stress and well below the stress needed to cause failure in the absence of corrosion (Eliaz et al. 2002). Internal residual stresses or external in-service loads can be high enough for SCC to occur, but the presence of stress raisers, such as notches, inclusions, machining marks or local corrosion usually decreases the resistance of the material to SCC initiation (Chatterjee et al. 2001). Sensitive microstructures can also be found in the HAZ of SS and Ni-base alloys and within welds (Scott 1996; Lu et al. 2015). Studies have showed that weld interfaces and transition regions play a key role in SCC susceptibility, especially due to the formation of hard layers. SCC and corrosion fatigue of DMWs are a major concern of the nuclear industry. (Seifert et al. 2008; Vaillant et al. 2007)

Crack initiation and propagation

Since SCC usually involves alloys forming a surface film (passive layer, de-alloyed layer or tarnish), it is divided into two steps: the initiation of a crack on an apparently smooth surface and the propagation of the crack (Rebak & Szklarska-Smialowska 1996). (A final step is the final failure of components, when the stress in the remaining part of the material exceeds the fracture strength, but it is not dealt with here.) For a given alloy, many parameters can
affect both crack initiation and propagation, as well as the cracking mode (intergranular or transgranular). Among them are the temperature, the nature and concentration of solute species, the pH and the electrochemical potential (Trethewey 2008). Strain hardening is known to promote both crack initiation and propagation. Most mechanisms proposed for SCC deal with crack propagation and not initiation, simply assuming the presence of a pre-existing defect, although SCC often starts from a smooth surface. In that sense, SCC crack initiation remains a challenge, even more so because the transition between the two stages is continuous (Scott 1996).

It is not fully understood how a smooth surface develops a crack. The first step usually involves the formation of a defect or surface discontinuity on the protective surface film. This defect can be formed either by localized mechanical damage due to machining, grain boundary sliding or oxidation, creep, vacancy accumulation or other material flaws. Inclusions such as MnS, segregation of Si and P, sensitized microstructure and the presence of secondary phases such as sigma phase and Laves phases are detrimental (Scott 1996; Raja & Shoji 2011; Hänninen 1979). The chemistry of the environment and microchemistry of the material play an important role in SCC initiation (Betova et al. 2012; Lu et al. 2011). The presence of Cr2O3 and Cr-rich spinel oxides at SCC crack tips can lead to dealloying and selective dissolution (Bruemmer & Thomas 2001). In addition, the pH and the amount of dissolved hydrogen, oxygen, CO2 and hydrogen peroxide raise the electrochemical corrosion potential and have a significant effect on crack initiation time and propagation rate (Jones et al. 1989).
Pitting corrosion is a major cause of SCC initiation (Lu et al. 2005; Galvele & de De Micheli 1970). Pits form easily on ground surfaces. Indeed, local rupture of the passive film can lead to a small anode/large cathode situation which enhances local dissolution and promotes pit formation. Pits can also form at inclusions such as MnS (Frankel 1998). A key element is the transition from a pit to the crack, as the conditions for pitting and for cracking are entirely different (Trethewey 2008).

Once a crack has initiated, it can propagate. Cracking can be intergranular (IGSCC) or transgranular (TGSCC), with the appearance of a brittle mechanical fracture. SCC is a remarkable process because normally ductile metals display brittle-like fracture behavior (Sieradzki & Newman 1987). Intergranular or transgranular, cracks generally follow a path perpendicular to the tensile stress while often showing branching (Eliaz et al. 2002). Mixed mode of cracking can also be present. Intergranular corrosion is a preferential attack on the grain boundary vicinity. Grain boundary precipitation (carbides) and segregation (impurities) play a major role as they increase the reactivity of the grain boundary, notably by the enrichment of one alloying element or the depletion of a corrosion-resisting element. As an example, the sensitization of SS due to the precipitation of chromium carbides is a well-known issue (Briant et al. 1982; MacDonald & Urquidi-MacDonald 1991).

Eventough attempts have been made to form a unified theory, there is no universal mechanism of SCC in the sense that no mechanism can completely describe all cases of SCC. However, considerable progress has been made over the past 40 years. Different mechanisms have been proposed, that vary from one material-stress-environment system to another. The main idea is currently that a continuous spectrum of mechanisms operates in each system, with higher or lower contribution from the environmental or mechanical factors, depending on the situation (Rebak & Szklarska-Smialowska 1996). These mechanisms suggest either an exclusive or a limited role of dissolution in the cracking process. Some SCC mechanisms are continuous as they propose that the propagation of cracks is controlled by dissolution (purely electrochemical mechanisms). However, fracture surfaces indicating brittle mechanical failure with very little dissolution have led to the development of discontinuous mechanisms based on cleavage (Sieradzki & Newman 1987). In these discontinuous mechanisms, embrittlement of the material is first controlled by dissolution, and then followed by crack advance due to mechanical fracture (electrochemical-mechanical mechanisms).
Dissolution mechanisms

For SCC mechanisms based on localized dissolution of the alloy, anodic SCC is a commonly used term, referring to the anodic dissolution of the metal following a film rupture. On the other hand, cathodic SCC is never called as such, but includes mechanisms based on embrittlement by hydrogen produced during a cathodic reaction. The dissolution mechanisms propose the anodic dissolution of the metal as a crack propagation mechanism, where stress is simply helping the corrosive environment to reach the metal. The main mechanisms are the active path mechanism, the film-rupture model, the slip-dissolution model, the corrosion tunnel model and the coupled environment fracture model (CEFM).

The active path model is based on the chemical heterogeneity at the grain boundaries due to grain boundary precipitation or segregation. Change in the microchemistry of the GB vicinity creates an anode-cathode situation with the bulk metal, which leads to localized dissolution at the GB. Stress keeps the crack open, improving transport of reacting species. It is one of the earlier SCC models developed for SCC of stainless steels (Fang et al. 1994; Sheinker & Wood 1972). It is, however, unlikely to occur for alloys resistant to sensitization or producing rapidly protective oxide films. In that case, the active path has to be strain-generated as showed for the next models.

The film-rupture model is the older and best known of these models. It is based on the repeated fracture of a protecting film at the crack tip by localized plastic deformation, followed by the anodic dissolution of the bare metal which causes crack propagation (Newman 1981; Vermilyea 1972). The crack propagates as the rate of film rupture is greater than the passive film growth at the crack tip, especially in preferential zones having lower repassivation properties (Scott 1996). The crack tip then repassivates, and the process starts again. This model, however, can only operate if a steep plastic strain gradient is present at the crack tip (Sieradzki & Newman 1987).

In the slip-dissolution model, local plastic deformation produces a slip step in the protective film, with consequent dissolution of the bare metal until the film repair. As for the film-rupture model, the periodic propagation of the crack results from the succession of 3 steps: rupture of the passive layer, dissolution of the bare metal and repassivation (Smith & Staehle 1967; Ford 1982; Ford & Andresen 2011) (see Fig. 2.2). In order to retain a crack geometry, the rate of the anodic reaction on the adjacent walls must be sufficiently low relative to the crack growth rate. In other words, the crack walls must be passivated, while the dissolution occurs at the crack tip. If the repassivation rate is too slow, the crack tip is blunting. If the repassivation rate is too high, little dissolution can occur.
The strain rate at the crack tip is critical in the slip-dissolution model (Parkins 1972), and crack growth is due to the emission of dislocations from the crack tip (Lynch 1983). The slip-step dissolution model is often used but commonly understood as the simplest film-rupture model, since the role of the slip-step is reduced to the film rupture. Many other names have been given (slip dissolution-repassivation model, film rupture slip dissolution model, slip-oxidation mechanism, film rupture and repassivation model, etc.) but they can be undeserved and confusing. This model has obtained a prominent position in the nuclear reactor industry in the study of aqueous intergranular SCC since the 90’s (Ford & Andresen 2011) although it has its critics for not taking into account the effect of creep on the crack tip strain rate (Gutman 2007; Hall 2009). The corrosion tunnel model and the CEFM are further based on the slip-step dissolution model. In the corrosion tunnel model, groups of small corrosion tunnels form from the slip steps and grow until the stress in the remaining ligaments causes ductile deformation and fracture. In the CEFM, cracks propagate by anodic dissolution, but this dissolution is assumed to be controlled by a cathodic process occurring at the crack mouth and the following transport of corrosion products inside the crack to the crack tip (MacDonald et al. 1994).

**Fig. 2.5.** Schematic of the slip rupture of an oxide film, leaving the bare metal susceptible to dissolution before repassivation (Was 2017)

For austenitic alloys such as stainless steels or Ni-base alloys in nuclear power systems, the intergranular SCC mechanisms in high-temperature primary water are usually based on the slip-step dissolution and film-rupture models (Ford 1982; Ford & Andresen 1994; Rebak & Szklarska-Smialowska 1996; Andresen & Ford 2011) but other mechanisms such as IASCC and HIC play a significant role. Especially, the slip-dissolution model is not accepted as a mechanism for transgranular SCC (Pugh 1985).
Cleavage mechanisms

The previous models assume that crack propagation is related to the anodic dissolution of the metal after rupture of a passive film by localized strain. However, suggestions have been made that these strains are in fact not enough to break the film (Sieradzki 1990). They also fail to explain TGSCC, which, unlike IGSCC, does not follow a chemically active path. Recent theories have focused on the discontinuous nature of crack propagation and the cleavage features observed on the fracture surfaces, leading to the development of cleavage models. These are the tarnish rupture mechanism, the film-induced cleavage mechanism, the adsorption-induced cleavage mechanism and the surface-mobility mechanism.

The tarnish rupture model has been used to explain discontinuous transgranular crack growth (Chatterjee et al. 2001). A thick brittle surface film, or tarnish, forms on the metal that fractures by cleavage under the applied stress, leaving the bare metal to react rapidly with the environment. The film then grows again, and the cycle is repeated. The model is, however, not valid for IGSCC as the thick tarnish does not penetrate at the crack tip or the GBs.

In the film-induced cleavage model, anodic dissolution of the metal leads to the formation of a brittle surface film (Pugh 1985; Newman & Sieradzki 1987). This film can be a de-alloyed layer or an oxide. The crack proceeds through the film and is injected in the bulk metal. The crack propagates by cleavage for a limited distance before becoming progressively blunted by plastic deformation (see Fig. 2.3). Once the crack stops, the process starts over (Newman et al. 1989). The main difference with the tarnish rupture model is that the crack does not propagate only into the surface film, but also into the ductile matrix, but this hypothesis can be hard to validate (Ricker et al. 1993).

Fig. 2.6. Schematic diagram of the steps of the film-induced cleavage model for transgranular stress corrosion cracking, with a) formation of the surface film, b) rupture of the film by the applied stress, c) a sharp high-velocity crack is injected into the metal matrix, d) crack arrest and e) nucleation of a film on the blunted new crack tip (Ricker et al. 1993).

The adsorption-induced cleavage model is based on the hypothesis that adsorption of surface active species from the surrounding environment to the surface of the crack tip reduces the bond strength between adjacent atoms in the
metal lattice next to the surface. The stress required for cleavage fracture is reduced and the adsorption promotes the formation of dislocations near the crack tip (Westwood et al. 1967; Lynch 1983). Adsorption of hydrogen can lower the surface energy of the metal in ways similar to the adsorption-induced cleavage mechanism, but it is kept separated from SCC and is included among other models involving hydrogen embrittlement (Lynch 2011b; Rebak & Szklarska-Smialowska 1996).

Fig. 2.7. Schematic illustration of a crack in a solid, subjected to an increasing force F, with the bond A-A₀ representing the crack tip, and B a surface active liquid metal atom (Westwood et al. 1967).

Fig. 2.8. Schematic illustration of the concepts forming the atomic surface mobility model (Galvele 1995).

The **atomic surface mobility model** is based on the surface diffusion of atoms from the highly stressed crack tip vicinity to a new site of lower stress on the crack side. The crack advances one atomic space for each of these movements. The coefficient of surface self-diffusion will dominate the crack growth rate and
the role of the environment is to change the surface self-diffusivity of the metal. (Galvele 1993; Galvele 1995)

**Irradiation-assisted SCC**

Due to radiation induced by the nuclear reactions and the irradiation damages resulting in materials, irradiation-assisted stress corrosion cracking (IASCC) has been studied over the years and has been identified as a potentially critical phenomenon for core internals in light water reactors. The mechanism of IASCC is not fully understood, and it may have great significance for the life times of core components (Scott 1994).

IASCC is a result of the interaction of irradiation, material, environment, temperature and stress. In the material, the collision of an energetic particle with the lattice can displace one or several atoms through the lattice, leading to radiation damage. The extent of radiation damage is a function of temperature: at low temperatures, the vacancies stay in equilibrium and form clusters (black spot), while at high temperatures (>300°C), vacancy clusters are unstable and lead to void swelling (gas bubbles growing to form voids) and creep. Radiation induced segregation and precipitation are also among radiation damages, while radiation-matter interaction can lead to transmutation of alloying elements into detrimental species. The affected components eventually suffer from embrittlement and dimensional instability. In the environment, radiolysis of water into other species affects the corrosion potential. Radiation damage combined with a potentially more aggressive environment can make SCC initiation easier and accelerate crack propagation (Shoji et al. 1998; Was & Bruemmer 1994).

IASCC is a time-dependent phenomenon, which needs a minimum residence time or threshold fast neutron fluence to occur, but can then occur at very low stresses. The complexity of IASCC arises from the fact that irradiation has an impact on all the important variables (microstructure, composition of the environment and temperature). In addition, the fluence and time dependencies of IASCC are not known precisely at low temperatures (Aaltonen & Hänninen 1997).

**Hydrogen-induced cracking**

Hydrogen-induced or hydrogen-assisted cracking (HIC or HAC) was categorized as one SCC mechanism, since hydrogen plays a role in a number of cracking mechanisms. Indeed, corrosion reactions often result in the formation of hydrogen, which can diffuse or be absorbed in the metal lattice, reducing mechanical properties. Combined with stress, it can result in crack propagation
(Turnbull 1993). However, cracking of SCC resistant alloys or cracking occurring under constant stress in the presence of hydrogen but without visible corrosion reaction have led to consider HIC as a separate form of EAC. Hydrogen embrittlement (HE) refers to the action of hydrogen in reducing the mechanical properties (ductility or tensile strength) of alloys to a high degree, increasing cracking susceptibility. HIC refers to the cracking of an alloy under constant stress when hydrogen is present (Lynch 2011b; Gangloff 2003).

High-strength steels are particularly susceptible to this type of attack (Gangloff 2003). Nickel-base alloys are more resistant to hydrogen embrittlement than ferritic steels but, due to the slow diffusivity of hydrogen in nickel, hydrogen embrittlement must be taken into account. Hydrogen has played an important role in the PWSCC susceptibility of Alloy 600 (Smuk et al. 1999). Cracking along DMWs has often been associated with the exposure to hydrogen in service (Magudeeswaran et al. 2008).

Hydrogen is present in water, air and many other substances. It can enter the metal lattice during casting, manufacturing, surface cleaning, welding and during service life in hydrogen-rich environments. It can also be dissolved into an alloy during corrosion reactions. As such, anodic dissolution can have an indirect effect by controlling the amount of hydrogen. In nuclear power systems, hydrogen is deliberately added to the coolant to limit the effect of radiolytic oxygen. The interaction between hydrogen and the microstructure influences the hydrogen embrittlement sensitivity. Precipitates and inclusions act as hydrogen trapping sites, mostly at grain boundaries (Symons et al. 2001; Angelo et al. 1995). Grain size, nature and distribution of secondary phases and the degree of cold work are then among the major parameters affecting hydrogen embrittlement. Materials with impurities like sulfur and phosphorus segregated at grain boundaries have been found to be more susceptible to hydrogen-induced cracking. (Beidokhti et al. 2009; Zhao et al. 2008)

Depending on the source of hydrogen, hydrogen embrittlement can be internal or external, occurring because of hydrogen from the bulk metal or from exposure to a hydrogen-rich environment. Hydrogen is then transported to a localized region of high triaxial stress, such as a crack tip, where it can cause embrittlement and initiate a crack or accelerate the crack propagation. Therefore, three factors affect the process: the origin of the hydrogen, its diffusion and the embrittlement process itself. (Gangloff 2003)

Cracks resulting from HIC can be either intergranular or transgranular. They are not as branched as in SCC. Due to the embrittlement, there is usually little
macroscopic plastic deformation, resulting in a brittle fracture. But careful fractureographic examinations show that hydrogen embrittlement is associated with locally enhanced plasticity at the crack tip. As the distribution of hydrogen can be highly non-uniform, localized deformations can lead to highly localized failure by ductile processes, while the macroscopic deformation remains small (Cwiek & Zielinski 2006; Eliaz et al. 2002).

The most common mechanisms of HIC are related to internal high pressure bubbles, brittle hybrid formation, decohesion of the metal lattice, reduction of the surface energy by adsorption, interaction with dislocations, and enhanced plasticity. As for SCC, the mechanisms proposed for HIC are numerous. Most of them are based on empirical observations of the fracture surfaces, explaining that they focus on different aspects. The two main families consist of mechanisms explaining either solely an apparently brittle fracture or point out the role of localized plasticity (for more recent mechanisms based on observations using characterization tools with higher resolution). The scale of the interaction between hydrogen and dislocation is leading now to atomistic simulation (Song & Curtin 2011). Most recent research works have focused on the interaction between hydrogen and dislocation nucleation (Kirchheim 2010; Barnoush & Vehoff 2010).

In the group of models focusing on brittle fracture, the internal high-pressure bubble model involves the diffusion and entrapment of gaseous hydrogen to internal defects (microstructural voids or existing cracks) and a subsequent pressure build-up. The pressure, alone or in combination with a stress applied to the metal, is sufficient to initiate a crack or propagate an existing crack (Zappfe and Sims, 1941). This process can easily occur if the structure is exposed to a hydrogen-rich environment. The loss of ductility and the resultant cracking are dependent on the temperature and the strain rate. At high temperatures, a strong correlation exits between the hydrogen carrying capacity of dislocations and the ductility loss (Chatterjee et al. 2001; Eliaz et al. 2002; Lynch 2011b; Cwiek & Zielinski 2006). Another form of brittle cracking is explained by the brittle hydride model, in which brittle H-rich hydride phases form ahead of the crack tip and facilitate crack growth by cleavage (Birnbaum, 1979; 1990; Eliaz et al. 2002; Chatterjee et al. 2001). The decohesion model is the oldest of HE mechanisms. It involves atomic hydrogen migrating into the microstructure of the metal resulting in the reduction of the interatomic bond or cohesive strength of the metal lattice (Troiano, 1960, Oriani, 1972). Hydrogen accumulates at regions of high triaxial stress ahead of the crack tip, and can promote bond rupture and
microcracks, which then link with the main crack. It provides a point of nucleation for a crack or accelerates the crack propagation process (Scheider et al. 2008; Cwiek & Zielinski 2006). Another version of this model involves the adsorption of hydrogen at the crack tip or at imperfections on the metal surface, which reduces the surface energy of the metal and facilitates the initiation of a crack from a surface defect or the propagation of an existing crack (Petch, 1956, Oriani, 1972). The adsorption of hydrogen can have, however, an important role at internal interfaces between the metal matrix and particles (Rice, 1976). Furthermore, as in the adsorption-induced SCC, hydrogen adsorption at the crack tip can weaken atomic bond and promote dislocation emission from the crack tip (Lynch, 1979, 1997). These three models are the most straightforward in explaining genuine brittle fracture by intrinsic embrittlement (Delafosse & Magnin 2001).

Localized plasticity observed on the fracture surface has led to the development of several models pointing out the interaction of hydrogen with dislocations, for example, the emission of dislocations resulting from the accumulation of hydrogen at precipitates and second phases (Scheider et al. 2008; Barnoush & Vehoff 2010). In another example, hydrogen lowers the stacking fault energy and induces coplanar deformation at a crack tip, causing anchoring of dislocations and embrittlement. By lowering the interatomic bonds, hydrogen adsorption can also induce the dislocation injection to the metal from a crack tip and the crack propagation by localized slip (Cwiek & Zielinski 2006). In the hydrogen-enhanced localized plasticity model (HELP), absorption of hydrogen facilitates the dislocation generation and movement. It increases plasticity locally and the highly localized deformation leads to crack propagation. It explains the localized plastic features of HAC fracture surfaces. It has been observed in situ in TEM foils, but it has not been proved that it occurs in bulk specimens (Birnbaum, 1990; Birnbaum at al. 1997; Ferreira et al. 1998; Scheider et al. 2008; Cwiek & Zielinski 2006).

Finally, the corrosion-enhanced plasticity model (CEP) gathers most of the previous features (Magnin et al. 1996). In this model, vacancies are created at the crack tip by anodic dissolution and hydrogen is produced by cathodic reaction. This model assigns an indirect role to corrosion by localizing and enhancing plasticity at the crack tip along some slip planes. Hydrogen segregates in these slip planes and activates dislocations, which form pile-ups by interacting with obstacles. The resulting high local stress can initiate cracking. It has been argued that this is purely a SCC mechanism since it involves corrosion reactions...
As for SCC, no model can account so far for all features found in failures associated with hydrogen. Moreover, as the numerous denominations (HIC, HAC, HEAC, HE) show, there is still not a clear understanding of the role of hydrogen and its interaction with other forms of EAC.

As plants age, most important corrosion issues will center on stress corrosion cracking and the accelerating role of irradiation and cold work. It can be argued that the major SCC issue in PWRs is that of the nickel-base alloys used in steam generator tubes, as it represents almost 75% of the surface area of the primary circuit in contact with the coolant. The focus of this thesis is therefore on the microstructural factors affecting the SCC resistance of Ni-base alloys used in the primary circuit of PWRs.

### 2.3. Life extension of nuclear power plants and thermal ageing of materials

According to the IAEA, 273 out of the 442 operating reactors have been in service for more than 30 years as of 2016. As most nuclear power plants (NPP) were originally designed to operate for 30 to 40 years, it means that more than 60% of the existing NPPs will reach the end of their planned life in the near future. Three options are offered: these plants will be decommissioned and replaced by new NPPs or alternative sources of energy, or their planned service life is extended. In parallel, the privatization of electricity production and the deregulation of electricity markets (Tooraj & Pollitt 2005; Nagayama 2009) has had a significant impact on nuclear power, which has now to meet the market conditions and competition (Hewlett 1994; Kessides 2010). For nuclear power, construction accounts for most of the costs (capital cost), whereas for gas power plants, fuel costs are the highest (Adamantiades & Kessides 2009). High initial costs and long construction times make it more difficult for new NPPs to be competitive as new and more efficient coal and gas power plants with lower initial costs and faster construction times are being developed. This has led to a significant interest in extending the operational licenses of existing plants beyond the planned 30-40 years (Carter 2006).

Typically, the service life of current reactors has been or is being extended first to 60 years and new designs are planned to operate for over 60 years. This extension of the original design life for an additional 20 years means that the integrity of reactor components has to be maintained for an extra 50% of the planned service life. It introduces a wide range of potential materials aging issues that have to be considered in the renewal license process (Zinkle & Busby 2009). Typically, from 5 to 10 years before an NPP reaches the end of its design
life, preliminary analyses have to be carried out to determine the need for component replacements and/or upgrades to meet the new expected service life (U.S. Department of Energy 2012). Another approach is to make modifications to the operating parameters to enable higher power levels to be achieved, which usually means an increased flow and/or temperature.

Alltogether, the recent activities aimed at extending the service life of current reactors and to develop new reactor designs with greater capability are intended to meet the market conditions in order to maintain nuclear power as a baseload source of energy, but they put higher demands on materials that are already facing extreme conditions of stress, corrosion and radiation (Grimes et al. 2008; Guerin et al. 2009). It is therefore of tremendous importance to understand the behavior of materials and the challenges they will face in the new PWRs or during their extended service life, in order to delay or prevent failures. Electrical cables, insulation and instrumentation are the most susceptible to age-related degradation, but material degradation due to corrosion is the main costly problem affecting a small but important portion of piping and major equipment (Golay & Moinzadeh 1986).

The exposition of the materials over extended times to relatively high temperatures results in thermal ageing, which is defined as the degradation of a material over time caused by changes at the atomic level due to temperature. A general feature of thermal ageing of alloys used in NPPs is the reduction of mechanical properties such as ductility due to changes in the microstructure that, in turn, can increase the susceptibility to SCC and other mechanisms (May et al. 2010; Meyer et al. 2011). The models for the mechanisms of SCC, IASCC and HIC have been developed to account for different failure features that can be found depending on the alloy and the environment. No mechanism or model has so far been able to account for all types of failures, and damages resulting from thermal ageing certainly can affect the mechanisms, while it is difficult to predict or simulate the nature or amount of these damages for extended times up to 100 years. Indeed, the effects of phase precipitation at high temperatures on the mechanical and corrosion properties of these materials have been studied extensively but there is usually less data available concerning the effect of long-term thermal aging at lower temperatures (300-600 °C) (May et al. 2010). The simulation of long-term thermal ageing is performed isothermally using Arrhenius methodology. The samples are aged in a thermal chamber to bring them to the same state as after long-term service time. For reliable simulation, the testing parameters (ageing temperature, ageing time and activation energy) are most important and the accelerator factors should not be too high (Plaček
It means that such tests require usually tens of thousands of hours. They are, however, an important part for the qualification and long-term behavior characterization of materials used in NPPs.

Thermal ageing is therefore an ongoing issue in NPPs, especially in cast stainless steels, duplex stainless steels, high-Cr ferritic stainless steels and stainless steel welds. It is well known that thermal ageing of cast duplex SSs at service temperatures increases both hardness and tensile strength, decreases ductility and fracture toughness, and shifts the ductile-to-brittle transition to higher temperatures (Chung 1992; Chopra & Chung 1985). Cast, welds and duplex stainless steels have a duplex structure of austenite and ferrite phases. When subjected to a range of temperatures as low as 300 ºC, they may undergo phase precipitation of such as Cr-rich carbides at phase boundaries, nitrides, sigma phase and other intermetallic phases. It can result in brittle-like fracture with cleavage of the ferrite phase or crack at the ferrite/austenite phase boundary. For example, spinodal decomposition is responsible for a well-known embrittlement at 475 ºC resulting in severe reduction in ductility and toughness of materials with δ-ferrite, which separates into Cr-rich/Fe-depleted α’-phase and Cr-depleted/Fe-rich α-phase, and sensitization due to G-phase formation (Vitek et al. 1991). It results in δ-ferrite hardening, a decrease in fracture toughness, sensitization at the δ-ferrite/austenite phase boundary and increased SCC crack growth rates (Lucas et al. 2016). While the embrittlement can occur after several hundred hours of aging at 475 ºC, it is also operative at lower temperatures as low as 300 ºC after several tens of thousands of hours of exposure (May et al. 2010; Chandra et al. 2012).

Thermal ageing can affect Ni-base alloys in the range of temperatures between 300 to 550 ºC, in ways that are similar to those found in stainless steels. For example, Ni-base alloys exhibit an atomic re-ordering reaction under 550 ºC, based on the formation of an intermetallic phase, leading to hardness increase and a reduction in ductility (Marucco et al. 1995). As Ni-base alloys are used in critical applications of PWRs and as the service life of many NPPs is in the process of being extended, concerns arise on the effect of thermal ageing on the integrity of NPPs in the long term. As pointed out in previous chapters, Ni-base alloys are key materials in the safe operation of PWRs, they are used in the primary circuit for critical applications, and the main issue concerns their SCC resistance. Therefore, thermal ageing of Ni-base alloys and its possible effects on their SCC resistance are the main focus of this doctoral thesis.
3. Alloys 690, 52 and 152

3.1. Nickel-base alloys

3.1.1. Main use

Nickel-base alloys are within the gamma austenitic range of the ternary Ni–Fe–Cr phase diagram, which constitutes the backbone of material selection in the primary circuit of PWRs. Due to their high strength and good corrosion resistance at high temperatures, they are extensively used in high-temperature applications. These alloys have low corrosion rates due to the formation of a chromium-rich protective surface layers that grow very slowly at operating temperatures (Zinkle & Was 2013). The two major examples of industrial Ni-base alloy families are the INCONEL alloys and the INCOLOY alloys. Among these, Alloys 600 and 800 are especially corrosion resistant at high temperatures and have been used extensively in heat-treating equipment. In PWRs, Ni-base alloys are used for high-strength components (springs, fasteners and bolts), critical applications (vessel head penetrations, steam generator tubes) and welds. Ni-base weld consumables Alloys 82 and 182, following the Alloy 600 composition, have been widely used in dissimilar metal welds (DMW) throughout nuclear power systems. Alloy 690 is now replacing Alloy 600, mainly for steam generator tubes and vessel head penetration tubes, while its associated weld consumables Alloy 52 and 152 are used in DMWs. Nickel-base alloys have evolved for many years to meet more demanding in-service requirements. (Yonezawa 2012)

3.1.2. Historical developments of Alloy 690

The first steam generators manufactured in the mid-60’s used austenitic stainless steel tubing. Stress corrosion cracking (SCC) issues led to the use of Ni-Cr and Ni-Cr-Fe alloys for critical applications such as the reactor pressure vessel, piping and steam generators in the 60’s. Mill-annealed (MA) Alloy 600 (Ni-16Cr-9Fe) was originally developed in the 50’s as an alternative material to austenitic stainless steel for steam generator tubing with higher resistance to SCC in chloride solutions. Its associated weld consumables are Alloy 82 and 182. However, susceptibility to SCC led to the first corrosion-related failures in the
70’s. More inspections since the 80’s revealed the presence of cracks and leaks due to intergranular cracking in Alloy 600 tubes of PWRs due to intergranular stress corrosion cracking (IGSCC). Cracks initiated mostly in the HAZ of Alloys 182 and 82 welded to base metal Alloy 600. This was due to the presence of corrosion environment, residual stress, and material sensitization effects. This particular type of IGSCC in high temperature, high purity water is called primary water SCC (PWSCC) (Scenini et al. 2005; Andresen et al. 2007). It led to the development of a thermally treated Alloy 600 (Alloy 600TT) in the 70’s, with enhanced resistance to PWSCC and excellent in-service performance. However, PWSCC was eventually detected in Alloy 600TT, initially in highly strained mechanical plugs for SG tubes. In parallel, the nuclear industry continued to optimize the metallurgy and alloying leading to the thermally treated Alloy 690 (Alloy 690TT) in the late 80’s (Harrod et al. 2001). Alloy 690TT (Ni-30Cr-10Fe) has since then been the material of choice for new and replacement components in the primary circuit of PWRs. It is used mostly for control rod drive mechanism (CRDM) nozzles, pressurizer nozzles and SG tubing, although Alloy 800Mod (Fe-33Ni-22Cr) remains a possible choice (Alexandreanu et al. 2012).

Alloy 690 and its weld metals Alloy 52 and 152 were developed with up to 30 wt.% chromium in order to increase the PWSCC resistance. Studies showed a marked improvement in crack initiation times and CGR as compared to Alloy 600 and its associated weld metals Alloy 82 and 182 (Sui et al. 1997). Alloy 690TT has since been used not only for cold-finished materials such as SG tubes but also for hot-finished materials for several components of the pressure boundaries of PWR primary coolant systems due to its excellent resistance to PWSCC (Yonezawa 2012). Up to date no crack initiation has been observed in service for Alloy 690 components, although SCC crack propagation has been shown to be possible. However, the thermal stability of Alloy 690 in the long-term performance of nuclear power plants operating as long as 60-80 years remains of crucial importance (Young et al. 2013). In addition, the susceptibility of welds to SCC, IGSCC and PWSCCs depends not only on the properties of the base and weld metals, but also on the microstructural changes taking place at the interface (HAZ, fusion line) during welding and post-weld heat treatment (Ahluwalia 2012). The behavior of Alloy 690, Alloy 52 and 152 after long-term exposure to the PWR conditions, and especially thermal ageing, is therefore of major importance.
3.2. Main characteristics of Alloy 690

3.2.1. Typical microstructure

Alloy 690 (or Alloy 690TT) is an austenitic, solid-solution strengthened nickel-base alloy with a face-centered-cubic (fcc) structure (see Fig. 3.1). For nuclear applications, its composition is mainly 58 wt.% Ni, 28-31 wt.% Cr, 7-11 wt.% Fe and less than 0.04 wt.% C. It is usually heat treated with a mill anneal at high temperature followed by a thermal treatment (TT). The alloy has a low solubility for carbon, and its microstructure normally contains carbides. The aim of the heat treatment is to reduce intragranular carbide precipitation in favor of intergranular carbide precipitation.

![Fig. 3.1. Microstructure of Alloy 690 showing intragranular Cr-carbides, twin boundaries and TiN particle (golden) at GB.](image)

The microstructure of Alloy 690 consists of a single austenitic phase with annealing twins formed after the heat treatment. It shows random grain orientation, with little to no texture. Even after the heat treatment, intragranular carbides are still dispersed in the matrix, but precipitation mainly occurs at the grain boundaries. Intergranular carbides can be semi-continuous or continuous. The precipitate phases are chromium carbides of the type $M_7C_3$ and $M_{23}C_6$. However, as the higher chromium content affects the stability of the $M_7C_3$ carbides, the most common precipitates both in the matrix and at the grain boundaries are $M_{23}C_6$ carbides, which nucleate often during the first stages of precipitation, mainly at GBs, twin boundaries and intragranular sites such as TiN particles.
M23C6 is a more general notation for Cr23C6 carbides, as Ni, Mo and Fe can often substitute partially for Cr. They have a size of about 0.5 μm. The amount of M23C6 carbides varies with carbon content and thermal exposure of the material (Shen et al. 2014; Olszta & Toloczko 2011). The crystallized M23C6 carbides forming during solidification are called primary carbides and those precipitated during later thermal treatment are called secondary carbides. Primary M23C6 carbides are incoherent with the metal matrix in Alloy 690TT, but secondary M23C6 carbides are mostly coherent with the matrix (Yonezawa et al. 2015). M23C6 carbides have either fcc or complex cubic structures (Inoue & Masumoto 1980; Yong-Hua et al. 1989). M23C6 carbides have a fcc structure with a lattice parameter between 1.057 to 1.068 nm, about three times that of austenite, producing the typical electron diffraction pattern showed in Figure 3.2.a (Ramirez & Lippold 2004). In addition to GBs, M23C6 carbides precipitate on incoherent and coherent twins, where they form long plates parallel to the twin boundaries, typically in {111} planes (see Fig. 3.2.b). Their formation mechanism is controversial, with studies pointing out the pinning of dislocations due to nucleation of carbides on the twin boundary and the growth of M23C6 in the stacking fault, while others suggest that the mechanism is related to residual stress (Sourmail 2001).

![Fig. 3.2. TEM imaging of intergranular M23C6 carbides (Sourmail 2001).](image)

In addition, the formation of Ti(C, N) and TiN particles appears to be unavoidable although they are less numerous. The size of TiN particles varies between 1-8 μm and they are dispersed randomly in the matrix. They appear golden in color under optical microscopy, with a predominantly rectangular shape. They have a hexagonal crystal structure and the vicinity of large, faceted TiN is a preferential site for nucleation for M23C6 (Kuo & Lee 2002; Dutta et al. 2007). The
gamma austenitic phase crystallizes first, titanium carbo-nitrides (mainly TiN) crystallize next and M$_{23}$C$_6$ carbides crystallize near the end of solidification.

![Image](image.jpg)

**Fig. 3.3.** Characteristics of M$_{23}$C$_6$ carbides, with a) a typical diffraction pattern at an Alloy 52 grain boundary with M$_{23}$C$_6$ carbides, showing a cube-on-cube orientation relationship and the 3:1 ratio between the lattice parameter of the carbides and that of the austenite matrix (Ramirez & Lippold 2004) and b) M$_{23}$C$_6$ plates growing from a twin boundary (Sourmail 2001).

### 3.2.2. Chemical composition and properties

Alloy 690 has a good resistance to SCC in many environments. It has been tested extensively for resistance to SCC in high-temperature water such as encountered in nuclear steam generators, showing that the alloy is highly resistant to cracking in chloride containing water, oxygen-containing water and deaerated water. To give a comparison, stressed steam generator U-bend tubes of Alloy 690 in polythionic acid showed no cracking after exposure for 720 h, while sensitized 304 SS cracked within 1 h.

At room and elevated temperatures, Alloy 690 displays high yield strength (283 MPa at RT) and ultimate strength (714 MPa at RT), and good ductility (elongation to fracture at RT is 48%). Its Young’s modulus is 211 GPa, but drops to 190 and 175 GPa at 216 and 538 °C, respectively. According to manufacturer’s datasheets (Special Metals), Alloy 690 retains a substantial level of tensile properties at high temperatures, with temperatures over 540°C required to produce significant decrease in strength. In addition, Alloy 690 has a high degree of metallurgical stability, forming no embrittling intermetallic phases, such as sigma phase, during long-time exposure at elevated temperatures. Datasheets show that room temperature tensile properties and impact toughness of annealed Alloy 690 are not significantly affected by exposure to critical intermediate temperatures for 12,000 h and longer (UNS No6690/W.Nr.2.4642 2002). The data provided, however, concerns Alloy 690 aged at temperatures over 565 °C. The choice of the ageing temperature is critical, and can affect the results, as will be seen in Chapter 6.
3.3. Thermo-mechanical history

3.3.1. Processing and inhomogeneous microstructure

The main product forms of Alloy 690 are hot-rolled plate, hot-extruded bar and tube. Thin section, small diameter tubes such as steam generator tubes are made using a cold-finishing process, while thick and large diameter pipes or forged materials, such as control rod drive mechanism (CRDM) adapter nozzles and RPV nozzles are made using a hot-finishing process (Yonezawa et al. 2005). Alloy 690 products can be water quenched or furnace cooled, and the microstructure of the alloy depends on the thermo-mechanical processing history of the product. Hot-extruded bars show significant intergranular precipitation, while tubes show a preferential orientation of the grains parallel to the tube axis and fine grain structure at the surfaces. In addition, two kinds of banding are observed in Alloy 690 depending on the manufacturing method: carbide banding and grain size banding (see Fig. 3.3). It is suggested that the banded structure and the large chromium carbides observed along the GBs in Alloy 690TT depend on differences in chemical composition and fabrication process. The main explanation for banding is that prior GB carbides do not dissolve when the working temperatures are too low, retaining the prior GBs and creating bands of fine grains adjacent to coarser grains. It can also be caused by TiN particles of a high stability, which pin grain boundaries during recrystallization (Shen et al. 2014). Banding appears more readily in billets and plates, while extruded Alloy 690 usually shows an ideal microstructure. Banding is detrimental as an inhomogeneous microstructure can retain more residual strain and affect the SCC resistance (S. W. Kim et al. 2015).

![Fig. 3.4. Longitudinal sections of an Alloy 690 billet showing a) carbide banding and b) grain size banding and isolated coarse grains (Willis et al. 2011).](image-url)
3.3.2. Effect of heat treatment on the IG carbide precipitation

Heat treatments for nickel-base alloys are generally i) annealing at temperatures between 700 and 1200°C depending on the composition, ii) stress relieving at temperatures between 430 and 870°C, iii) stress equalizing, iv) solution treating and v) age hardening. Their goals are mainly to soften the alloy by decreasing its hardness, removing residual stresses and restoring ductility, or to harden it by increasing the strength properties. In the case of Ni-base weld metals, post-weld heat treatments (PWHT) are often used to achieve the full strength of the weld. The most common softening heat treatment is annealing, which consists of heating the alloy above a critical temperature, maintaining in temperature and cooling. The three stages of annealing are i) recovery, during which dislocations are removed or rearranged, ii) recrystallization, especially in highly strained zones, and iii) grain growth.

Solution annealing (SA) heat treatments are used for Alloy 690 to minimize the effects of cold work and banding, although banding can remain an issue if the annealing temperature is too low. The grain size increases and hardness decreases with increasing the temperature and the duration of the solution annealing heat treatment. A typical procedure for Alloy 690 is solution annealing at 1100 °C for 30 min and water quenching (WQ). SA dissolves most of the M23C6 carbides, resulting in carbide-free GB structure (Zagal et al. 2008). In addition to the homogenization of the alloy, heat treatments of Alloy 690 also aim to reduce intragranular carbides in favor of intergranular carbides. Low temperature heat treatments following solution annealing will precipitate M23C6 carbides in the GB region but will barely affect the grain size. Intragranular carbides will also precipitate. Typical heat treatments are performed at 700 °C for up to 72 h, followed by WQ. However, ageing of Alloy 690 at lower temperatures will also lead to the precipitation of intergranular carbides over longer times. Studies point out that the heat treatment at 700 °C starts to precipitate discrete intergranular carbides within 4 to 12 h. The amount of carbides increases with the duration of the heat treatment and the morphology of the intergranular carbides changes from discrete to near-continuous over longer times (Casales et al. 2002; Dutta et al. 2007). As seen in Fig. 3.4, the size of the carbides increases with the temperature of the low temperature heat treatment. The discontinuity of the carbides was noticed to increase with the temperature of the heat treatment (Hong et al. 2005).
Fig. 3.5. Carbide morphology of Alloy 690 after a) solution anneal at 1150°C for 1 h, b) solution anneal at 1150°C for 1 h then heat treatment at 700°C for 1 h, c) as-received and d) solution anneal at 1150°C for 1 h then heat treatment at 800°C for 1 h (Hong et al. 2005)

3.3.3. Sensitization at grain boundaries

Many studies have shown that the grain boundary misorientation strongly affects the precipitation of Cr-rich carbides. Coarse and discrete carbides precipitate at random high-angle grain boundaries, while dense fine and faceted carbides precipitate on low-angle grain boundaries (Lim et al. 2004). Carbides precipitate mainly at the dislocation junctions on the grain boundaries with high density dislocation networks. They grow dendritically, and the surface energy of grain boundary influences the carbide shape, size and distribution (Li et al. 2010). The consequence of the intergranular precipitation of carbides is to create a chromium-depleted zone near the grain boundaries. The depleted zone usually gets wider as the ageing temperature and/or duration is increased. It is a traditional cause of IGSCC susceptibility in austenitic alloys, but intergranular carbides have mostly been considered to be beneficial in the case of Alloy 690 (Hwang et al. 2013; Jiao et al. 2010).

Solute and impurity atoms segregate at the grain boundaries before the nucleation of carbides and affect the precipitation behavior of carbides. B, C and Si segregate to the grain boundaries in Alloy 690. In addition, Cr atoms migrate from the matrix to the vicinity of the grain boundary due to their strong interaction with C atoms. They co-segregate with the C atoms in some regions of the
grain boundary prior to the formation of $\text{M}_{23}\text{C}_6$ carbides (see Fig. 3.5) (Li, Xia, Liu, et al. 2013).

At the early stage of carbide nucleation, when the density of excess C atoms is too small for the nucleation of $\text{M}_{23}\text{C}_6$, chromium atoms are not consumed quickly and the chromium-depleted zone near the grain boundary commonly observed is not present, yet (Thuvander et al. 1999). The $\text{M}_{23}\text{C}_6$ carbides form later due to the excess of segregated Cr and C atoms. The precipitation of carbides substantially consumes the carbon in solution. Carbide growth slows down before stopping once the amount of carbon available is too low. However, volume diffusion of chromium from the matrix continues (Casales et al. 2002). The evolution of Cr concentration at grain boundary is therefore: i) enrichment at the grain boundary before carbide nucleation, ii) depletion at the grain boundary after carbide precipitation, and iii) self-healing after the growth of carbides, resulting from the diffusion of chromium from the matrix to the depleted zone (Li, Xia, Zhou, et al. 2013). Sensitization at the grain boundaries and self-healing are both related to the diffusion of chromium, but diffusion along the grain boundaries is faster than volume diffusion from the matrix. It explains that healing occurs after longer heat treatment, once carbides have already precipitated (see Fig. 3.6) (Casales et al. 2002).

Heat treatments induce segregation of impurities to grain boundaries, chromium depletion and carbide precipitation at the grain boundaries and in the matrix. In addition to heat treatments which are planned, alloys can experience similar levels of temperatures in the heat-affected zone of welds. Both in the heat-treated alloy or in the HAZ, the chemical composition and the structure of the grain boundaries play a critical role in the resistance to intergranular attack and IGSCC of Alloy 690. Particularly, the nature of the intergranular carbides

![Fig. 3.6. Concentration profiles of Cr, C, B and Si across the grain boundary (Li, Xia, Liu, et al. 2013).](image)
and their effects on both the stress concentrations and on the surrounding chemical composition are of crucial importance and have been a major source of failures for former Alloy 600 and associated Alloy 82 and 182.

![Fig. 3.7. Evolution of the Cr concentration profile from the grain boundary to the grain matrix depending on the duration of the sensitization heat treatment at 700 °C (Casales et al. 2002).](image)

### 3.4. Alloy 690 in weldments

#### 3.4.1. Alloy 52 and 152 weld metals

Many welds found in NPPs are made from metals of different compositions, such as when cladding structural LAS with SS for corrosion resistance or joining of metals with differences in structure and properties (Nelson et al. 1999). A typical example is a weld between a ferritic LAS and an austenitic stainless steel using a nickel-base filler metal in PWRs. The dissimilar metal welds (DMW) are an advantage in terms of cost reduction and performance, but they create major weak points in the structure. In order to minimize the risk of weld failures, a crucial point is the selection of a filler metal. The filler metal must have enough strength, ductility and corrosion resistance for service. In addition, it must match the properties of the two base metals: coefficient of thermal expansion, tensile and yield strength, chemical dilution without forming defects or increasing susceptibility to cracking (Karlsson 1995).

Ni-base alloys, in addition to their own mechanical and corrosion resistance properties, present intermediate thermal expansion properties compared to those of ferritic LAS and austenitic base metals, and have a low solubility for carbon. As compared to SS filler metals, nickel-base alloys have increased the service life of DMWs by reducing carbon migration at the interface and differential expansion strains (Payne 1969). However, Ni-base alloys are in practice...
more difficult to weld than SS fillers. Their weldability and the resulting mechanical properties depend on the solidification behavior, which in turn depends on solute redistribution of alloying elements. Ni-base filler metals are subject to ductility dip cracking (DDC), hot cracking and reheat cracking. Hot cracking is a major problem in the welding of austenitic alloys (Hänninen et al. 2007). It is associated with low melting point eutectics such as FeS, TiC and NbC or Laves phase, which extend the solidification temperature range (McCracken & Smith 2011). The formation of hot cracks is usually explained by the presence of a liquid film under tensile stress at GBs. The presence of the liquid is often related to the segregation of impurities and depends on the chemical composition of the alloy. Hot cracking is reduced with smaller solidification temperature ranges. (Hänninen et al. 2008)

Alloy 600 and its associated weld metals Alloy 82 and 182 show good weldability and they have been used extensively in BWRs and PWRs, most notably in the steam generator tubing and the reactor pressure vessel nozzle safe end welding. They proved, however, susceptible to SCC, IGSCC and PWSCC, and have led to in-service failures. The filler metals Alloy 52, 152 and 52M were developed based on the composition of Alloy 690 as a replacement (Bruemmer et al. 2005; Lee & Wu 2010). They can take into solution Ni, Cu, Cr, and Fe upon dilution from base metals and, with higher chromium content, they show better SCC resistance than Alloy 82 and 182. With lower niobium content, Alloy 52 has a smaller solidification temperature range than Alloy 82, which is beneficial against hot cracking (Kuo & Lee 2002). There are less precipitates in Alloy 52 than in Alloy 82, especially less Nb-enriched precipitates, and the precipitates are mostly TiN and TiC in the interdendritic zones and at the GBs. The precipitation is increased with PWHT (Lee & Jeng 2001). The main consequence is a coarser dendritic structure and lower average hardness of Alloy 52, which also has a lower tensile strength than Alloy 82.

Despite their better PWSCC resistance, Alloy 52 and 152 suffer from ductility dip cracking (DDC). This has led to the development of Alloy 52M and 152M with increased amount of boron and zirconium at GBs. Further, Alloy 52MSS has been developed with higher Nb and Mo addition to resist DDC. Mo and Nb segregate in the interdendritic regions, and precipitate as MC (mostly NbC) carbides at higher temperatures as opposed to the M23C6 carbides that form at low temperatures in Alloy 52 and 52M. They are therefore effective to pin GBs, creating serpentine GBs that resist sliding and thus improve DCC resistance (Kiser et al. 2010). However, increased Nb content and related NbC eutectic reactions increase the solidification cracking susceptibility and are detrimental to hot
cracking resistance. Laves phase may also form due to the segregation of Nb and further extend the solidification temperature range (McCracken & Smith 2011; Alexandrov et al. 2011).

The main defects present in Alloy 152, 52 and 52M welds are IG cracks. The fewest cracks are present in Alloy 152, and the greatest number of weld cracks is found in Alloy 52M. These cracks are related to secondary phase precipitates. Among them, TiN is the prevalent feature leading to weld cracks. The presence of these cracks may have significant impact during the service life. They can act as stress concentrators or be a preferential corrosion site. This makes them particularly susceptible to SCC. (Bruemmer et al. 2009)

Despite the fact that they are used commercially for the welding of Alloy 690, there are few papers available in the literature regarding the characteristics of these weld metals (Kuo & Lee 2002), but a strong research effort is starting to give results. In particular, there is still little knowledge about their long-term behavior since no in-service experience is available, yet. It is a crucial issue, especially for nuclear systems, which have a long (and extending) service life and for which failures are potentially very severe. Previous failures and new concerns are mostly related to the interfaces of the welds, that is, the transition zones between the weld metal and the base metals. These narrow zones undergo different metallurgical changes during welding, PWHT or long-term ageing, which have to be characterized in order to comprehend the long-term behavior of the components (Lundin 1982; Nelson et al. 2000).

3.4.2. Use in dissimilar metal welds

A DMW will generally present at least two fusion lines, between the weld metal and the base metals or buttering layer. The transition zones of the DMW interface are usually classified as heat-affected zone (HAZ), partially-melted zone (PMZ) and unmixed zone (UMZ). The HAZ of the base metal is subject to solid-state transformations (carbide dissolution, grain growth) without changes in composition. In the PMZ of the base metal, temperatures between the liquidus and solidus lead to various amounts of liquation, which have huge influence on the microstructure (localized melting of secondary phases, constitutional liquation of certain particles). The composition remains identical to that of the base metal. The UMZ is a stagnant boundary layer of completely melted and re-solidified base metal mixed with the filler metal, leading to a composition gradient. The composition gradient is very important in terms of microstructure and performance. The classification of microstructural zones can become more com-
plex in the case of weld repairs such as overlays, resulting in a weld with an increased number of materials and zones: aged and new base metals, aged and new weld metal, aged and new HAZ (Hyde et al. 2001). DMWs have often been observed to fail before the components reach their expected service life. The characterization and control of the HAZ, PMZ and UMZ is, therefore, of particular concern since they are involved in most of the in-service failures (Nelson et al. 1998). Especially, the interface depends greatly on the nature of the metals to be joined: ferritic/austenitic and austenitic/austenitic interfaces present very different features. The intermetallic compounds formed in these regions have to be investigated to determine their strength and susceptibility to cracking and corrosion (Nelson et al. 2000). A typical example is the weld of a ferritic LAS to Alloy 690 or austenitic SS using Alloy 52 or 152 filler metal.

3.4.3. Heat-affected zone of Alloy 690

This type of interface occurs between an austenitic Ni-base alloy or SS base metal and a nickel-base weld metal. A typical example in a modern PWR is the interface between Alloy 690 and one of its weld metals Alloy 52 or 152 at the joint between the RPV and its head penetration tubes. The interface is by nature rather homogeneous, since both sides of the fusion line are austenitic, with very low carbon contents. The fusion lines show fewer changes as compared to the ferritic/austenitic interfaces and it can be difficult to distinguish between Alloy 690 base material, HAZ, PMZ and UMZ. However, typical DMW microstructures are observed such as GB thickening and liquation in the HAZ, which are increased by PWHT along with the formation of Type II boundaries (Soares et al. 2007). An approximation of Alloy 690 interface (see Fig. 3.7) can be based on a grain size change from the base metal to the HAZ to PMZ to UMZ.
Further, the transition from the UMZ to the weld metal is indicated by carbides precipitated along the dendrite cores as the PMZ region with elongated grains has few particles on its boundaries. Cr3C is the major precipitate, along with TiC particles (Moss & Was 2012). In addition to the changes in the carbide precipitates, and although the microstructures change in a less dramatic fashion than in ferritic/austenitic fusion lines, the HAZ of Alloy 690 and the interface with the weld metal can retain residual strain to levels comparable to highly cold-worked materials. It can increase greatly the susceptibility to SCC and IGSCC (Lu et al. 2015).

3.4.4. Ferritic-austenitic interface with Alloy 52 and 152

The other type of interface commonly encountered in Alloy 52/152 DMWs in PWRs is the ferritic/austenitic interface. A typical example is the weld of a ferritic LAS such as SA 508 to stainless steels using Alloy 52 or 152 filler metals. These alloys present severely different composition, especially concerning the carbon and chromium content. Due to these differences, a composition gradient forms at the interface. A complex microstructure occurs due to the mixing and diffusion of alloying elements, notably carbon migration. The reduced chromium and nickel contents in the transition region due to dilution effects tend to increase the SCC susceptibility while the formation of hard and soft layers,
driven by the composition gradients, lead to mechanically weak points in the UMZ or PMZ and increase the strength mismatch at the interface. The key microstructural factors in the formation of these zones are carbon-depleted zone (CDZ), carbides, martensite and Type II boundaries. (Peng et al. 2005; Rajeev et al. 2001; Lundin 1982)

CDZ results from the carbide dissolution and carbon migration from the LAS HAZ to the nickel-base weld metal near the fusion line. The difference in chromium content and the high amount of other carbide formers (Nb, Mo) result in different carbon activities, promoting the carbon diffusion. This phenomenon is usually increased markedly by PWHT (Sudha et al. 2002). In the LAS, it leaves a layer of ferritic grains with low hardness and promoting creep at high temperatures (Lundin 1982). The phenomenon is accentuated by the grain coarsening at the fusion line, due to the high temperatures underwent by the material. Martensite has often been observed within the UMZ of the weld. It is due to the formation of intermediate compositions with high hardenability turning to martensite upon rapid cooling from welding. It leads to steep mechanical property gradients at the interface and has been related to failures of DMWs (Nelson et al. 1998). In addition to the martensitic layer, carbon migration from the LAS side to the weld metal can result in carbide precipitation in the weld metal which is a preferential cracking site. Ni-base alloy weld metals have reduced the width of the martensitic layer and the carbon migration from the LAS side as compared to the stainless steel weld metals. However, the low diffusivity of carbon in Ni-base weld metals results in the accumulation of carbon close to the fusion line. It can lead to carbon build-up of about 1.5 wt.% C. A narrow (3-5 μm) planar solidification front can also be observed close to the fusion line inside the weld metal. It shows neither dendritic structure nor precipitation, and has very steep composition gradients and high hardness levels (between 500-800 HV0.1) due to the carbon build-up (Alexandrov et al. 2013). The precipitation of carbides when the solubility limit of carbon is exceeded is also associated with high hardness levels and brittle microstructures susceptible to hydrogen-assisted cracking. The presence of martensite/austenite mixtures at the weld interface is often observed due to the non-uniform distribution of alloying elements within the transition zone as well as swirls of base metal with mixed BCC/FCC structures turning into martensite after PWHT (Nelson et al. 1999; Nelson et al. 2000). Type II boundaries are parallel to the fusion line, typically less than 100 μm away in the weld metal. They result from the different crystal structure of the materials: after austenization of the LAS at high temperature, the original fusion line becomes an austenitic/austenitic boundary, which can
migrate into the austenitic weld metal. The distance between the Type II boundary and the fusion line is then controlled by the composition and temperature gradients within the transition region. They are a common feature related to the failure of DMZ. The presence of Type II boundaries reduces SCC resistance and leads to intergranular cracking under simulated reactor coolant conditions (Chung et al. 2011). The weld interfaces have to be characterized as they represent a major weak point of the structure. In PWRs (as well as in BWRs), the heat-affected zones of the welds have been a usual location of failures (Hänninen et al. 2006).

As mentioned in the previous chapters, the other main source of concern for Ni-base alloys is the integrity of steam generators. Ni-base alloy families typically include a base metal and its associated filler metals based on the same composition, such as Alloys 600 and 82/182 or Alloys 690 and 52/152, which are studied simultaneously. Indeed, the characterization of the microstructures and long-term SCC behavior of the nickel-base alloys used both in DMWs and steam generators is a crucial aspect of the structural integrity assessment of PWRs.

3.5. SCC resistance of Alloy 690 components

Historically, Alloy 600 was found to be difficult to crack in high-temperature, high-purity water in laboratory, encouraging the belief that it would be resistant in service. At first, few cracking-related failures were reported even after years of operation. After an incubation time of 10 to 12 years, however, many plants began to experience cracking. Similarly, Alloy 690 has always been considered very resistant to corrosion and SCC. For that reason, most research has been conducted on fretting wear, which is purely mechanical and occurs as the result of a low amplitude motion between contacting components, as it was considered a more likely source of damage on Alloy 690 components (Hong et al. 2005). Operating experience and testing continue to show excellent PWSCC resistance of Alloy 690 under normal PWR conditions (Fyfitch et al. 2012), but there is no evidence to affirm that Alloy 690 is immune to IGSCC. Cracks can grow at moderate or high rates in PWR primary water under certain conditions. Issues rise especially with the effect of residual strains at the weld interfaces and within the base metal because of cold work and thermal ageing. Another common thought is that GB carbides in nickel-base alloys are always beneficial to SCC resistance, which may prove to be false (Andresen et al. 2012). A concern today is that the incubation time for the cracking of Alloy 690 may simply be longer than that of
Alloy 600, which would only postpone the start of cracking in many plants. Current studies are therefore focused on the microstructures, processes and water chemistries that may increase the susceptibility of Alloys 690 and 52/152 to SCC crack initiation and growth (Zinkle & Was 2013). Especially, there is a need to consolidate the knowledge base on the PWSCC of Alloys 690, 52 and 152, for both the PWSCC initiation and propagation. An extensive work has been done following the failures related to Alloys 600, 82 and 182. The determination of factors of improvement (FOI) of Alloys 690, 52 and 152 over Alloys 600, 82 and 182, requires the use of the exactly same SCC test conditions: processing, loading and environmental conditions. Since the initiation time for the PWSCC of Alloy 690 is much longer than that of Alloy 600, it also requires longer ageing tests. There is especially a need to obtain PWSCC initiation data for Alloy 690 and 52 in order to develop inspection requirements for components.

3.5.1. Effect of chemical composition and IG carbide precipitation

With more than 30 wt.% Cr, the chemistry of Alloy 690 results in a higher PWSCC resistance than that of its predecessor Alloy 600. The high chromium content increases its resistance to general corrosion, whereas the high nickel content increases its resistance to caustic and chloride SCC (Crum et al. 1982). The analyses of Alloy 600 tubes taken from steam generators have showed that carbide distribution was of great importance in the PWSCC process: cracking was found in tubes with intragranular carbides while tubes with grain boundary carbides were free of cracking (Aaltonen & Hänninen 1997). The good PWSCC resistance of Alloy 690 is attributed to a high equilibrium chromium concentration at the intergranular carbide interface with the matrix (Yu & Yao 1990). Indeed, it is known to be more resistant to IGSCC after thermal treatment, where intragranular carbides dissolve at high temperatures and precipitate at the grain boundaries upon cooling. Greater grain boundary carbide coverage in Alloy 690 has been seen to increase the resistance of Alloy 690 to SCC in high–temperature high–purity water (Jiao et al. 2010; Kai et al. 1989). Corrosion susceptibility is associated with the chromium-depleted zone along the grain boundaries, resulting from the precipitation of M\textsubscript{23}C\textsubscript{6} carbides. However, the high carbon solubility in Alloy 690 allows a fast carbide precipitation and chromium will continue to diffuse from the matrix once the carbon in solution has been consumed, recovering the SCC resistance (Casales et al. 2002). The high chromium content reduces sensitization due to chromium depletion during carbide precipitation at GBs (Yu & Yao 1990). From a mechanical point of view, the removal of intragranular carbides promotes accommodation of the loads within grains,
while intergranular carbides act as low energy dislocation sources, promoting a homogeneous deformation. The SCC resistance is higher when the distribution of intergranular carbides is continuous or semi-continuous rather than discrete (Casales et al. 2002; Dutta et al. 2002). Intergranular carbides effectively promote SCC crack tip blunting and decrease the crack tip stress state, increasing the SCC resistance (Bruemmer et al. 2013). The $\text{M}_2\text{C}_6$ carbide morphology is, however, of great importance. Discrete carbides are considered beneficial, but they are harmful when precipitating as continuous films at GBs (Yonezawa et al. 2015).

Once a crack is initiated, however, propagation under PWR condition is possible (Zagal et al. 2008). As mentioned in the chapter dealing with SCC mechanisms, pitting corrosion is a major cause for SCC initiation. Pits form readily on inclusions, and the shape, size and volume fraction of these inclusions play therefore an important role (Trethewey 2008). The presence of larger TiN particles in Alloy 690 is detrimental, as the maximum degree of misfit is found at the interface between the particles and the matrix. They are therefore a preferential site for pitting corrosion and can act as passive film breakdown sites (Dutta et al. 2007).

The question of how the cracks propagate is still open, although it is a general issue concerning most SCC mechanisms. The most used mechanism to explain the SCC of Alloys 690, 52 and 152 is the slip-dissolution model, in which local plastic deformation produces a slip step in the protective film, with consequent dissolution of the bare metal until the film repair (see Chapter 2.2.2). However, the effect of dissolved hydrogen on SCC growth in Alloy 690 in high temperature water still requires investigation. Alloy 600 presents a maximum SCC growth rate in the proximity of the Ni/NiO phase transition. For Alloy 690, although the dependence on the amount of dissolved hydrogen is lower than that of Alloy 600, introducing hydrogen to deaerated water promotes SCC growth (Peng et al. 2012). The addition of hydrogen to Alloy 690 reduces the ductility and fracture toughness and the degree of embrittlement increases with increased carbide precipitation. One explanation is that carbides, acting as hydrogen trapping sites, increase the local hydrogen concentration at their interface with the matrix, resulting in lower fracture strain (Symons, 1998). Intergranular carbide precipitation affects the strain energy of the grain boundary and results in a hardness difference between the grain boundary vicinity and the matrix. It can be detrimental to the SCC resistance, where strain localization is the major factor (Bruemmer et al. 2013).
The chemistry of Alloy 690 promotes a good IGSCC resistance. However, the structural factor remains crucial in controlling the passive film breakdown when considering the film-rupture model. Although extensive intergranular precipitation seems to increase the SCC resistance, features such as banding, inclusions, micro-voids at grain boundaries, fractured second phase particles and brittle intermetallic phases all weaken the passive film and enhance the CGR. Deformation by cold work, residual strain or carbide-band structure can increase the CGR to more than $10^{-8}$ mm/s (Peng et al. 2012). In addition, intergranular cracking in austenitic alloys is still an unsolved issue up to now. It has been related to corrosion, with IGSCC and PWSCC of Alloy 600.

Another important traditional concern with Alloy 600 has been the creep mechanisms in Alloy 600 MA in primary water, studied as a possible factor of increased PWSCC susceptibility. Creep is important not only for its intrinsic effect on the material behavior, but also for its effect on the integrity of the oxide film. Operating temperatures are relatively low but dislocation creep of the alloy can be expected (Frost & Ashby, 1982). The Creep damage mechanism views IG cracking as the results of creep void nucleation and growth at GBs (Angeliu et al. 1995). Grain-boundary sliding (GBS) was observed in Alloy 600 MA and Alloy 600 TT has been proposed as a link between IG strain rates and IGSCC growth rates. It has been considered an issue for Alloy 600. Grain boundaries act as barriers for dislocations, causing lattice dislocations to pile up at grain boundaries. However, at the higher temperatures, dislocations can propagate to an adjacent grain more easily. The dominant creep mechanisms for Alloy 600MA in primary water was identified as edge dislocation climb and the non-conservative motion of jogged-screw components, although thermally activated dislocation glide mechanism can be another possible mechanism (Yi & Was, 2001). Increased chromium and carbon were found to improve the creep and IGSCC cracking resistance (Donati et al. 1988). The influence of carbon in the improvement of the creep resistance was attributed to the pinning of mobile dislocations by carbon atoms and the delay in the recovery process of dislocation climb at grain boundaries (Hertzberg & Was, 1998). On the other hand, increase in the chromium content reduces greatly the stacking fault energy of the alloy and inhibit dislocation climb and cross-slip (Stiller et al. 1996). For that reason, grain boundary creep and grain boundary sliding are usually not considered an issue for Alloy 690 with 30 wt.% Cr, although an increase in IG carbide precipitation was found to be detrimental to creep resistance in Alloy 600 (Noel et al. 1996).
However, intergranular cracking can occur as an inherent phenomenon without corrosion: cracking of Alloy 690 in water is primarily intergranular, and no oxidation is found along the grain boundary ahead of the crack tips (Hou et al. 2011). Residual strains produced by cold work, in the HAZ after welding or during thermal ageing are also a source for increased IGSCC susceptibility.

3.5.2. Effect of cold work and HAZ

It has been reported that high cold work increases significantly the SCC susceptibility of Alloy 690. IGSCC was observed in cold-worked Alloy 690TT in PWR primary water in the range between 320°C and 360°C (Arioka et al. 2011). Cold work accelerates the CGR, sometimes to alarming levels close to those of Alloy 600 (Andresen et al. 2012). However, the effect of cold work on the SCC susceptibility is not well understood. An important effect of cold work is to increase the strength and hardness of the material. It increases the dislocation density and hinders further dislocation movements, which usually leads to an increased SCC susceptibility. Hardness increase was observed from 166 HV (0% CR) to 182 HV (11% CR) and to 223 HV (24% CR). The amount of misorientation in the alloy increases proportionally to the amount of cold work until 10% CR (Tsutsumi & Couvant 2012).

In addition, cold work has been seen to damage the grain boundaries of Alloy 690TT. Grain boundary damage includes fracture of the intergranular carbides and TiN particles, formation of voids at the carbide interfaces with the matrix and strain concentration (Peng et al. 2012). The increased CGR in cold-worked Alloy 690 appears to correlate with the grain boundary damage, as fractured carbides, voids and micro-cracks at the grain boundary provide a path for IG cracks. Grain boundary damage also reduces the internal friction against grain boundary sliding (Olszta & Toloczko 2011). Cracked carbides, cavities and pores have been observed at grain boundaries near tips of IGSCC cracks in cold-worked Alloy 690TT, and the formation of micro-cracks from the collapse of vacancies is a possible IGSCC mechanism in cold-worked materials in high-temperature water (Arioka et al. 2011). It was concluded that the CGRs of PWSCC in cold-worked Alloy 690 were affected not only by the level of cold work but also by the grain size and the cracking of primary M23C6 carbides, whose presence and number strongly depend on the chemical composition and fabrication process (Arioka et al. 2011).

However, cracking in cold-worked Alloy 690 can be also independent of the grain boundary damage. Cracks have been found to stop at fractured carbides. Carbide fracture, which occurs in a plane normal to the grain boundary (Peng
et al. 2012), seems therefore to enhance IGSCC crack blunting. Cracks have been seen to change their propagation path slightly from the damaged grain boundary to follow the matrix-carbide interface instead. One likely explanation is that cold work creates localized deformation and strength increase, which are particularly high at the grain boundaries (Peng et al. 2012). Added to the local strain already produced by intergranular precipitation, this strain concentration at grain boundaries can result in hardening and promote IG cracking. It can also be a reason for increased CGR in cold-worked alloys in high-temperature water (Bruemmer et al. 2013; Hou et al. 2011).

Alloy 690 components are not typically found in highly cold-worked condition and the high CGRs observed in highly cold-worked Alloy 690 have been considered not representative of the practical situation of in-service Alloy 690 components in PWR (Arioka et al. 2011). However, welding and the resulting heat-affected zone can lead to similar high levels of strain. Examples of SCC have been reported near weld interfaces, all associated with high residual strain levels. The distribution of the residual strains at weld interface has been noted as 40 to 50% in the weld metal, 20% in the UMZ and PMZ, about 15% in the base metal HAZ and 8 to 10% within the base metal (Andresen et al. 2012).

### 3.5.3. Effect of thermal ageing

Another source of increased SCC susceptibility has traditionally been thermal ageing. Thermal ageing at 475 °C is a well-known source of embrittlement in duplex and cast stainless steels and stainless steels welds. Alloy 690 is said to have a good high temperature stability and not to form embrittling phases during thermal ageing, but it has been shown that high-chromium alloys may be susceptible to in-service embrittlement via the formation of the long-range ordered Ni2Cr phase (Marucco et al. 1995; Young et al. 2013). The occurrence of short-range ordering (SRO) in Alloy 600 during slow strain rate tests in 360 °C water was observed for the first time, linked to an increased SCC (or IGSCC) susceptibility of Alloy 600 (Y. S. Kim et al. 2015). A study evaluating effects of varying degrees of long-range order on the PWSCC resistance of a model Ni-30.7 Cr wt.% alloy showed a CGR of $1.2 \times 10^{-7}$ mm/s after 2000 h at 475 °C, similar to CGRs of Alloy 690 with more than 20% plastic strain (Young 2017). Manufacturer’s data on the thermal stability of Alloy 690 show that tests were made at temperatures higher than 560 °C (UNS No6690/W.Nr.2.4642 2002), which may be too high to observe the above-mentioned ordering reactions and embrittlement. It is therefore of particular importance to consider the thermal ageing
of Alloy 690, especially regarding long and extending service life time at temperatures in PWRs. The formation of the ordered intermetallic Ni2Cr phase upon long-term exposure to relatively low in-service temperatures, lower than 450 °C, has to be considered. The brittle phase resulting from long-range ordering (LRO) affects the mechanical properties of the alloy, increasing hardness and decreasing ductility. It leads to concerns regarding the long-term structural stability of Alloy 690 components (Barnard et al. 2014; Delabrouille et al. 2009). In addition, long-term thermal ageing of Alloy 690 promotes intergranular precipitation of the embrittling α’-Cr phase at 550-600 °C, with the amount and size of particles increasing with the ageing time and temperature (Marucco 1995).

3.6. Short-range ordering of Alloy 690

3.6.1. Ordering reactions

Although studies have mainly been carried out on model alloys, most commercial Ni-Cr alloys show a reversible ordering reaction based on the formation of the ordered orthorhombic intermetallic Ni2Cr phase below 550 °C (Kim et al. 2000). Ordering reactions are a kind of phase transformation, in which an atomic rearrangement in regular patterns occurs below a critical temperature. It is the result of the stronger attractive force developed between different atoms as compared to similar atoms. Ordering reactions can be classified into two categories: i) thermal ordering, which is thermally activated without stress or strain, or results from pure diffusion and ii) strain-induced ordering, which appears when strain is applied, or in the plastic zone during crack propagation (Kim et al. 2013). Ordering occurring during thermal aging at a high temperature may be enhanced during high-temperature deformation due to strain-induced ordering (Kim & Kim 2011). Short-range ordering (SRO) develops at the early stages of ageing in Alloy 690, or can result from furnace cooling or solution annealing heat treatments after quenching, deformation or irradiation. The kinetics of SRO are rapid and independent of the alloy composition, and it can develop at temperatures above the critical temperature, where LRO is not possible. During SRO, the size of the order domains does not exceed a few nanometers, making it difficult to observe directly (Marucco 1995). SRO can further transform into LRO upon prolonged ageing at temperatures under 550 °C. LRO follows a nucleation and growth process. Nucleation can be both homogeneous and heterogeneous and the nucleation rate increases with decreasing tempera-
The growth is slower at lower temperature, as it depends on atomic diffusion (Marucco & Nath 1988). Above the critical temperature, typically between 525-575 °C, LRO does not occur anymore since nucleation decreases. The critical temperature and, thus, the degree of ordering, depends on the composition. LRO is promoted near the Ni2Cr stoichiometry (30.7 wt.% Cr) and the Ni3Cr stoichiometry (22.8 wt.% Cr) (Marucco et al. 1995). While Alloy 690 will produce the Ni2Cr phase, Alloy 600 can produce the Fe3Ni and Ni3Fe phases. Even near the stoichiometry, the transformations are slow, usually requiring ageing times over 30 000 h and typically around 60 000-100 000 h.

Differential scanning calorimetry (DSC) applied to Alloy 600 shows an exothermic ordering reaction around 520 °C (Kim et al. 2013). When the temperature of the ordered alloy is raised above the critical temperature, a disordering reaction occurs. It can be seen as the reverse of the ordering reaction. The ordered Ni2Cr phase loses the ordered structure and disperses the excess chromium. DSC of Alloy 690 shows an endothermic reaction due to disordering at temperatures higher than 550 °C. This is an endothermic reaction due to the consumption of energy needed for the rearrangement of the atoms (Smallman, 1985). For shorter times above the critical temperature, a metastable order is retained even above the critical temperature, because the long-range diffusion of chromium does not have time to occur. The activation energies for a model Ni2Cr alloy range from 73 to 87 kJ/mol (Delabrouille et al. 2009). The activation energy for Alloy 690 ordering reaction has been determined as 240 kJ/mol, and it generally ranges from the energy for vacancy migration in nickel (135 kJ/mol) to bulk diffusion of chromium in nickel (275 kJ/mol) (Young et al. 2013). The exothermic ordering reaction temperature is higher in Alloy 690 than in Alloy 600, meaning that Alloy 690 may present slower ordering reactions. However, more accurate determination of LRO activation energy is needed as only few studies have been dedicated to determine the apparent activation energy of LRO. Both solution-annealed and heat-treated Alloy 690 show lattice contractions upon aging at 350 and 420 °C, indicating the occurrence of SRO by thermal aging. Ageing at 350 and 420 °C also increases the hardness of Alloy 690 (Kim & Kim 2016).

### 3.6.2. Influence of the chemical composition

The ordering reaction is affected by the composition of Alloy 690 and is reduced when moving away from the Ni2Cr stoichiometry. However, the effect of alloying on LRO is not well understood. The ordering behavior is principally deter-
mined by the Ni/Cr ratio and the ordering kinetics become slower when the ratio departs from the Ni2Cr stoichiometry (Kim et al. 2000). However, other alloying elements affect the transformation. The effect of Fe is of particular importance. It has been said that increasing the iron content would effectively delay the initiation of LRO and that Fe content of more than 9 wt.% would effectively prevent the formation of ordering (Delabrouille et al. 2009). However, it was showed more recently that increasing the Fe content does not prevent the formation of ordering but actually lowers the critical temperature above which the disordering reaction occurs. At the Ni2Cr stoichiometry, the critical temperature is 550 °C, while it becomes as low as 400 °C for 10 wt.% Fe (see Fig. 5.1). Therefore, Alloy 690 with 9 wt.% Fe does harden, but at lower temperatures (Young et al. 2013).

For similar Fe content, the degree of SRO increases linearly with the Ni content. Mo and W have a stabilizing effect by promoting the ordered Ni2(Cr, Mo, W) phase (Marucco et al. 1995). In addition, alloying with 2.47 wt.% Mo accelerates ordering at temperatures higher than 418 °C but apparently not at lower temperatures (Young et al. 2013). Other alloying additions investigated like Si, Mn and Nb do not have significant effects on the ordering reactions. To be noted is that carbon in solution appears to delay the establishment of SRO by trapping excess vacancies (Kim et al. 2000). Complex alloys like Alloy 690 may prove to be more resistant to ordering as compared to similar model alloys (for example, Alloy 690 compared to Ni-30Cr-9Fe).

![Fig. 3.9. Evolution of the critical temperature in alloys near the Ni2Cr stoichiometry with increasing at.% Fe (Young et al. 2013).](image)

### 3.6.3. Effect of heat treatment and cold work

The prior condition of the material and the thermo-mechanical treatments influence greatly the ordering levels in the material. WQ materials show the lowest
activation energy (135 kJ/mol), which increases with furnace cooling (155 kJ/mol) and further with cold work (205 kJ/mol) (Young et al. 2013). In addition, DSC of Alloy 600 in the water-quenched (WQ), air-cooled (AC) and furnace-cooled (FC) conditions shows that the exothermic ordering reaction at 520 °C is attenuated first with AC and further by FC (Kim et al. 2013). Water-quenched specimens retain more disordered structure, from which SRO will quickly develop (Marucco & Nath 1988). Upon slow furnace cooling from solution annealing temperatures, ordering is likely to occur already during cooling and produces a rather advanced precipitation stage and some level of ordering. Although it makes further ordering reaction more difficult, it will effectively reduce the initiation time for ordering during ageing (Young et al. 2013). Cold work after furnace cooling destroys the SRO structure and increases the ordering initiation times back to the levels of the water-quenched material and has been seen to increase the initiation time for ordering during ageing (Young et al. 2013). Cold work has been shown to create dislocations which act as sink for irradiation-induced defects, reducing the ordering kinetics for irradiated materials. However, it also produces a large amount of lattice defects, promoting SRO formation and carbide precipitation during re-heating (Kim et al. 2000). Few studies have pointed out that cold work can promote ordering or reduces the temperature at which the exothermic ordering reaction occurs (Delabrouille et al. 2009; Kim et al. 2000)

3.7. Consequences of ordering on SCC susceptibility

The consequences of ordering are mainly dimensional instability due to changes in the lattice parameter and changes in the electrical and thermal characteristics as well as mechanical properties. An increase in the electrical resistivity due to the formation of SRO in the early stages of ageing after water quenching is commonly known as the K-state, and is attributed to the scatter of electrons by SRO nuclei. When the nuclei grow to a critical size corresponding to the wave length of Fermi electrons, a maximum resistivity is reached. The resistivity decreases below the critical temperatures due to LRO (Marucco et al. 1995). The reduction in resistivity is also attributed to the Cr-depletion of the matrix, caused by the ordered phase precipitation.

Measurements of the lattice parameter show that ordering leads to a significant lattice contraction during ageing below 550 °C, with a maximum effect at 475 °C at low Fe contents. SRO causes contraction around 0.03 % while LRO can lead to contractions up to 0.3 % after 30000 h. The extent of contraction depends of the level of ordering in the alloy (Marucco et al. 1995). It increases
the level of internal stresses and leads to a significant hardness increase, an increase in the yield stress (from 241 MPa to 483 MPa upon ageing for 2000 h at 475 °C) and decrease in the elongation to fracture (from 65 to 10%), while changing the fracture mode from ductile micro-void coalescence to brittle intergranular fracture (Young et al. 2013; Kim et al. 2013). The high level of lattice contraction caused by the ordering reaction can lead to negative creep. During creep testing above the critical temperature or at high stress levels, the creep component prevails. Below the critical temperature, the observed strain can be negative, due to the formation of SRO or LRO based on Ni₆Cr. The excessive stresses generated in constrained component due to lattice contraction may lead to failure (Dahl & Hald 2004). In addition, ordering can promote heterogeneous planar slip or heterogeneous deformation. A dislocation moving along a slip plane in the ordered lattice has to destroy the atomic bonds across the slip plane. Since successive dislocations will produce less and less disorder, the movement becomes easier on this slip plane, confining the deformation. It produces widely spaced coarse slip steps and is a concern for EAC resistance (Young et al. 2013).

There is an ongoing discussion as to whether or not ordering directly contributes to the SCC mechanism of Alloy 690 by promoting cracking without the intervention of corrosion, or if its role is limited to a general degradation of mechanical properties. A study pointed out lattice contraction due to SRO as the leading factor for IGSCC of Alloy 600 (Y. S. Kim et al. 2015). Further, SRO was directly observed during slow strain rate tests of Alloy 600 in water at 360 °C. A direct correlation between SRO levels and PWSCC susceptibility was drawn as FC Alloy 600 with lower ordering levels was more PWSCC resistant than WQ Alloy 600 with higher lattice contraction (Kim et al. 2013). In a similar fashion, another study showed evidence that SCC of Alloy 690 may be related to SRO. It highlighted a direct correlation between the enhanced resistance to SCC of heat-treated (TT) Alloy 690 over solution-annealed (SA) Alloy 690, linked to the lower lattice contraction of the former over the latter upon ageing (Kim & Kim 2016). In contrast, another study of the same Alloy 690 conditions stated that the enhanced SCC resistance of the heat-treated Alloy 690 was due to the beneficial role of grain boundary carbides forming during thermal ageing (Kuang et al. 2015). However, it was showed that the negative strain rate dependence of SCC initiation in SA- and TT-Alloy 690 was related to the rate of SRO, increasing with decreasing strain rate. Secondary intergranular cracks forming in TT-Alloy 690 or FC-Alloy 600 during SCC tests in primary water at 360 °C, independently of the strain rate, were showed to be caused by lattice contractions due to SRO.
prior to SCC tests and, therefore, were not stress corrosion cracks. It was deduced that the enhanced SCC initiation in cold-rolled Alloy 690 with decreasing strain rate was related to the rate of SRO but not to corrosion, making SRO an intrinsic driving force for SCC of Alloy 690 (Kim & Kim 2016). Furthermore, the activation energy of the ordering reaction in Alloy 690 was found to be around 240 kJ/mol, which is similar to the activation energy of IG crack initiation. Another study, however, refutes the hypothesis that an intrinsic force is driving the crack propagation in Alloy 600 and 690. SCC tests run on model Ni-Cr-Fe alloy close to the Alloy 690 composition and Alloy 690 showed that thermal ageing was detrimental to IGSCC resistance only with the development of LRO. In that way, ordering would not be an intrinsic driving force for cracking but, similar to cold work, it will promote SCC susceptibility by increasing the crack tip strength and decreasing the toughness of the ordered alloy (Young 2017). To conclude, whether SRO constitutes an intrinsic driving force for cracking or whether LRO increases the strength and decreases the toughness of the alloy at SCC crack tips, the studies agree that thermal ageing and ordering are a concern for Alloy 690 components in PWRs exposed to temperatures above 270 °C for extended times since its composition is close to the Ni2Cr stoichiometry (Barnard et al. 2014; Young et al. 2013).
4. Conclusions of the literature review and aims of the study

This part of the thesis aimed at showing the role of Ni-base alloys in PWRs, and of Alloy 690, 52 and 152 in particular, which are used in the RPV, steam generator tubes and DMWs of PWRs. In addition, it was showed that SCC and PWSCC, and their possible interaction with irradiation and hydrogen, are among the biggest concerns for the integrity of Alloy 690 components. Although the SCC and PWSCC resistance of Alloy 690 is significant, the possibility remains that although no cracks have formed in-service until now, cracking is only delayed as for Alloy 600 but with a longer initiation time. It is well known that cold work increases tremendously the PWSCC susceptibility of Alloy 690, and that strain levels similar to that of highly cold-worked material (typically, 20% reduction) can be found in the HAZ of Alloy 690. It is also well known that the interfaces of DMWs of Alloy 82 and 182 are very sensitive to SCC and therefore the narrow transition zones of DMW interfaces with Alloy 52 and 152 have to be characterized extensively.

The direction of the research effort on Alloys 690, 52 and 152 is now to characterize materials with lower levels of cold work (lower than 15%) and to determine factors of improvements over Alloy 600, which requires especially extensive data on the PWSCC initiation for Alloy 690. In addition, current plants are ageing and their service life is being extended, and future plants are planned to operate up to 80 or 100 years, warranting a particular look at thermal ageing of components and its influence on the degradation mechanisms. Already, it has been pointed out that the LRO forming in Alloy 690 during ageing is detrimental to the SCC resistance to levels similar to highly cold-worked materials. Pushing further the role of ordering, a hypothesis is being investigated that the initiation time for cracking of Alloy 600 is intrinsically driven by SRO (Kim et al. 2000; Y. S. Kim et al. 2015; Kim & Kim 2016). To investigate similar role of SRO in the case of Alloy 690, Alloy 690 material was provided to be studied in this doctoral thesis. Whether ordering is directly acting as a driving force for cracking, or more generally degrading mechanical properties and facilitating SCC initiation, it remains a source of concern for the long-term degradation of Alloy 690 SCC
resistance in PWRs. The testing of thermal stability and long-term thermal ageing is, however, tedious, and most studies have dealt with model Ni-Cr and Ni-Cr-Fe alloys, as the effects of other metallurgical features, such as $\alpha'$-Cr precipitation, can overlap those of the ordering reaction. In addition, experiments done in other studies have showed that the LRO is more easily developing in model alloys than in commercial melts of Alloy 690. It means that ordering is found in Alloy 690 mostly as SRO, which is difficult to detect due to the small size of the ordered domains, lower lattice contraction, lower hardness increase, and the absence of an extended intermetallic phase that can be observed by TEM diffraction. Data on the effect of thermal ageing of a commercial melt of Alloy 690 is therefore valuable, as is the detailed examination of SRO levels and their effect on mechanical properties. In addition, there is very little or no data concerning the thermal ageing of Alloy 52 and 152 weld metals and weld interfaces. The focus of this thesis has therefore been on the effect of thermal ageing on Alloy 690 and Alloy 52 weld metal, with a particular focus on SRO of Alloy 690 and on the DMW interfaces with Alloy 52.
5. Experimental methods

5.1. Materials of the study

5.1.1. Alloy 690 samples

Alloy 690 samples were provided by Prof. Youg Suk Kim from the Korean Atomic Energy Research Institute. The alloy is a commercial melt from INCO, its composition is given in Table 8.1, with notably 9.18 wt.% Fe. Table 8.2 shows the four original conditions of the alloy prior to ageing: solution annealed (SA) and water-quenched (WQ), then thermally-treated (TT) for 17 h at 700 °C and/or cold-rolled to a 20% reduction ratio (CW). For clarity, these conditions are named here SA-Alloy 690 (solution annealed then water quenched), SACW-Alloy 690 (solution annealed, water quenched and cold worked), TT-Alloy 690 (solution annealed, water quenched and thermally treated) and TTCW-Alloy 690 (solution annealed, water quenched, thermally treated and cold worked). The as-received conditions were then thermally aged for 3000 and 10 000 h at 350, 420, 475 and 550 °C, resulting in 32 aged conditions showed in Table 8.3, and a total of 36 conditions with the four as-received ones. For clarity, the name of the aged conditions is based on the name of the as-received condition, followed by the ageing temperature and ageing time. For example, the Alloy 690 that was solution annealed, thermally treated and cold worked, then aged at 420 °C for 3000 h is named TTCW-420C-3K, or TTCW420C3K shortly. The Alloy 690 samples were provided as small blocks of about 50x8x8 mm. Samples used in different experiments were then cut out from these blocks by electric discharge machining (EDM) (see Fig. 5.1.).

Table 5.1. Chemical compositions (in wt.%) of Alloy 690 used in this study.

<table>
<thead>
<tr>
<th>Alloy 690</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>Cu</th>
<th>C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>62.6</td>
<td>28.7</td>
<td>9.18</td>
<td>0.21</td>
<td>0.12</td>
<td>0.08</td>
<td>0.0048</td>
<td>0.037</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>
5.1.2. Alloy 52 weld metal samples

The study of Alloy 52 weld metal was done using RPV safe-end DMWs between LAS and SS with Alloy 52 weld metal. Two mock-up welds were used. One laboratory RPV safe-end mock-up weld was made at Aalto University and studied as-welded (AW) and after post-weld heat treatment (PWHT). The post-weld heat treatment was done at 550 ± 15 °C for 17 h followed by 610 ± 15 °C for 7 h.

Another RPV safe-end mock-up weld from Mitsubishi Heavy Industry (MHI) using a similar PWHT was provided by TVO. It was studied as-received (AR) and after thermal ageing for 5000 and 10 000 h at 400 °C carried out at VTT. Both mock-up welds were representative of the RPV safe-end in the EPR design (Fig. 5.2.a), using a narrow gap and no buttering layer between the LAS side and the weld metal (see Fig. 5.2.b). Ageing at 400 °C for 10 000 h is calculated to be equivalent to 60 years of operations at PWR in-service temperatures, in terms of GB segregation of phosphorous in RPV LAS (Joly et al. 2013). The weld mock-ups consisted in both case of SA 508 and 316L base metals, SS 308 cladding on
the RPV side and Alloy 52 weld metal (see Fig. 5.2.c and Table 8.4 for chemical compositions). The welds were investigated to study the effect of PWHT and thermal ageing on the weld interfaces and on the Alloy 52 weld metal. Samples were extracted with EDM to facilitate the characterization (see Fig. 5.2.d). Since the first DMW mock-up made at Aalto University was studied within the SINI project, and the second DMW mock-up was studied within the NIWEL project, the five conditions are called SINI-AW, SINI-PWHT, NIWEL-AR, NIWEL-5000h and NIWEL-10000h.

Fig. 5.2. Schematic of a) the emplacement of the RPV nozzle and b) typical features of the narrow-gap dissimilar metal weld of the RPV nozzle to its safe-end used in the Olkiluoto 3 EPR, with c) a slice from the as-received mock-up weld and d) a sample extracted by EDM from the slice and mounted in a polymer matrix.
Table 5.4. Chemical compositions (in wt.%) of the materials used in the DMW mock-ups.

<table>
<thead>
<tr>
<th></th>
<th>SA508 Gr. 2</th>
<th>AISI 316L</th>
<th>AISI 308L</th>
<th>Alloy 52 (SINI)</th>
<th>Alloy 52 (NIWEL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.21</td>
<td>0.023</td>
<td>0.007</td>
<td>0.03</td>
<td>0.023</td>
</tr>
<tr>
<td>Si</td>
<td>0.17</td>
<td>0.53</td>
<td>0.37</td>
<td>0.13</td>
<td>0.15</td>
</tr>
<tr>
<td>Mn</td>
<td>0.78</td>
<td>1.29</td>
<td>1.9</td>
<td>0.24</td>
<td>0.26</td>
</tr>
<tr>
<td>P</td>
<td>0.002</td>
<td>0.031</td>
<td>0.013</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>S</td>
<td>0.009</td>
<td>0.002</td>
<td>0.001</td>
<td>&lt;0.001</td>
<td>0.0007</td>
</tr>
<tr>
<td>Cr</td>
<td>0.45</td>
<td>17</td>
<td>20.3</td>
<td>29.2</td>
<td>29.93</td>
</tr>
<tr>
<td>Ni</td>
<td>0.85</td>
<td>10.1</td>
<td>10.3</td>
<td>59.28</td>
<td>58.86</td>
</tr>
<tr>
<td>Mo</td>
<td>0.62</td>
<td>2.04</td>
<td>0.1</td>
<td>0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Nb</td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>N</td>
<td>0.014</td>
<td>0.04</td>
<td>0.04</td>
<td></td>
<td>0.021</td>
</tr>
<tr>
<td>Ti</td>
<td>0.002</td>
<td></td>
<td></td>
<td>0.51</td>
<td>0.54</td>
</tr>
<tr>
<td>Fe</td>
<td>Bal.</td>
<td>Bal.</td>
<td>Bal.</td>
<td>9.8</td>
<td>10.43</td>
</tr>
<tr>
<td>Al</td>
<td>0.016</td>
<td></td>
<td></td>
<td>0.72</td>
<td>0.66</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0.003</td>
<td></td>
<td></td>
<td>0.009</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td></td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

5.1.3. Metallographic preparation

Samples were cut from the Alloy 690 blocks or from the DMW slices using EDM in order to reduce deformation during cutting. Samples for scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), X-ray diffraction (XRD), nanoindentation and atomic force microscopy (AFM) were all prepared in the same way. The sections were mounted in a conductive polymer matrix, Struers PolyFast, then they were ground with Struers SiC grinding papers up to 4000 grit and then polished with 3 µm and 1 µm Struers DiaPro diamond solutions. The last deformation layers were removed in a Buehler Vibromet 2 polisher with a colloidal silica alkaline suspension for 16 to 20 h. Sample surfaces were ultrasonically cleaned using a Triton solution in order to remove SiO particles deposited during the final stage of polishing. This preparation aimed at providing a surface with as little residual deformation as possible in order to be characterized with EBSD, and the same surface finish was used for all the experiments in order to make the comparison of the results more relevant and to reduce the measurement errors due to residual deformation (especially for nanoindentation and XRD). Sample preparation for transmission electron microscopy (TEM) will be dealt in more detail in Chapter 8.2.3.
5.2. Characterization methods

5.2.1. Scanning electron microscopy

The development of scanning electron microscopy (SEM) dates back to the 1920s following discoveries on the interactions of charged particles with electric and magnetic fields by Busch, and the concept of wave-particle duality by De Broglie. It was seen that electron wavelengths were almost five orders of magnitude smaller than the wavelength of photons, thus leading the way to microscopes with a better resolution than light instruments. The first SEM was developed in 1942 by Zworykin, reaching a resolution of 50 nm (Bogner et al. 2007).

A SEM consists mainly of a microscope column including an electron gun and a system of electro-magnetic lenses, computers to drive the microscope and detectors to collect signals. Electron guns consist of 3 parts: an electron source (cathode), a Wehnelt cap and an anode. The Wehnelt cap is polarized to act as a repulsive convergent electrostatic lens, condensing the cloud of electrons extracted from the filament before the acceleration by the anode. Below the Wehnelt cap, the anode attracts the electrons and accelerates them with a high voltage up to 40 kV to form a beam.

![Schematic diagram of a conventional thermionic electron gun (Goldstein et al. 2012).](image)

Two kinds of electron guns are found depending on the type of electron source: thermionic guns and field-emission guns (FEG). In thermionic guns, the electron source is typically a tungsten filament or a LaB₆ crystal that are heated so that electrons overcome the energy needed to extract an electron from a solid to the vacuum in the vicinity of the surface (a.k.a. the work function). LaB₆ crystals
have a higher brightness and longer lifetime than tungsten filaments. FEG uses tungsten crystals with a sharp tip, which either emit electrons at room temperature by quantum mechanical tunneling thanks to a high electric field (cold field emission), or are recovered by a thin ZrO layer to reduce the work function and heated to extract electrons (Schottky field emission). The main benefits of FEG over thermionic guns are a higher brightness and smaller energy spread, resulting in a smaller beam size and enabling the use of low-energy imaging, limiting the effect of chromatic aberrations and increasing the resolution. However, they require ultra-high vacuum ($10^{-8}$ Pa) and they have a lower probe current (especially in the case of cold field emission) than conventional guns.

Fig. 5.4. SEM images of two different electron sources used in electron guns, with a) a tungsten filament (thermionic gun) and b) a sharp tungsten tip (cold field emission gun) (Goldstein et al. 2012).

Once the beam exits the Wehnelt cap, it is divergent and must be focused with the system of electro-magnetic lenses in the column, which deflect the electron beam using electrically charged plates or a magnetic flux. However, electromagnetic lenses generate much more aberrations than optical. Spherical aberrations affect magnetic lenses (and optical lenses as well), where electrons along the beam axis are deflected less than electrons on the periphery, resulting in several focus points. In addition, chromatic aberrations are a feature unique to magnetic lenses, in which electrons with different energies are being deflected differently. The total sum of aberrations is the main resolution limiting factor of a SEM (with SE, about 5-10 nm with a conventional gun and down to 1 nm with a FEG-SEM).

The electron beam with an energy up to 40 keV is now focused on the surface of a specimen. A reflection image is obtained by scanning the beam over the surface. Most of the energy from the incident beam will be dissipated in the lattice in the form of heat. However, the interaction between the incident beam and the matter also generates various signals that are collected by different detectors in order to provide information using chemical or topographic contrast,
or to provide a chemical analysis of local composition. Generated by the incident beam (usually 10-40 keV), these signals are mainly: Auger electrons (up to 2000 eV), secondary electrons (SE, up to 50 eV), high-energy backscattered electrons (BSE, from 50 eV to 40 keV) and characteristic X-rays (from 500 eV to 40 keV).

Fig. 5.5. Schematic of the interaction volumes for various electron-specimen interactions, showing the SE signal coming from the surface while BSE and characteristic X-rays are coming from the bulk (Witke 2016).

Fig. 5.6. Schematic of the formation of a) backscattered electron, b) secondary electron, c) characteristic X-ray and d) Auger electron during the interaction of the incident electron beam with matter.

BSEs are the result of an elastic scattering within the specimen, where the trajectory of the incident beam changes without energy loss. Due to scattering, they interact with the material in an interaction volume that increases in size with the atomic number (Z) of the material and the energy of the incident beam and they are released in a continuous spectrum. The size of the interaction volume
is such that only medium resolution can be achieved. However, the Z dependence of the interaction volume means that heavier elements will generate more BSE, resulting in a chemical contrast.

On the other hand, the generation of SE, Auger electrons and characteristic X-rays is the result of an inelastic scattering, where the incident electron beam loses energy in the interaction with the material (see Fig. 5.6). SEs are the result of an ionization of atoms, in which an electron from the outer shell of an atom is knocked away during the collision with the incident beam. As for BSEs, they are released in continuous spectrum, which means that they are not characteristic of atoms. However, outer electrons are not strongly bound to the nuclei, which means that they can be ejected with a low energy. SEs have therefore low energies and only those generated close to the surface will be collected before they are re-absorbed. The emission area of SEs has therefore a small depth and width, and they are used to image topographic details with high resolution.

Metallographic characterization was performed using SEM to obtain information on general microstructures, carbide precipitation, weld interfaces and fracture surfaces. The main focus of the SEM study was on the IG carbide precipitation in Alloy 690 and Alloy 52, on the SA 508 HAZ microstructure and the interface with Alloy 52 in the NG-DMW. The SEM characterization was carried out at Aalto University using a field emission gun (FEG) Zeiss Ultra 55. SE and InLens detectors were mainly used, as they reveal topographic details on the surface, such as IG carbides, weld interfaces that have been slightly etched by the caustic silica suspension, or fracture surfaces. BSE were used in the imaging of carbides as the chemical contrast helps to differentiate them from the matrix.

5.2.2. Energy dispersive X-ray spectroscopy

Although produced during inelastic scattering of the incident beam, X-rays and Auger electrons differ from SEs as they are the result of the deexcitation of an atom after the loss of an electron from the inner shells in the collision with the incident beam. During the atomic relaxation, an electron from the higher energy outer shell moves to the inner shell to fill the electron vacancy by releasing energy in a radiative (X-ray) or non-radiative (Auger electron) way, which are characteristic of emitting atoms. Auger electron generation occurs when the photon X-ray first generated during deexcitation is re-absorbed internally and results in the emission of an outer shell electron (see Fig. 5.6). X-rays have a higher energy and a longer mean free path. They are therefore generated from an interaction volume the size of which depends on the incident energy and the atomic number. On the contrary, Auger electrons have a weaker energy and
mean free path as they come from the outer shell. As a result, X-rays are used for chemical analysis with a medium resolution, while Auger electrons are used for surface chemical analysis.

Energy-dispersive X-ray spectroscopy (EDS) is based on the analysis with an in-SEM detector of the energy spectrum of X-rays emitted during the interaction of atoms with the incident beam. The identification of atoms provides a qualitative analysis, while the estimation of atomic concentrations from the peak intensities in the spectrum gives a quantitative analysis. EDS can be used as a fixed probe to analysis of the chemical composition at a local point on the SEM image, or in a scanning mode to map the dispersion of given elements.

EDS was used to analyze the chemical compositions of the Alloy 690 IG precipitates and composition gradients in the Alloy 52 weld metal at the weld interfaces. The method was used mostly for qualitative analysis.

5.2.3. Electron backscatter diffraction

Electron backscattered diffraction (EBSD) is a crystal orientation-based technique using a special phosphor screen detector mounted in the SEM chamber. The incident beam scans the sample surface and the EBSD detector receives the backscattered beam. Electron backscattering patterns (EBSP) are produced by the interaction of the incident beam with the crystal lattice. They show diffraction contrasts, with bands of higher intensity (Kikuchi lines) resulting from the channeling of electrons along low-index lattice plane and their exit out of the lattice in diffraction cones (Kossel cones) following Bragg’s angles and characteristic of the diffracting planes. The center of the bands is the imaginary intersection of the lattice plane with the phosphor screen, the star-like centers are

![Fig. 5.7. Schematic of the characteristic X-ray formation after the incident electron beam kicks out an electron from the shell (Oxford X-ray fluorescence 2009).](image-url)
zone axes of the crystal lattice, the angles between bands are interplanar angles and the widths of the bands are proportional to Bragg’s angles and related to Miller indices of each plane. Each scanning point gives therefore information on the local crystal structure and orientation, by simply comparing the widths and positions of several bands in the pattern and comparing them with the simulated bands of a known crystal structure (a.k.a, indexing of the EBSP). The sample is tilted at a fixed angle of usually 70° to increase the pattern intensity. The band positions are extracted via a Radon or Hough transform. It transforms all points on a line of the EBSP into a single point in the Hough space, which sums all the intensities along the straight line of the EBSP divided by the number points along the line. A bright line in the diffraction pattern becomes a peak in the Hough space. A peak is more easily detected in the Hough space than a line in the EBSP (low sensitivity to image noise), its center yields the coordinates of the band center, and the spread of the peak is a measure of the Bragg angle (and therefore of the Miller indices of the crystal plane).

Fig. 5.8. Schematic of the formation of a backscatter Kikuchi band (Schwarzer 1997) and a simulated electron backscattering pattern (EBSP) for nickel with Kikuchi lines and zone axis taken from Alloy 690 sample studied for this thesis.

EBSD is used mostly for texture analysis using orientation imaging microscopy (OIM), which consists of the reconstruction of crystalline orientations by automatically indexing Kikuchi lines for a large number of points on a selected area of the sample. There is also considerable interest to use EBSD in the study of elastic and plastic strains. Elastic strains distort the crystal lattice. This distortion is visible in the EBSP as a shift in some zone axis and changes in some diffraction band widths. Very careful image analysis of high-resolution EBSP is needed to measure elastic strains. On the other hand, plastic strain is known to decrease the quality of EBSP and misorientation based techniques are validated
for the quantification of plastic strain (Lehockey et al. 2000). Local misorientations represent a change in crystal lattice orientation between different points in the material. Contrary to elastic strain, plastic strain is accommodated in the crystal lattice by the formation of dislocations (Wright et al. 2011). Misorientations increase in the lattice where dislocations accumulate, and are therefore closely related to strain. However, two kinds of dislocations are generated. Statistically stored dislocations (SSD) represent dislocations that are stored in the material but result in a net Burgers vector of zero and are therefore not visible in the local misorientation maps. Only the areas where the net Burgers vector is not zero result in a change in crystallographic orientation. These dislocations are named geometrically necessary dislocations (GND). Local average misorientation techniques are therefore not well suited to quantify the actual magnitude of plastic strain, which results from the addition of SSDs and GNDs (Wright et al. 2011). However, EBSD is very much capable to study the localization of effective plastic strain, a measure of strain hardening (dislocation density build-up). As such, local average misorientations can give a good indication of the qualitative hardness profile, or effective plastic strains, across a surface (Shen et al. 2016; Wright et al. 2011).

![Fig. 5.9. Illustration of the uses of EBSD, with a) phase identification at a ferritic (red)/austenitic (blue) weld interface, b) grain boundary nature identification (twin boundaries in red) and c) local kernel average misorientation (higher misorientation in green and yellow).](image)

General EBSD was carried out with the FEG Zeiss Ultra 55 equipped with a 2-diode HKL EBSD detector and using the HKL fast-acquisition software for acquisition of the orientation maps and phase identification for grain texture and grain size analysis. A newer FE Zeiss Merlin VP Compact equipped with a 5-diode Bruker e-Flash detector was used for the plastic strain analysis at grain boundaries with a Bruker Quantax software. The e-Flash detector provided EBSP with a higher resolution (1600×1200), resulting in a higher angular resolution. The accelerating voltage was set to 20 kV, and the aperture was opened to 120 mm. The working distance was between 19-20 mm. EBSD was used to characterize the grain size of different Alloy 690 conditions and in the LAS HAZ of the LAS/Alloy 52 narrow-gap DMW, to study the formation of PMZ at the
weld interface. High-angular resolution EBSD was used to study strain localization at GBs in Alloy 690.

5.2.4. Transmission electron microscopy

Transmission electron microscopy (TEM) was used already before the development of SEM. The first electron microscope was a TEM developed in 1931 by Ernst Ruska and Max Knolls. A TEM operates with a much higher beam energy than SEM (typically from 100 to 400 kV) and generates signal by passing the beam through a thin sample (typically less than 200 nm). The incident electron beam is either transmitted through the sample depending on its thickness and electron transparency (transmitted beam), elastically scattered (diffracted beam), inelastically scattered (energy loss) or converted to X-rays. As a result of the high velocity of the electrons and the reduced interaction volume with the thin sample, TEM offers magnifications higher than SEM and can reach sub-Ångstrom resolution (Rose 2009).

Fig. 5.10. Schematic of the TEM electron beam after crossing the specimen and passing through the objective lens (distance u from the object), with diffraction forming in the back focal plane (distance f from the objective lens, where f is the focal length), and the projected image forming in the image plane (distance v from the objective lens) (Williams & Carter 2013).

The usual limit for point resolution with a TEM at 300 kV is about 2 Å. In addition to scattering contrast, TEM provides a diffraction contrast for crystalline materials enabling the analysis of microstructures (transmitted and diffracted beams), it also enables local chemical analysis with EDS (X-rays) or electron energy loss spectroscopy (EELS), and phase contrast (with high resolution TEM). The EDS with TEM has a better resolution than in SEM (spot size 10-100 nm). EELS analyses the discrete energy loss of the incident beam through the specimen, which is characteristic of the ionization threshold of the atoms, and enables the analysis of light elements thanks to energy resolution. Figure 5.10
shows the typical path of the electron beam in the TEM column. After crossing the thin sample, the beam is focused by the objective lens on a phosphor screen or a CCD camera. In the focal plane of the objective lens (reciprocal space), diffraction patterns are formed by electrons scattered by the sample. In the image plane of the objective lens (real space) is a projection of the area of the sample that was irradiated by the electron beam. Diffraction patterns and image are therefore simultaneously present in the TEM, and either one can be selected via an intermediate lens before being magnified by the projective lens on the phosphor screen/CCD camera.

Figure 5.11 shows the three principal modes used in TEM. In imaging mode (selection of the image plane), two different imaging ways are possible by inserting an objective aperture in the back focal plane to select or block different beams: bright field (BF) imaging and dark field (DF) imaging. In BF imaging, only the direct transmitted beam is selected by the objective aperture, and brighter areas correspond to locations where the most electrons have been transmitted. In DF
imaging, the transmitted beam is blocked by the objective aperture to select only one or more diffracted beams. The brighter areas in DF correspond to locations where the beam has diffracted the most. The diffracted beams have strongly interacted with the specimen and can provide useful information on particles, precipitates and dislocations. For selected area diffraction (SAD), an aperture in the plane of the first intermediate image defines the region of which the diffraction is obtained. (Williams & Carter 2009)

![Image of TEM disk preparation](image)

**Fig. 5.12.** Illustration of the preparation of TEM disks, with a) the Alloy 690 plate, the metal puncher and the resulting 0.3 mm thick disks and b) the disk holder for further grinding.

TEM was used to study the effect of thermal ageing on Alloy 690, with a particular focus on the imaging and chemical analysis of IG carbides, and with the hope of observing interlattice reflections typical of ordering in diffraction patterns. TEM examinations were carried out at VTT using a Philips CM200 FEG-STEM. Compositional analyses were carried out utilizing a Noran Voyager energy dispersive X-ray analyser and Gatan System Six software. A liquid nitrogen cold-finger was also employed in order to help reduce hydrocarbon contamination in the microscope. Some observations were made using the newest FEI Talos F200X FEG-STEM.

Thin disks were prepared from Alloy 690 for TEM examination. First, 0.5 mm thick plates were cut by EDM from the Alloy 690 blocks, and grinded on both side with 800 to 2000 grit papers to reach a thickness of 0.3 mm in order to remove residual deformations and be able to punch through the plates. Then, disks were punched through the plates with a metal puncher using a hammer (a pneumatic puncher is also possible, but the hammer works faster and induces less residual deformations). These disks were then grinded with a 2000 grit pa-
per to reach a thickness of 80 to 100 μm. The thin disks were then electropolished using a Struers TenuPol-5 with a fresh electrolyte Struers A2-II (methanol-perchloric acid mix) at -40 °C. The electropolishing stops when light can pass through holes in the disks, and the areas of interest are electron transparent regions usually located on the side of the holes.

5.2.5. Hardness measurements

Microhardness

Hardness tests are very useful for materials characterization and quality control of manufacturing processes. Hardness can be correlated to tensile strength for many metals and alloys, and is also an indicator of machinability, wear resistance, toughness and ductility (ASTM E384-16). However, hardness, as a material property, is very difficult to define since it depends on how it is measured. Indentation hardness measurements use a hard tip applied with a given load on the surface of the material to determine its resistance to plastic deformation. The size of the indentation depends on the force applied on the indenter, and determines therefore the scale of the hardness test. Typically, three categories of tests are used: macroindentation tests (from 10 to 1000 N), microindentation tests (from 10mN to 10N) and nanoindentation tests (from 10μN to 10 mN). Due to a reduced size of indentations, microhardness tests are suited for the evaluation of specific phases and regions, or hardness gradients too low for macrohardness testing, while nanoindentation allows the evaluation of thin films, individual GB regions and specific grains.

In conventional macro- and microhardness tests, indentations can reach penetration depths of the order of 0.01 to 1 mm. Typical tests are the Brinell and Rockwell tests that use ball-shaped indenters, or the Vickers and Knoop tests that use a square based or elongated pyramid diamond tip, respectively (see Fig. 5.12.a). The Vickers test is the most commonly used in the microhardness characterization of metallic alloys, while the Knoop test is best suited for brittle materials such as ceramics and thin films.

In microhardness tests, the calculation of Vickers hardness is made from the resulting indentation by dividing the test load by the area of the indentation. Most often, the area of the indentation is obtained by measuring the diagonals of the indentation (see Fig. 5.12.b). Vickers hardness is not altered by the choice of the test load, from 250 mN to 10 N, because the indent geometry is constant as a function of indent depth.
Vickers tests provide quantitative hardness measurements with high stability over a wide range of loads, although it is recommended that a number of indents are made and the average and standard deviation are calculated. At loads lower than 250 mN, however, it becomes difficult to measure extremely small indents (<20 \(\mu\)m) by light microscopy with high precision and reproducibility, and tests should be considered to be qualitative in nature. To address this issue, instrumented microindentation has been developed since the 90’s. Typically, a conventional microhardness tester is instrumented with a piezoelectric load cell and capacitance displacement gages to measure load and displacement during indentation (Pharr & Cook 1990). The major advantage of this technique is that no subjective assessment of the indentation size is needed, as relevant information on the Vickers hardness and Young’s modulus are directly extracted from load–depth curves, which are representative of the mechanical response of the material. Instrumented microhardness was typically used for small indentation loads, typically below 100 mN (Oliver & Pharr 1992), but it has been generalized for higher loads up to 1000 mN (Petit et al. 2007) and for nanoindentation (Oliver & Pharr 1992; Pharr 1998; Oliver & Pharr 2004).

Vickers tests were used with a 1 kg load to characterize the general microstructure of Alloy 690 conditions. After that, instrumented microhardness tests were performed using a CSM Instruments Micro-Hardness Tester (MHT) with a load of 350 mN to study the hardness variations in Alloy 52 weld metal and the hardness gradients in the LAS HAZ and at the weld interface. The step size between indentations in the hardness profiles at the weld interface was 50 \(\mu\)m. However, steep hardness gradients of narrow transition made the use of a smaller step size necessary. In addition, the hardness variations related to the development
of ordering in Alloy 690 were expected to be too small to be studied with typical microhardness loads. Both issues justified the use of nanoindentation.

**Nanoindentation**

Nanoindentation was developed in the early 70’s for modern applications such as thin films, microelectronics and biomaterials characterization. Compared to other methods of mechanical testing in the sub-micron range, nanoindentation has a relatively simple setup and specimen preparation. As for microhardness with loads <250 mN, nanoindentations are difficult to be measured with the traditional optical microscopy. Atomic force microscopy techniques can be used but the determination of the nano-indentation hardness uses an intrumented depth-sensing indentation. Commonly, a diamond Berkovich tip with a geometry known to high precision (see Fig. 5.13.a) is pressed into the specimen until a given maximum depth or load are reached, and then removed. Synchronously, the load and the displacement of the indenter are recorded. A typical nanoindentation test consists of a quasi-static loading to full load followed by a hold-time and an unloading to zero load (see Fig. 5.13.b). Nanoindentation uses a model for the deformation of an elastic half space by an elastic punch, which relates the contact area at peak load to the elastic modulus and estimates the contact area from the indenter shape function (see Fig. 5.14.a).

Fig. 5.14. Typical features of nanoindentation, with a) indentation mark of a Berkovich tip (Oliver & Pharr 1992) and b) a representation of a load-displacement curve for an instrumented indentation experiment. The quantities shown are $P_{\text{max}}$: the peak indentation load; $h_{\text{max}}$: the indenter displacement at peak load; $h_f$: the final depth of the contact impression after unloading; $S$: the initial unloading stiffness; and $h_c$: the contact depth (Oliver & Pharr 1992).
The analysis is usually made using the Oliver and Pharr method (Oliver & Pharr 1992). This model assumes that deformation upon unloading is purely elastic, that the compliance of the sample and of the non-rigid indenter tip combine as springs in series with a reduced modulus, defined as in Eq. 5.1. It also assumes that the contact can be modeled using an analytical model for a rigid indenter of defined shape in contact with a homogeneous isotropic elastic half space using Eq. 5.2.

$$\frac{1}{E_r} = \frac{(1 - v^2)}{E} + \frac{(1 - v_i^2)}{E_i}$$  \hspace{1cm} (5.1)$$

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$ \hspace{1cm} (5.2)

where $E_r$ is the reduced modulus, $E$ and $v$ are Young’s modulus and Poisson’s ratio for the specimen, $E_i$ and $v_i$ are the same parameters for the indenter, $S$ is the experimentally measured stiffness of the upper portion of the unloading data, $E_r$ is the reduced modulus, and $A$ is the projected area of the elastic contact. These equations apply to tips with a wide range of shapes. $E_r$ and $E$ can, thus, be calculated by knowing $S$ and $A$.

The Oliver and Pharr method is based on the notion that, at peak load, the material conforms to the shape of the indenter to some depth; if this depth can be established from the load-displacement data, the projected area of contact can be estimated directly from the indenter shape function $F$ in Eq. 5.3:

$$A = F(h_c)$$ \hspace{1cm} (5.3)
where A is the projected area of contact, h_c is the contact depth, and F is the indenter shape function. F has to be determined experimentally prior to analysis. The contact depth h_c is determined from the load-displacement data. In the Oliver and Pharr method, it is assumed that the unloading data is described by a power law relation in Eq. 5.4.

\[ P = \alpha (h - h_f)^m \]  

(5.4)

where P is the load and \( \alpha \), m and \( h_f \) are material constants. The initial unloading slope S is then found by analytically differentiating this expression and evaluating the derivative at peak load and displacement. From the point of view of the analysis using equations given above, it is the initial unloading data that is the most significant. Knowing S enables to know the contact depth h_c from the load-displacement data and the value of the projected area A in Eq. 5.3. It is then possible to calculate \( E_r \) from Eq. 5.2 and \( E \) from Eq. 5.1. In addition to the modulus E, it is possible to determine the hardness H, defined as the mean pressure the material will support under maximum load., with Eq. 5.5.

\[ H = \frac{P_{\text{max}}}{A} \]  

(5.5)

where A is the projected area of contact at peak load \( P_{\text{max}} \). The value H is different from the conventional Vickers hardness definition, in which the area is determined by measurement of indentation size, because the contact area A measured from the load-displacement curve involves an elastic component that will not be observed in the residual deformation left once the indenter is removed. Indeed, there is usually some degree of elastic recovery during unloading as the elastically strained material outside of the plastic zone relaxes and tries to resume its original shape, as seen in Fig. 5.14.b. (Oliver & Pharr 1992; Fischer-Cripps 2006). As seen in Fig. 5.15, the mean contact pressure, or indentation stress, is linearly proportional to the indentation strain for a completely elastic contact. As load is further applied, the plastic zone grows in size and this results in a leveling off of the indentation stress. Further increase in load results in a proportional increase in the contact area and so the mean contact pressure becomes constant (ignoring any strain hardening effects). Under these conditions of a fully developed plastic zone, the mean contact pressure can be called the hardness H of the specimen (Fischer-Cripps 2006).
Several parameters are taken into account to minimize errors in nanoindentation measurements. First, instrumental errors include the initial penetration point determination, frame compliance and the determination of the area function $F$ from Eq. 5.3. The determination of the initial contact between the indenter and the specimen is very important because the contact point determines the reference from which the displacement measurement is made. Frame compliance arises during loading from the deflections of the load frame instead of displacement into the specimen material. In addition, the hold-time at full load is often applied to account for creep effects before the indenter is unloaded. Creep and thermal drift in nanoindentation testing are very important sources of error and are difficult to distinguish.

Materials issues can also add to the error. Piling-up is an important unresolved issue in nanoindentation testing, especially for more ductile materials (see Fig. 5.16). Sinking-in represents the fact that, even for a purely elastic contact, the contact occurs below the specimen free surface. On the contrary, for a contact with plastic deformation, the surface can raise at the edge of the indentation and it decreases both the penetration depth and the computed contact area $A$. As a result, both the hardness and the elastic modulus $E$ are overestimated and it can lead to a substantial error. The piling-up effect can only be adjusted by direct measurement of the contact area with AFM or by calibrating the area function $F$ on a reference specimen similar to the test specimen to accommodate piling-up within $F$. It is, however, possible to ignore the effect and treat the resulting values of $E$ and $H$ as comparative values (qualitative approach) (ISO 14577). In addition to the piling-up effect, significantly smaller penetration depths and lower loads imply that specimen preparation is likely to
influence test results, notably with residual deformations from sample preparation (ASTM E384 – 16). For quantitative analysis, the grain size of the material also has to be taken into account, due to local interaction between dislocations that nucleate below the indenter tip and the surrounding GB interfaces for smaller grains (<900 nm for nickel) (Yang & Vehoff 2007).

Nanoindentation was used in this study to measure low hardness variations in Alloy 690 before and after ageing, and local hardness gradients at the LAS/Alloy 52 weld metal interfaces. Measurements were carried out on the same CSM instrument as microhardness (MHT) testing but with a nanoindentation hardness tester (NHT) module. The indenter was a pyramidal Berkovich diamond tip, the applied force was 1.5 mN, the indentation step size was 5 μm, the loading/unloading rates were 7.5 mN/min and the hold time was 10 s. Thermal drift and creep were not assumed to be significant. Vibro-polishing in a colloidal silica alkaline suspension for 16 to 20 h was aimed at reducing residual deformations. The piling-up effect was not corrected but tests were used mainly for a qualitative comparison between different conditions of a same material. In Alloy 690, measurements consisted of grids of at least 20 by 20 indentations, in order to cover several grains and include only measurements from grain interiors in the averaged result. The aim was to distinguish between hardness variations related either to lattice contraction or to GB precipitation, as seen in Fig. 5.18. The resulting hardness levels were taken as an average of these 400 indentations, from which data related to the zone of influence of GB was removed. The remaining hardness levels in several grain interiors were rather homogeneous for each Alloy 690 conditions, with a standard deviation of 5% and 7% from average noted for non-CW and CW conditions, respectively. The difference between the load from microhardness (350 mN) and nanoindentation (1.5 mN) is so that hardness
results from both methods cannot be compared directly, but a qualitative comparison of hardness variations is possible.

Fig. 5.18. Example of a) a 25x25 matrix of indentations for Alloy 690, and b) the corresponding hardness map, showing homogeneous hardness levels in the interior of several grains, and hardness variations localized at GBs.

5.2.6. Atomic force microscopy (AFM)

The atomic force microscopy (AFM) is part of a range of scanning probe microscopes (SPM) from the 80’s, and follows the development of the scanning tunneling microscope (STM). It has become an important tool for imaging surfaces down to the atomic scale. In the AFM, a sample is scanned by a tip mounted on a cantilever spring.

The small size of the tip (from a few nanometers to a few tens of nanometers) means that the interaction with the samples does not result only from a direct contact. Three different forces can be involved depending on the distance between the tip and the surface. During contact with the sample and surface deformation by the cantilever, an elastic repulsion force is dominant (Hertz model). When the tip is near the surface (tens of Ångströms), the dominant interaction is the Van der Waals force. For larger distance, the electrostatic interactions dominate. As a result, three types of AFM scanning modes are used: contact-mode, non-contact mode and semi-contact or tapping-mode (semi-contact and non-contact are often considered to be part of a single category).

In the contact mode, the probe tip directly touches the sample surface during scanning. The interaction between the tip and the sample is measured by monitoring either the deflection of the cantilever (constant scanner height) or the height of the scanner (constant deflection). When using a constant height, a
A topographic image of the surface results from the spatial variation of the cantilever deflection. The deflection of the cantilever is usually measured by monitoring the reflection of a laser beam focused onto the end of the cantilever. This technique is often used for atomic scale resolution imaging. When using the height of the scanner, a feedback loop moves the scanner up and down to keep the deflection of the cantilever constant. The scanner vertical motion generates data for the topographic image. This is the usual technique when using contact-mode AFM.

In the non-contact mode, the tip does not touch the surface. The cantilever arm is oscillated at the resonance frequency and the amplitude of the oscillation is kept constant by a feedback loop. Near the surface, Van der Waals and electrostatic forces modify the spring constant of the cantilever and, thus, its resonance frequency. The change in the resonance frequency of the cantilever provides topographic data in that case. Non-contact AFM was originally developed to avoid surface damage accompanying contact-mode AFM imaging. In the semi-contact mode or tapping-mode, the oscillation of the cantilever arm is such that the tip is in intermittent contact (“taps”) with the sample surface. Tapping-mode AFM provides higher resolution than the purely non-contact AFM, while still minimizing inelastic surface deformation by reducing the duration of tip-specimen contacts.

In tapping-mode, the tip will be successively in direct contact and non-direct interaction with the surface, experiencing therefore both attractive (Van der Waals) and repulsive (elastic contact) forces. It is possible to monitor the amplitude of oscillation, and to generate surface topography data from amplitude variations. In addition, the phase angle of probe oscillation (the difference between the input oscillation signal and the actual oscillation of the cantilever after contact with the sample) can be recorded. Phase imaging is very useful as it is sensitive to surface stiffness and adhesion between the tip and surface, and can therefore reveal other material properties apart from topographic data, such as local mechanical properties and chemical composition. In particular, phase imaging provides a map of stiffness variation on the sample surface, where stiffer regions have a more positive phase shift and appear brighter. The stiffness is proportional to the effective modulus and therefore related to the Young’s modulus of the material (Magonov et al. 1997; Schmitz et al. 1997).

AFM was used to characterize Alloy 690 GBs before and after ageing, in order to investigate strain localization. It was performed using a Veeco Dimension 3100 AFM system with an XY closed-loop scanner using TappingMode™ with
RTESPs (Rotated Tapping Etched Silicon Probes). Analysis of the data was accomplished using Gwyddion, a modular program for SPM data visualization.

5.2.7. X-ray diffraction

When an incident beam of monochromatic X-rays interacts with a material, the main effect is the scattering of X-rays from atoms within the target material. In the case of crystalline materials, the scattering of incident X-rays by the sample produces constructive interference when conditions satisfy Bragg’s law (see Eq. 5.6).

\[ n\lambda = 2d \sin \theta \]  

(5.6)

Bragg’s law relates the wavelength \( \lambda \) of the incident X-ray beam to the incident angle \( \theta \) and the lattice spacing \( d \) of a crystalline sample; \( n \) is an integer. The intensities of the diffracted waves depend on the lattice of the crystal structure.

X-ray diffraction (XRD) is the most common method measuring the intensity of a diffracted X-ray beam from crystalline materials. It measures the X-ray diffraction intensity as a function of scattering angle by using a diffractometer. Indeed, most crystalline materials are polycrystalline. When a material with randomly oriented crystallites interacts with an X-ray beam, the beam sees all possible atomic planes. As a result, by scanning the sample through a range of \( 2\theta \) angles, it is possible to go through all possible diffraction directions of the lattice and to detect the corresponding diffraction peaks as a function of the incident angle (diffractogram, see Fig. 5.18.a).

Fig. 5.19. Example of a) a XRD diffractogram (HCP cobalt cold-worked and annealed at 230 °C, using a Co K\(_{\alpha}\) radiation) (Warren 1969) and b) the unfiltered emission spectrum of a Mo anode bombarded by an electron beam (Guinebretière 2007).
XRD is a powerful tool for the identification and quantification of crystalline phases in multiphase samples based on their diffraction patterns. Indeed, diffraction peaks are related to lattice spacing, and are therefore characteristic of each crystal. Typically, the identification of the crystalline phases is done by comparing the measured lattice spacings with standard reference patterns. XRD can be used to measure the average lattice parameters of known materials, determine the orientation of single crystals, find the crystal structure of unknown materials, and measure residual stress of crystalline regions.

![XRD Diffractogram](image)

Fig. 5.20. Example of a) a discontinuous signal recorded in a XRD diffractogram and b) a calculated continuous curve fitting the same data and showing the positions of simulated peaks (Guinebretière 2007).

In a typical XRD equipment, a cathode ray tube first generates X-rays. It is done by producing an electron beam and bombarding a target material to produce characteristic X-rays. These X-rays consist of two main components, Kα and Kβ (see Fig. 5.18.b), and their wavelengths are characteristic of the target material (typically, Cu, Fe, Mo or Cr). Crystal monochromators filter these X-ray spectra to produce monochromatic X-rays for diffraction. The X-ray beam is then collimated and directed onto the sample. Slit systems are inserted into the X-ray path to minimize angular dispersion and to improve spatial resolution for the incident and diffracted X-ray beams. The sample and detector both rotate at an angle of θ and 2θ, respectively, to scan a range of 2θ angles from typically 5° to
70°. A detector records the intensity of the reflected X-rays and converts the signal to a count rate. The diffractograms obtained are discontinuous (see Fig.5.19.a) and their interpretation requires a fitting of the discontinuous signal with a continuous function (see Fig.5.19.b). Fitting can be done peak by peak or by using whole-pattern fitting simulations. A typical method makes use of the Rietveld refinement, in which the fitting accounts not only for the peak positions but also for the peak intensities. The processing of the diffraction diagrams enables to extract three important values from each peak: the angular position, the integrated intensity and the intensity distribution. Especially, peak positions enable to determine the interplanar distances of the material. (Guinebretière 2007).

X-ray and electron diffraction are similar, but the electron-matter interaction is typically much stronger than the X-ray photon-matter interaction. As a result, X-rays have a longer mean free path in the material (sample preparation is therefore not critical), but larger interaction volumes are needed to generate detectable X-ray signals. XRD provides therefore an overview of the microstructure of the sample, but smaller domains (<30 nm) cannot be resolved by this technique.

XRD was used to measure variations in the lattice parameter of Alloy 690 before and after ageing. XRD experiments were performed on a PANalytical X’Pert Pro MPD diffractometer using programmable slit optics and adjustable sample stage. The surface position of the samples was set using a height dial that was first calibrated against the (111) reflection of a standard silicon sample. The first five reflections ((111), (200), (220), (311), (222)) of the Alloy 690 samples were measured, and lattice parameters were determined by Rietveld refinement using PANalytical Highscore Plus 4.5 software. High preferred orientation of some samples was corrected using spherical harmonics. The standard error of the measurement was evaluated at 0.00012 Å using the standard silicon sample, and the experimental error was 0.005% for successive measurements on similar Alloy 690 SA samples. Due to time and budget limitations for the use of XRD in an external facility, only a few conditions were characterized with XRD several times. Therefore, the experimental error observed for Alloy 690 SA before ageing, which was re-measured 4 times, is used as a confidence interval for other conditions as well. The samples were observed with EBSD and deemed free of notable residual surface deformation that could affect the results.
5.3. Conclusion of the experimental methods

The experiments carried out for this thesis aimed at a detailed characterization of Alloy 690 and Alloy 52. Notably, the effect of heat treatment and thermal ageing on general microstructures and then on more localized areas, such as weld interfaces and grain boundaries, were characterized. The following section presents the results of these experiments.

First, the characterization of the as-received and aged Alloy 690 conditions is presented, from general microstructures to SRO levels and precipitations at grain boundaries. A second part shows the effects of thermal ageing on the Alloy 52 weld metal, while a special focus is given to the transition zones of DMWs in a third and last part.
6. Results

6.1. Thermal ageing of Alloy 690

6.1.1. Microstructures and hardness

Figure 6.1.1 shows an optical view of a typical TT-Alloy 690, which is the most commonly found product of Alloy 690. Dark intra- and intergranular precipitates are found and expected to be M23C6 carbides according to the literature. TiN particles appear golden in optical microscopy and are present in all conditions both inside grains and at GBs. Figure 6.1.2 shows the microstructures of the SA, SACW, TT and TTCW-Alloy 690 before ageing. The main visible difference is that heat treatment promotes IG carbide precipitation in TT- and TTCW-Alloy 690, while the grain boundaries of SA- and SACW-Alloy 690 remain mostly free of precipitates. Channeling contrast in the SEM pictures already reveals the presence of strain in the cold-worked Alloy 690 conditions, which is further seen in kernel average local misorientations maps (KAM) with EBSD (see Fig. 6.1.3). Cold work induces a clear increase in strain levels, and the localization of strains near grain boundaries. EBSD also reveals that twin boundaries and a smaller grain size are promoted by thermal treatment in the TT-Alloy 690, as compared to SA-Alloy 690 (Fig. 6.1.2). The influence of thermal ageing on the general microstructure of Alloy 690 conditions is seen as an example in Figures 6.1.3, 6.1.4 and 6.1.5, showing EBSD mapping of Alloy 690 in the as-received conditions and then aged at 475 °C for 3000 h and 10 000 h, respectively (Mouginot et al. 2015). Strains seem to become more homogeneous upon ageing in SACW- and TTCW-Alloy 690, but thermal ageing does not seem to influence strain levels significantly. This is further seen in Figure 6.1.6, showing the macro-hardness levels in all Alloy 690 conditions before and after ageing at 420 and 550 °C for 10 000 h. The grain size is smaller in TT-Alloy 690 than in SA-Alloy 690 before ageing, but grain growth is visible in TT-Alloy 690 upon ageing at 475 °C (see Fig. 6.1.3, 6.1.4 and 6.1.5). The influence of the ageing temperature on the grain size of TT-Alloy 690 is further seen in Figure 6.1.6.
Fig. 6.1.1. Optical images of TT-Alloy 690, with a) the general microstructure of Alloy 690 with equiaxed grains, twinning and golden TiN particles, b) a close-up of intragranular carbides looking like carbide banding and c) a close-up of a TiN particle.

The main effect of thermal ageing on the microstructure of Alloy 690 is actually the promotion of IG precipitation, as seen in Figures 6.1.7, 6.1.8, 6.1.9 and 6.1.10 for SA-Alloy 690, TT-Alloy 690, SACW-Alloy 690 and TTCW-Alloy 690, respectively. Especially, ageing at 475 and 550 °C greatly modifies the structure of GBs, with extensive IG precipitation occurring in the previously precipitate-free SA- and SACW-Alloy 690 conditions, and the development of large precipitated areas in TT- and TTCW-Alloy 690. In SACW- and TTCW-Alloy 690, precipitation occurs extensively in highly strained areas, as seen in Figures 6.1.9, 6.1.10 and 6.1.11, and recrystallization can occur next to highly strained GBs upon ageing at 550 °C (Mouginot et al. 2017a).

In relation to higher strain levels, Figure 6.1.12 shows that the Vickers hardness of SACW- and TTCW-Alloy 690 is about twice that of SA- and TT-Alloy 690, with little influence of thermal ageing on the hardness level. However, small variations are visible.
The hardness of TT-Alloy 690 is higher than that of SA-Alloy 690 before ageing, but it reaches similar hardness levels upon ageing. The hardness of TTCW-Alloy 690 is also higher than that of SACW-Alloy 690, but it decreases upon ageing, while the hardness of SACW-Alloy 690 increases upon ageing at 420 °C but decreases upon ageing at 550 °C. Vickers hardness with 1 kg load is useful for general characterization purposes, but difficulty arises from the fact that many factors influence the measured hardness level: grain size, IG precipitation, ordering, stress relaxation and recrystallization. The need to discriminate between the factors influencing the hardness level, in order to characterize the SRO level, made the use of much smaller loads necessary (Mouginot et al. 2017b).

**Fig. 6.1.2.** SEM imaging of the different conditions of Alloy 690 (SA, TT, SACW and TTCW) before ageing. The main visible difference with SEM is the IG carbide precipitation in TT- and TTCW-Alloy 690 after heat treatment.
Fig. 6.1.3. EBSD mapping of the microstructure of the SA-, SACW-, TT- and TTCW-Alloy 690 conditions before ageing with band contrast (twin boundaries in red) on the left and kernel average local misorientations (KAM) on the right.
Fig. 6.1.4. EBSD mapping of the microstructure of the SA-, SACW-, TT- and TTCW-Alloy 690 conditions after ageing at 475 °C for 3000 h, with band contrast (twin boundaries in red) on the left and KAM on the right.
Fig. 6.1.5. EBSD mapping of the microstructure of the SA-, SACW-, TT- and TTCW-Alloy 690 conditions after ageing at 475 °C for 10 000 h with band contrast (twin boundaries in red) on the left and KAM on the right.
Fig. 6.1.6. EBSD mapping with band contrast (twin boundaries in yellow) of the microstructure of TT-Alloy 690 before ageing (TT) and after ageing at 420, 475 and 550 °C for 10 000 h, showing the grain size growth with ageing temperature.

Fig. 6.1.7. SEM imaging showing the evolution of IG precipitation in SA-Alloy 690 before ageing (SA) and after ageing at 420, 475 and 550 °C for 10 000 h.
Fig. 6.1.8. SEM imaging showing the evolution of IG precipitation in TT-Alloy 690 before ageing (TT) and after ageing at 420, 475 and 550 °C for 10 000 h.

Fig. 6.1.9. SEM imaging showing the evolution of IG precipitation in SACW-Alloy 690 before ageing (SACW) and after ageing at 420, 475 and 550 °C for 10 000 h.
Fig. 6.1.10. SEM imaging showing the evolution of IG precipitation in TTCW-Alloy 690 before ageing (TTCW) and after ageing at 420, 475 and 550 °C for 10 000 h.

Fig. 6.1.11. EBSD mapping of TTCW-Alloy 690 aged at 550 °C for 10 000 h with band contrast on the left and KAM on the right. Unresolved (dark) areas in KAM correspond to IG precipitation.

6.1.2. Hardness variation and link with SRO

After the characterization of the general microstructures of the different Alloy 690 conditions and the resulting understanding of the scale at which changes related to thermal ageing occur, a more detailed characterization was started. Notably, a close attention was paid to small hardness changes occurring upon thermal ageing as a means to deduce indirectly the level of SRO and the effect of both the original alloy condition and the ageing temperature on these changes. Small variations are noted with Vickers hardness tests using a 1 kg (or about 9.8 N), with a clear influence of cold work and heat treatment on the original conditions, but small effect of thermal ageing. Especially, the influence of
grain size, IG precipitation, strain localization and SRO are overlapping and contradictory.

![Fig. 6.1.12. Vickers hardness levels (using 1 kg load) in all Alloy 690 conditions before (AR) and after ageing for 10 000 h at 420 and 550 °C. The hardness of cold-worked conditions is about twice that of the non cold-worked conditions. Standard deviation from average of 2 and 4 % for non-CW and CW conditions, respectively.](image1)

![Fig. 6.1.13. Hardness from the nanoindentation test for the SA-, SACW-, TT- and TTCW-Alloy 690 conditions before ageing (AR) and after ageing at 350, 420, 475 and 550 °C for 10 000 h. Standard deviation from average of 5 and 7 % for non-CW and CW conditions, respectively.](image2)

An idea is that the effects of grain size, IG precipitation and strain localization (in CW samples) interact in an indentation over a large area with grain boundaries, while SRO occurs in the lattice in grain interiors. As showed in Figure 5.18 in Section 5.2.5, the use of nanoindentation with an instrumented tester and a 1.5 mN load to create large matrices of indentation enables to discriminate between the influence of GBs and the hardness levels inside several grains. Figure 6.1.13 shows the results of these nanoindentation tests for all Alloy 690 conditions before ageing and after ageing at 350, 420, 475 and 550 °C for 10 000 h. Each point of the graph is an averaged value of at least 400 indentations, from which data points close to GB zones have been removed. For clarity, errors bars
are not showed on the graph, but a standard deviation of 5 and 7 % from average was observed in the non-CW and CW samples, respectively.

Before ageing, cold work increases the hardness of the alloy (from 371 to 465 HV_{IT} for SA- to SACW-Alloy 690 and from 413 to 507 HV_{IT} for TT- to TTCW-Alloy 690, respectively). Thermally treated conditions are harder than the water-quenched conditions (371 and 413 HV_{IT} for SA- to TT-Alloy 690, respectively). In all conditions, thermal ageing at 350 and 420 °C for 10 000 h increased the hardness of Alloy 690. At 350 °C, the hardness increase is more obvious for the cold-worked conditions SACW- (from 465 to 535 HV_{IT}) and TTCW-Alloy 690 (from 507 to 538 HV_{IT}) than for the SA- and TT-Alloy 690 conditions. For all conditions, the hardness increase is the strongest at 420 °C, especially for the TT condition (from 413 HV_{IT} before ageing to 544 HV_{IT} after 10 000 h at 420°C). At 475 and 550 °C, the hardness increase was more limited in the TT-Alloy 690 condition and a hardness decrease was observed in the SACW- and TTCW-Alloy 690 conditions. In the SA-Alloy 690 condition, a hardness increase was still noticeable at 475 °C, while the hardness upon ageing at 550 °C was similar to the level obtained upon ageing at 350 °C (Mouginot et al. 2017a).

![Fig. 6.1.14. Variations of the grain size in TT-Alloy 690 as compared to SA-Alloy 690 before ageing and after ageing at 420 and 550 °C.](image)

The nanoindentation measurements are not influenced by grain size variations or the development of IG precipitation, which explains that the results are different from that of Vickers hardness testing with 9.8 N. In particular, Vickers hardness of TT-Alloy 690 is higher than that of SA-Alloy 690 before ageing, but is seen to decrease with increasing ageing temperature, while IG precipitation increases, which correlates well with an increase in grain size (see Fig. 6.1.14 and 6.1.15). The grain size was calculated by grain area detection with EBSD, using a magnification of 500x with a step size of 0.06 μm. A threshold of 10 or
100 pixels per grain can be applied depending on the standard used (Mouginot et al. 2017b). The error in the grain size measurement was calculated as the ratio of the standard deviation by the square root of the number of measured grains.

Fig. 6.1.15. EBSD mapping of SA- and TT-Alloy 690 before ageing and TT-Alloy 690 after ageing at 420 and 550 °C for 10 000 h, showing the grain size variation.

Fig. 6.1.16. Lattice parameter variation from SA- to TT-Alloy 690 before ageing and in TT-Alloy 690 upon ageing at 350, 420, 475 and 550 °C for 10 000 h.

Further, the Vickers hardness increase in SA-Alloy 690 following an increase in ageing temperature to reach the hardness level similar to that of TT-Alloy 690 upon ageing at 550 °C can be attributed to IG precipitation increasing upon ageing in SA-Alloy 690 to reach the microstructure similar to that of TT-Alloy 690.
Nanoindentation tests do not show the same trends as Vickers hardness tests, as the grain size and IG precipitation do not affect them. For this reason, an assumption is made that the hardness variations observed from the nanoindentation measurements are due to changes in the ordering levels in Alloy 690. This assumption is strengthened by lattice parameter measurements obtained by XRD. Figure 6.1.16 shows the changes in the average lattice parameter measured for the TT-Alloy 690 condition before and after ageing at 350, 420, 475 and 550 °C for 10 000 h, and compared to the as-received SA-Alloy 690 condition. The lattice parameter decreased significantly after thermal treatment, as compared to the SA-Alloy 690 condition. Lattice contraction in the TT-Alloy 690 condition increased even further upon ageing at 420 °C. Ageing at 475 °C led back to a lattice parameter similar or higher than the as-received TT-Alloy 690 condition, while ageing at 550 °C increased the lattice parameter significantly to levels close to the SA-Alloy 690 condition. These experiments are indirect but suggest strongly a SRO peak in all conditions of Alloy 690 upon ageing at 420 °C, which is supported by the literature on the subject (Mouginot et al. 2016; Mouginot et al. 2017a). A confidence interval of 0.005 %, based on the experimental error observed for successive measurements on Alloy 690 SA, was added.

Going further, the work was focused on TT-Alloy 690 as it showed the highest variations in the nanoindentation measurements and therefore, supposedly, the best chance to observe SRO directly. In addition, Alloy 690TT is the standard condition used in power plants, adding value to the results.

### 6.1.3. Direct observation of SRO

Ordering in Ni-base alloys is usually studied using indirect methods such as measurement of hardness and lattice parameter variation, or changes in electrical resistivity. However, the formation of LRO can arguably be studied almost directly by observing electron diffraction patterns with a TEM. The presence of an ordered superlattice generates interlattice reflections in usually forbidden area between the main lattice diffraction spots. Difficulty arises from the fact that such extra-reflections can also be attributed to oxide layer formation on the surface of the sample or to precipitates in the lattice. In addition, the observation of interlattice reflections due to ordering is commonly accepted as being unfeasible for a commercial melt of Alloy 690.

An idea, following the hypothesis that SRO is linked to the PWSCC of Alloy 600 by strain build-up during thermal ageing, was to study the strain levels in TT-Alloy 690 using an EBSD detector with high angular resolution (i.e., able to
detect lower misorientations in the lattice). Figure 6.1.17 shows the HR-EBSD maps for TT-Alloy 690 before and after ageing at 420, 475 and 550 °C for 10 000 h. No significant change is observed between before and after ageing, although the misorientation levels are reduced upon ageing at 550 °C (Mouginot et al. 2017b).

![HR-EBSD mapping of TT-Alloy 690 before and after ageing at 420, 475 and 550 °C for 10 000 h, with the corresponding local misorientation profiles.](image)

**Fig. 6.1.17.** HR-EBSD mapping of TT-Alloy 690 before and after ageing at 420, 475 and 550 °C for 10 000 h, with the corresponding local misorientation profiles.
Figure 6.1.18 shows an overview of the TT-Alloy 690 material before and after ageing at 420 and 550 °C for 10 000 h. TEM study of TT-Alloy 690 does not show direct evidence of SRO, but ageing at 420 °C leads to the formation of dislocation tangles (indicated by red arrows in Fig. 6.1.18). These tangles are not observed before ageing or after ageing at 500 °C. TT-Alloy 690 samples showing an otherwise clean microstructure. Similarly, GBs of TT-Alloy 690 aged at 420
°C seem to show higher dislocation density than TT-alloy 690 before ageing, with a similar level of IG carbide precipitation, or upon ageing at 550 °C, with a higher level of IG precipitation (see Fig. 6.1.19) (Mouginot et al. 2017b).

A closer characterization of the dislocation tangles found in TT-Alloy 690 upon ageing at 420 °C shows that they are often centered on a small particle (see Fig. 6.1.19).
A study of the diffraction patterns in various locations of grain interiors, near GBs, on GBs and on the tangles did not reveal interlattice reflections due to ordering. As illustrated in Figure 6.1.21, all extra reflections in addition to the fcc lattice of the matrix can be attributed to carbides.

**Fig. 6.1.20.** TEM imaging of a dislocation tangle found in TT-Alloy 690 aged at 420 °C for 10 000 h, showing the bright field image of the tangle (right) and the corresponding dark field (left) with a highlighted particle at the center of the dislocation tangle.

**Fig. 6.1.21.** Illustration of the study of diffraction patterns of a GB in TT-Alloy 690 aged at 420 °C for 10 000 h (top left). The dark field image associated with the main reflections reveals a grain on one side of the GB (bottom left), while the rotated reflections correspond to the grain on the other side of the GB (bottom right). The interlattice reflections are associated with M23C6 carbides on the GBs (top right).
Another direct evidence of SRO in TEM is the formation of a mottled contrast due to nuclei of ordered phase (Marucco 1995). A similar feature was found and investigated in TT-Alloy 690 upon ageing at 420 °C. It is suggested that it is the result of an oxide film formation on the surface of the thin TEM sample rather than SRO.
6.1.4. Evolution of grain boundaries with thermal ageing

The study of SRO via nanoindentation carefully avoided GBs to focus on grain interiors, and TEM work on SRO focused on lattice reflections rather than carbides, but IG precipitation remains the main visible change caused by thermal ageing. Especially, ageing at 475 and 550 °C causes significant changes in all conditions. Figures 6.1.7 to 6.1.10 show the effect of ageing temperature on the extent of IG precipitation.

In addition, diffusion-induced grain boundary migration (DIGM) is promoted in SA- and TT-Alloy 690 at 475 and 550 °C, as seen in Figure 6.1.23, although IG carbides are seen to pin GBs already in TT-Alloy 690 before ageing (see Fig. 6.1.8). IG carbides are growing within the migrated zone, between the original GB and the new migrated GB. As illustrated in Figure 6.1.25, all IG precipitates studied with TEM in SA- and TT-Alloy 690 are Cr-rich M\textsubscript{23}C\textsubscript{6} carbides. The lattice parameter of M\textsubscript{23}C\textsubscript{6} carbides is about three times bigger than that of the austenitic fcc matrix, which results in a distance between diffraction points associated with these carbides about three times smaller in the reciprocal space. This diffraction pattern is typical of M\textsubscript{23}C\textsubscript{6} carbides in a fcc matrix (see Fig. 6.1.24.a) (Mouginot et al. 2017a).

Fig. 6.1.23. SEM imaging (top left) and EBSD mapping of the microstructure of the SA- and TT-Alloy 690 conditions after ageing at 550 °C for 10 000 h, showing evidence of DIGM.
Fig. 6.1.24. TEM bright field image of a precipitate in TT-Alloy 690 aged at 420 °C for 10 000 h (top left) and the selected area diffraction (SAD), with a) the diffraction pattern from this area, b) the corresponding dark field image of the same location using interlattice reflections, and c) a lower magnification dark field image using the same diffraction spots.

A special case was made of SACW- and TTCW-Alloy 690 conditions aged at 550 °C for 10 000 h. Figure 6.1.25 shows the extent of recrystallization and precipitation within the recrystallized area in SACW-Alloy 690 aged at 550 °C. A different kind of precipitate appears upon ageing within recrystallized areas. These precipitates appear rounder, bigger and darker than other typical M\textsubscript{23}C\textsubscript{6} located at GBs and twins (see Fig. 6.1.26). As seen with TEM EDS and as illustrated with a SEM EDS map in Figure 6.1.27 for SACW-Alloy 690 aged at 550 °C for 10 000 h, all the precipitates forming upon thermal ageing are Cr-rich.

Phase identification with EBSD, following the analysis of diffraction patterns typical of M\textsubscript{23}C\textsubscript{6} carbides, confirms that the vast majority of precipitates forming upon thermal ageing in non-CW Alloy 690 conditions are indeed Cr-rich M\textsubscript{23}C\textsubscript{6} carbides. They decorate mostly GBs, but precipitation occurs also at twin boundaries to some extent (see Fig. 6.1.28).
In CW Alloy 690 conditions aged at 550 °C for 10 000 h, however, the rounder and darker precipitates are identified as the ferritic α-Cr phase (see Fig. 6.1.28). M_{23}C_6 carbides still decorates the original GBs and twins, while α-Cr grows in the recrystallized areas. Although the formation of the α-Cr phase usually occurs at temperatures higher than 600 °C, the high amount of deformation induced by cold work seems to favor its precipitation at a lower temperature (Mouginot et al. 2017a; Mouginot et al. 2017b).

Fig. 6.1.25. SEM imaging of SACW-Alloy 690 after ageing at 550 °C for 10 000 h, showing a large recrystallized area starting from a former highly-strained GB.

In SACW- and TTCW-Alloy 690, twins are usually highly deformed, resulting in the precipitation of elongated M_{23}C_6 carbides (see Fig. 6.1.26). In SA- and TT-Alloy 690, however, another type of precipitate develops on twin boundaries upon thermal ageing. It results typically in thin dark lines growing perpendicular from the twin boundary, as seen in Figure 6.1.29. TEM analysis shows that these precipitates are Cr-rich M_{23}C_6 carbides plates (see Figure 6.1.30).

Finally, the effect of IG carbide precipitation and SRO on the strain distribution at GBs was investigated. A hypothesis was that lattice contraction occurring within the grains due to the development of SRO will generate strains accommodated between grains at GBs. To that end, high angular resolution EBSD analysis was carried out at high magnification on GBs of TT-Alloy 690 before and after ageing at 420, 475 and 550 °C for 10 000 h. The results are seen in
Figure 6.1.31, showing the strain localization around GBs using local kernel average misorientation maps (Mouginot et al. 2017b).

**Fig. 6.1.26.** SEM imaging of precipitates forming in recrystallized areas of SACW- and TTCW-Alloy 690 upon ageing at 550 °C for 10 000 h. Typical M23C6 carbides forming at GBs and highly deformed twins are marked with yellow arrows. Another type of rounder and darker precipitate is marked with red arrows.
Fig. 6.1.27. SEM imaging of a recrystallized area in SACW-Alloy 690 aged at 550 °C for 10 000 h, with the corresponding EDS mapping showing the distribution of Cr, Ni and Fe.

Fig. 6.1.28. EBSD mapping of TT- and TTCW-Alloy 690 conditions after ageing at 550 °C for 10 000 h, showing the distribution and nature of precipitates in the Ni matrix (black). In TT-Alloy 690, only Cr-rich M23C6 carbides are found at GBs and twins. In TTCW-Alloy 690, while Cr-rich M23C6 also decorate GBs, the dominant precipitation is α-Cr particles in the recrystallized areas.
No significant change is observed in the IG strain localization in TT-Alloy 690 before and after thermal ageing. It is interesting to note that upon ageing at 475 and 550 °C, when DIGM becomes significant, the higher strains remain located at the original position of the GBs, around IG carbides.

Going further, AFM mapping of the same TT-Alloy 690 conditions was carried out to observe the influence of IG carbides on hardness distribution at GBs (see Fig. 6.1.32). Phase imaging was used to image hardness variations between grains and GBs. The main conclusion is that thermal ageing does not significantly change the hardness distribution near GBs in TT-Alloy 690, and that the highest hardness is located at GBs due to IG carbides. TT-Alloy 690 aged at 550 °C for 10 000 h has an overall lower phase response than that of TT-Alloy 690 before ageing or upon ageing at 420 °C, which corresponds to a lower overall hardness. In addition, the area between original GBs and migrated GBs is softer than that of grain interiors. With a closer view of GBs, it is interesting to see that, typically, one side of the GBs is softer than the surrounding material, while the other side is harder (see Fig. 6.1.33). It is due to the relative grain orientations (Mouginot et al. 2017b).
Fig. 6.1.30. TEM imaging of precipitates at twin boundaries in TT-Alloy 690 aged at 550 °C for 10 000 h, with bright field image (top left), dark field images (top right, middle left) corresponding to interlattice reflections from the SAD (middle right). Scanning TEM EDS analysis shows that these are Cr-rich carbides (bottom right).
Fig. 6.1.31. HR EBSD mapping of GBs in TT-Alloy 690 before and after ageing at 420, 475 and 550 °C for 10 000 h, with the SEM imaging of the location (left) and the corresponding KAM levels (right).
Fig. 6.1.32. AFM mapping of TT-Alloy 690 before and after ageing at 420 and 550 °C for 10 000 h, with height imaging (left) following the amplitude of the cantilever oscillations, and phase imaging (right) following the difference between the initial frequency of the cantilever oscillation and the frequency after contact with the surface.
6.2. Characterization of Alloy 52 weld metal

The effect of thermal ageing on Alloy 52 weld metal was investigated using the same means than for Alloy 690. The weld metal microstructure away from the weld interfaces is, however, rather inhomogeneous. As a result, nanoindentation measurements with 1.5 mN loads resulted in very large scatter and could not be used. Microstructures were characterized first, with a special focus on GBs, and hardness variations from the weld crown to the weld root were measured.

6.2.1. Microstructures of the weld metal

As seen in Figure 6.2.1, the Alloy 52 weld metal microstructure shows elongated grains diverging from the weld center towards the two weld interfaces with the base metals. Figure 6.2.2 shows a closer optical view of the microstructure of
weld metal grains. Within each grain, a dendritic structure is visible, following certain growth direction. Precipitates are mostly located in the interdendritic regions. Grains are typically more than 1 mm long, and are separated by solidification grain boundaries where two dendritic structures of different orientations meet. No visible change in the Alloy 52 weld metal microstructure is observed upon ageing at 400 °C for 5000 and 10 000 h.

![Alloy 52 weld metal aged at 400 °C for 10 000 h](image)

Fig. 6.2.1. SEM imaging of Alloy 52 weld metal at the weld center in the NIWEL 10 000 h weld.

![Fig. 6.2.2. Optical picture of Alloy 52 weld metal after etching, with the microstructures from a) the NIWEL AR condition and b) the NIWEL 5000 h condition.](image)

A closer view of the solidification GBs is given in Figure 6.2.3. PWHT promotes the precipitation of Cr-rich IG carbides in the weld metal, and no significant change is seen after thermal ageing up to 10 000 h. Grain boundary migration is visible in all conditions, with a pinning effect from IG carbides, but there is no evidence that thermal ageing promotes GB migration further after PWHT.
Before and after ageing, some areas of the weld show more extensive IG precipitation, as seen in Figure 6.2.4. As in Alloy 690, the other main kind of precipitates found in Alloy 52 weld are TiN particles, distributed throughout the weld both inside grains and at GBs (see Fig. 6.2.5). They are not affected by the thermal ageing.

In Alloy 690, thermal ageing for 10 000 h affects GB structures significantly only at 475 °C and higher. It is therefore true that thermal ageing at 400 °C has little effect on the microstructure of Alloy 52 weld metal (Ahonen et al. 2016; Sarikka et al. 2017).

Fig. 6.2.3. SEM imaging of GBs in Alloy 52 weld metal from the NIWEL mock-up before and after ageing at 400 °C for 5000 and 10 000 h.
Fig. 6.2.4. SEM imaging of a large precipitated area at GBs in Alloy 52 weld metal aged at 400 °C for 5000 h.

Fig. 6.2.5. SEM imaging of Alloy 52 weld metal after ageing at 400 °C for 10000 h, showing a solidification GB decorated with IG carbides and darker, and bigger TiN particles.
6.2.2. Hardness variation

Microhardness measurements were carried out in the studied conditions before and after ageing at 400 °C for 10 000 h. The results are showed in Table 6.2.1. The hardness of the Alloy 52 weld metal increases from the weld crown to the weld root, with little influence of thermal ageing. The main difference between the hardness level of the weld crown before and after ageing results from a slight difference of position of the measurement, the microhardness for the NIWEL 5000 h weld crown being taken closer to the weld center.

Table. 6.2.1. Hardness variation in Alloy 52 weld metal from the weld crown to the weld root, before and after ageing at 400 °C for 5000 and 10 000 h.

<table>
<thead>
<tr>
<th>NIWEL</th>
<th>Crown</th>
<th></th>
<th>Center</th>
<th></th>
<th>Root</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>232</td>
<td>8</td>
<td>247</td>
<td>14</td>
<td>268</td>
<td>10</td>
</tr>
<tr>
<td>5000 h</td>
<td>243</td>
<td>13</td>
<td>249</td>
<td>8</td>
<td>270</td>
<td>15</td>
</tr>
<tr>
<td>10 000 h</td>
<td>239</td>
<td>15</td>
<td>245</td>
<td>17</td>
<td>257</td>
<td>12</td>
</tr>
</tbody>
</table>

There is little influence of thermal ageing at 400 °C up to 10 000 h on the microstructure and hardness levels in Alloy 52 weld metal in this DMW mock-up. However, transition zones in DMWs are traditionally susceptible to metallurgical changes and represent a critical location that has to be investigated along with the weld metal (Mouginot et al. 2014; Sarikka et al. 2016).

6.3. Characterization of the LAS/Alloy 52 weld metal interface

The transition zone from the LAS to the Alloy 52 weld metal is of particular interest since it joins two materials with different lattice structures (bcc for LAS and fcc for Alloy 52) and very different composition (high Cr/low C for Alloy 52, low Cr/higher C for LAS). Going from the LAS base metal to the Alloy 52 weld metal, the transition zones of interest are the LAS heat-affected zone (HAZ), the LAS carbon-depleted zone, the partially melted zone (PMZ) at the fusion line and the weld metal close to the fusion line.

6.3.1. Heat-affected zone of the LAS

As seen in Figure 6.3.1, the heat-affected zone (HAZ) of the LAS extends about 2.5 mm from the fusion line to the base metal. The LAS base metal (about 240 HV0.3) consists of coarse ferrite grains with bainite clusters. The microstructure refines progressively towards the fusion line due to the heat input from the welding process. First, an intermediate zone is found in the HAZ with partially refined grains, followed by a grain-refined zone of higher hardness (about 280
HV₀.₅). Closer to the fusion line, the heat input is such that grains coarsen. Last but not least, adjacent to the fusion line is a layer of coarse grains from which carbon has diffused to the low-C/high-Cr weld metal side of the interface. It is the carbon-depleted zone (CDZ, about 230 HV₀.₅). To be noted is the presence of bands in the LAS HAZ (see Fig. 6.3.1) appearing darker or lighter. The darker bands have a smaller grain size and are harder (about 300 HV₀.₅) than the rest of the HAZ.

Figures 6.3.2 to 6.3.4 show the evolution of the LAS HAZ microstructure in SINI-PWHT from the base metal to the grain-refined zone and the CDZ near the fusion line with Alloy 52 weld metal. PWHT used to temper the weld is a standard procedure for the actual components, but a side effect is seen in Figure 6.3.5, showing the difference in the CDZ width between the SINI-AW (about 10 μm wide) and the SINI-PWHT (more than 50 μm wide) conditions. NIWEL-AR has a similar condition than SINI-PWHT, as they have both followed the same standard PWHT. A CDZ about 60–70 μm wide is therefore visible in NIWEL-AR (see Fig. 6.3.6). However, thermal ageing of the NIWEL mock-up at 400 °C for 10 000 h, simulating 60 years of operations in a modern PWR, does not appear to influence the CDZ width (see Fig. 6.3.6). In addition, a comparison of the microstructures in the LAS HAZ between the NIWEL-AR and NIWEL-10 000 h does not reveal noticeable changes (see Fig. 6.3.7).

![Fig. 6.3.1. Optical image of the NIWEL DMW mock-up before ageing, showing the LAS base metal (extreme left), the LAS HAZ (darker zone) and the interface with Alloy 52 weld metal (extreme right). The magnification is low enough to see three weld passes, creating the wavy pattern of the fusion line. Banding is seen in the LAS HAZ.](image)
Fig. 6.3.2. SEM imaging of the SA 508 base metal in the SINI-PWHT condition.

Fig. 6.3.3. SEM imaging of the grain-refined zone of the SA 508 HAZ in the SINI-PWHT condition.
Fig. 6.3.4. SEM imaging of the grain-coarsened zone and CDZ of the SA 508 HAZ in the SINI-PWHT condition, next to the fusion line with Alloy 52 weld metal.

Fig. 6.3.5. Optical images of the SA 508/Alloy 52 weld metal interface in the SINI-AW and SINI-PWHT conditions (left and right, respectively), showing the effect of PWHT on the CDZ in the LAS side.

Fig. 6.3.6. Optical images of the SA 508/Alloy 52 weld metal interface in the NIWEL-AR and NIWEL-10 000 h conditions, showing CDZs of similar width.
Fig. 6.3.7. SEM images of the SA 508 HAZ microstructure in the NIWEL-AR (left) and NIWEL-10 000 h (right) conditions, taken next to the fusion line with Alloy 52 weld metal (a and e), 50 μm from the fusion line (b and f), 120 μm from the fusion line (c and g) and in the LAS base metal (d and h).

The grain size in the grain-refined zone of the LAS HAZ reaches low levels that are difficult to characterize with SEM. EBSD was used (see Fig. 6.3.8) to determine the grain size variations in the LAS HAZ of NIWEL conditions before and after thermal ageing (see Fig. 6.3.9). The variation for the NIWEL-5000 h gives
an idea of the expected trend. The large scatter between the different conditions, from 500 up to 1500 μm away from the fusion line, is related to the banding observed in Figure 6.3.1. For that reason, the main conclusion is that the grain size in the LAS goes from about 2.5 μm in the base metal, to about 1.5 μm in the grain-refined zone and back to 2.5 μm in the CDZ. No significant change due to thermal ageing is visible.

Fig. 6.3.8. EBSD mapping of the microstructures in the LAS HAZ of the NIWEL-5000 h condition, at different distances from the fusion line (FL).

Fig. 6.3.9. Grain size variation in the LAS HAZ of NIWEL mock-ups before and after ageing for 5000 and 10 000 h at 400 °C.
6.3.2. Partially melted zone

The partially melted zone (PMZ) is a martensite-like layer adjacent to the fusion line between a ferritic LAS and an austenitic weld metal, in which both the base metal and the weld metal are present. The LAS grains in the PMZ are small and elongated, with a feather-like appearance reminding of martensite (see Fig. 6.3.10). The transition of a straight fusion line between the LAS and Alloy 52 occurs typically at the beginning of a weld pass, when LAS starts to be swept away from the base metal into the weld metal (see Fig. 6.3.11). The progression of the PMZ development following a weld pass is clearly visible in Figure 6.3.12.

![Fig. 6.3.10. EBSD mapping of a PMZ at the interface between a ferritic LAS (red) and an austenitic Alloy 52M weld metal (blue) interface, with phase identification (left) and grain orientation (right) analysis.](image_url)

![Fig. 6.3.11. SEM imaging of the transition between a straight fusion line and the start of a PMZ in NIWEL-5000 h at the beginning of a weld pass.](image_url)
Along with the development of a PMZ, the start of the weld pass modifies the composition gradients at the LAS/Alloy 52 weld metal quite significantly. Figures 6.3.13 and 6.3.14 show composition gradients from EDS line scans over the fusion line in NIWEL-AR, first without PMZ and then over a PMZ. The results show that the PMZ has a composition still close to that of the LAS since it is comprised mostly of LAS grains. However, the Fe-, Ni- and Cr-composition gradients from the LAS to the weld metal are less steep after the PMZ. About 30 $\mu m$ away from the LAS is needed to reach the nominal weld metal composition without PMZ (see Fig. 6.3.13), while 120 $\mu m$ is needed after a PMZ (see Fig. 6.3.14). An EDS mapping shows that this phenomenon is a result of the location of the PMZ at the start of a weld pass (see Fig. 6.3.15). Indeed, the weld pass sweeps material from the LAS into the weld metal, generating the PMZ but also diluting a portion of the LAS into the weld metal. It results in a significant Fe enrichment in the weld metal in this area, which is seen when crossing the PMZ with an EDS line scan (see Fig. 6.3.14). In addition, PMZ are martensite-like layers that are typically harder than the surrounding LAS and weld metal, as seen in the nanoindentation profiles from Figure 6.3.16. The PMZ morphology or hardness levels are not visibly affected by thermal ageing in the NIWEL mock-up weld. (Ahonen et al. 2017; Sarikka et al. 2017)
**Fig. 6.3.13.** EDS line scan over a clean fusion line in NIWEL-5000 h, showing the steep composition gradients from the LAS (left) to Alloy 52 weld metal (right).

**Fig. 6.3.14.** EDS line scan over a fusion line with PMZ in NIWEL-5000 h, showing wider composition gradients from the LAS (left) to Alloy 52 weld metal (right).
Fig. 6.3.15. EDS mapping of the start of a weld pass in NiWEL-5000 h, showing the transition from a) a clean fusion line to b) a PMZ and eventually to c) a LAS swirl in the weld metal. The beginning of the weld pass increases the dilution of Fe (red) from the LAS to the Ni-rich (blue) weld metal.
6.3.3. Alloy 52 weld metal

The weld metal near the fusion line in ferritic/austenitic interfaces of DMWs presents typical features, and Alloy 52 is not the exception. Figure 6.3.17 shows an overview of such a typical interface from SINI-AW. It shows the grain coarsening zone and CDZ in the LAS side, a PMZ along the fusion line, and a Type II boundary in the weld metal side, marked by a different orientation of the weld metal lattice before and after the boundary.

Type II boundaries and precipitation at Type II boundaries are an important feature of the DMW interface as they have been related to premature failure of components. Figure 6.3.18 shows the evolution of a Type II boundary before and after ageing at 400 °C for 10 000 h in NIWEL-AR and NIWEL-10 000 h. No visible change due to thermal ageing can be observed.

Another typical feature of ferritic/austenitic DMW interface is the presence of a planar solidification front in the weld metal near the fusion line. It is characterized by the absence of a dendritic structure in a narrow zone, and is linked to steep composition gradients and carbon pile-up, which can result in high hardness levels and be a preferential site for cracking. Figure 6.3.19 shows such a featureless layer in SINI-AW and its widening after PWHT.
The main conclusions of the microstructural characterization are so far that PWHT widens the CDZ in the LAS side of the LAS/Alloy 52 weld metal interface, while thermal ageing at 400 °C up to 10 000 h does not change microstructure to a visible extent. Neither the Alloy 52 weld metal, nor the LAS HAZ or the PMZ and Type II boundaries at the weld interface show significant differences between the NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h conditions.

**Fig. 6.3.17.** EBSD mapping of the LAS/Alloy 52 weld metal interface in SINI-AW, with phase identification (top) and grain orientation (bottom) maps. It shows typical features of the ferritic (blue)/austenitic (red) DMW interface, such as CDZ, PMZ and Type II boundary in the weld metal.

**Fig. 6.3.18.** SEM imaging of a Type II boundary in a) NIWEL-AR and b) NIWEL-10 000 h DMW.

**Fig. 6.3.19.** Fusion line and Alloy 52 weld metal in a) SINI-AW and b) SINI-PWHT, showing the widening of featureless layer adjacent to the fusion line.
6.3.4. Hardness profiles

The result of metallurgical changes in the narrow transition zones of DMWs is mostly visible in hardness levels across the interface. This section presents the microhardness and nanohardness measurements made across the LAS/Alloy 52 weld metal interfaces of SINI-AW, SINI-PWHT, NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h.

Figure 6.3.20 and 6.3.21 show the microhardness profiles in the SINI mock-up before and after PWHT. A clear effect of PWHT is visible, as the smooth transition from the LAS to Alloy 52 weld metal in SINI-AW becomes a strong hardness mismatch at the fusion line, with the lowest hardness in the LAS (220 HVIT) and a hardness peak in Alloy 52 weld metal adjacent to the fusion line (650 HVIT).

Figures 6.3.22, 6.3.23 and 6.3.24 show the evolution of the hardness profile at the LAS/Alloy 52 weld metal interface in the NIWEL samples before and after ageing at 400 °C for 5000 and 10 000 h. NIWEL-AR shows a microhardness profile similar to that of SINI-PWHT, as they are both PWHT and not aged. The lowest hardness is found in the LAS (220-230 HVIT) and the highest hardness in Alloy 52 weld metal (536 HVIT). High scatter in the LAS HAZ is due to banding. Thermal ageing affects the hardness profiles significantly, as the hardness peak in Alloy 52 weld metal becomes lower upon ageing for 5000 h (377 HVIT) and even lower upon ageing for 10 000 h (331 HVIT). In the LAS HAZ, a hardness peak is found about 600 μm away from the fusion line in both the SINI and NIWEL samples. (Ahonen et al. 2017; Sarikka et al. 2017)

![Microhardness profile](image)

**Fig. 6.3.20.** Microhardness profile (350 mN) at the interface between LAS (negative values from the fusion line) and Alloy 52 weld metal (positive values from the fusion line) in SINI-AW.
**Fig. 6.3.21.** Microhardness profile (350 mN) at the interface between LAS (negative values from the fusion line) and Alloy 52 weld metal (positive values from the fusion line) in SINI-PWHT.

**Fig. 6.3.22.** Microhardness profile (350 mN) at the interface between LAS (negative values from the fusion line) and Alloy 52 weld metal (positive values from the fusion line) in NIWEL-AR (to which the same PWHT was applied than in the SINI-PWHT condition).
Fig. 6.3.23. Microhardness profile (350 mN) at the interface between LAS (negative values from the fusion line) and Alloy 52 weld metal (positive values from the fusion line) in NIWEL-5000 h.

Fig. 6.3.24. Microhardness profile (350 mN) at the interface between LAS (negative values from the fusion line) and Alloy 52 weld metal (positive values from the fusion line) in NIWEL-10 000 h.
Microhardness profiles show a clear difference between all the conditions, but the fact that significant changes occur over narrow transition zones (a few tens of microns at most) makes to use of nanoindentation particularly interesting. A smaller indentation size enables to obtain measurements with a better spatial resolution and characterize, for example, the width of the hard layers and their position compared to the fusion line, more precisely. To that end, the matrix of indentations near the fusion line and the corresponding hardness map is presented along with the nanoindentation hardness profile in each case.

Figures 6.3.25 and 6.3.26 show the hardness profiles obtained with nanoindentation over the LAS/Alloy 52 weld metal interface in the SINI-AW and SINI-PWHT conditions, respectively. A narrow layer (less than 10 μm) in the LAS adjacent to the fusion line has the lowest hardness in the SINI-AW, which corresponds to the narrow LAS CDZ. A hardness peak (667 HV<sub>IT</sub>) is visible at the fusion line where the indentations overlap with a narrow PMZ (<1 μm), but no hardness peak is visible in Alloy 52 weld metal. In Figure 6.3.26, however, a clear hardness peak is seen in Alloy 52 weld metal (840 HV<sub>IT</sub>), starting from the fusion line and extending over 25 μm. In addition, the low hardness layer in the LAS side is much wider (about 25 μm) than in the AW condition.

Figures 6.3.27, 6.3.28 and 6.3.29 show the evolution of the nanoindentation hardness profile across the LAS/Alloy 52 weld metal interface before and after ageing at 400 °C for 10 000 h. Before ageing, the hardness peak (858 HV<sub>IT</sub>) and the hardness map are very similar to that of SINI-PWHT, which was expected. The hard layer in Alloy 52 and the CDZ are, however, narrower (about 15 μm).

After 5000 h at 400 °C, the hardness peak in Alloy 52 weld metal is softening (733 HV<sub>IT</sub>) and the hard layer is narrower (about 5 μm). In addition, the hard layer is not adjacent to the fusion line anymore, but starts rather about 10 μm away in the weld metal. The CDZ reaches softer values (319 HV<sub>IT</sub>) than in the NIWEL-AR condition (330 HV<sub>IT</sub>), although the average value stays similar.

After 10 000 h, the same trend is observed, with the hardness peak in Alloy 52 weld metal softening further (637 HV<sub>IT</sub>) and being pushed further into the weld metal (about 20 μm). The hardness map also shows that the hard layer is not fully continuous along the fusion line anymore. The CDZ reaches even lower values (280 HV<sub>IT</sub>). (Ahonen et al. 2017; Sarikka et al. 2017)
Fig. 6.3.25. Nanoindentation hardness profile (1.5 mN) across the LAS/Alloy 52 weld metal interface in SINI-AW. An optical picture of the matrix of indentations near the fusion line and the corresponding hardness map are added to help visualize the hardness variation and their location at the interface.
Fig. 6.3.26. Nanoindentation hardness profile (1.5 mN) across the LAS/Alloy 52 weld metal interface in SINI-PWHT. An optical picture of the matrix of indentations near the fusion line and the corresponding hardness map are added to help visualize the hardness variation and their location at the interface.
Fig. 6.3.27. Nanoindentation hardness profile (1.5 mN) across the LAS/Alloy 52 weld metal interface in NIWEL-AR. An optical picture of the matrix of indentations near the fusion line and the corresponding hardness map are added to help visualize the hardness variation and their location at the interface.
Fig. 6.3.28. Nanoindentation hardness profile (1.5 mN) across the LAS/Alloy 52 weld metal interface in NIWEL-5000 h. An optical picture of the matrix of indentations near the fusion line and the corresponding hardness map are added to help visualize the hardness variation and their location at the interface.
Fig. 6.3.29. Nanoindentation hardness profile (1.5 mN) across the LAS/Alloy 52 weld metal interface in NIWEL-10 000 h. An optical picture of the matrix of indentations near the fusion line and the corresponding hardness map are added to help visualize the hardness variation and their location at the interface.
7. Discussion

In this section, the results are discussed first for the thermal ageing of Alloy 690 and then for Alloy 52 weld metal/LAS interface. Table 7.1 and 7.2 give the relative variations in hardness and lattice parameter depending on the ageing temperature and original condition of Alloy 690. Figure 7.1 and Table 7.3 show a compilation and analysis of the nanoindentation measurements for SINI-AW and SINI-PWHT. Figure 7.2 shows the correlation between hardness and grain size variations in the LAS in the case of NIWEL-5000 h DMW. Figure 7.3 and Table 7.4 show a summary of the microhardness measurements for NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h DMW. Figure 7.4 and Table 7.5 show a similar summary of the nanoindentation data for the same samples.

7.1. Alloy 690

The four conditions SA-, SACW-, TT- and TTCW-Alloy 690 present very different microstructures. Cold work nearly doubles the hardness of the material in both SACW- and TTCW-Alloy 690 as compared to SA- and TT-Alloy 690, respectively. In addition, heat treatment after solution annealing promotes IG carbide precipitation, and grain refining in TT-Alloy 690 as compared to SA-Alloy 690. Macrohardness variations can be explained by these factors. TT-Alloy 690 is harder than SA-Alloy 690 before ageing due to smaller grain size and a higher density of GBs decorated with IG carbides. Upon ageing with increasing ageing temperature, increasing grain growth reduces the hardness of TT-Alloy 690, while increasing amount of IG carbides in SA-Alloy 690 increases the hardness to levels similar to that of TT-Alloy 690. In the cold-worked conditions, TTCW-Alloy 690 is harder than SACW-Alloy 690 before ageing due to the presence of IG carbides. Thermal ageing of SACW-Alloy 690 promotes IG carbide formation and increases the hardness, while ageing at 550 °C promotes recrystallization and stress relaxation in both SACW-Alloy 690 and TTCW-Alloy 690, therefore reducing the hardness level. No evidence of SRO was found using a load of 9.8 N. The need to discriminate between the respective influence of grain size, IG
carbides and strain localization made the use of nanoindentation necessary, with positive results.

**Table 7.1.** Hardness variations of aged SA-, SACW-, TT- and TTCW-Alloy 690 conditions with ageing temperature, relative to the respective as-received condition.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>SA</th>
<th>SACW</th>
<th>TT</th>
<th>TTCW</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>+ 6 %</td>
<td>+ 15 %</td>
<td>+ 2 %</td>
<td>+ 6 %</td>
</tr>
<tr>
<td>420</td>
<td>+ 30 %</td>
<td>+ 26 %</td>
<td>+ 32 %</td>
<td>+ 14 %</td>
</tr>
<tr>
<td>475</td>
<td>+ 14 %</td>
<td>+ 4 %</td>
<td>+ 3 %</td>
<td>– 4 %</td>
</tr>
<tr>
<td>550</td>
<td>+6 %</td>
<td>– 1 %</td>
<td>+ 1 %</td>
<td>– 4 %</td>
</tr>
</tbody>
</table>

**Table 7.2.** Lattice parameter variations of the TT-Alloy 690 condition with ageing temperature relative to the as-received SA-Alloy 690 condition.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>TT condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>– 0,04 %</td>
</tr>
<tr>
<td>350</td>
<td>– 0,05 %</td>
</tr>
<tr>
<td>420</td>
<td>– 0,05 %</td>
</tr>
<tr>
<td>475</td>
<td>– 0,04 %</td>
</tr>
<tr>
<td>550</td>
<td>0 %</td>
</tr>
</tbody>
</table>

Using nanoindentation, and with relatively short ageing times (3000 and 10 000 h), strong suggestion of SRO was found in all Alloy 690 conditions with hardness increases upon ageing at 350 and 420 °C, and lattice contraction in the range of 0.04-0.05%. The use of nanoindentation, as explained in Chapter 5, enables to remove the influence of grain size and IG carbides on the hardness variation, while limiting the effect of strain localization at GBs in CW samples. The nanoindentation hardness variations are therefore assumed to relate to the levels of SRO in Alloy 690.

Considering the as-received TT-Alloy 690 condition, the heat treatment increased the hardness (Table 7.1) and decreased the lattice parameter (Table 7.2) as compared to water quenching after solution annealing, implying the occurrence of ordering in Alloy 690 during heat treatment. Indeed, the main microstructural change between TT- and SA-Alloy 690 conditions is Cr-rich IG M$_{23}$C$_{6}$ carbide precipitation, which decrease the hardness in the TT conditions due to a drop in solid solution hardening by carbon arising from carbide precipitation. Nonetheless, a higher hardness in TT- and TTCW-Alloy 690 than in SA-and SACW-Alloy 690 suggests the occurrence of SRO during the heat treatment, leading to a decrease in the lattice parameter and an increase in hardness. It can be related to a lower carbon content of the matrix following IG carbide precipitation during heat treatment, carbon atoms are not trapping vacancies anymore, the nucleation of SRO is promoted. The hardness results show that as-received SACW and TTCW conditions are harder than the SA and TT conditions, which
correlates with the higher strain levels typically induced by CW, as seen in the macrohardness results.

Upon ageing at 350 °C, hardness increases in all conditions (Table 7.1). The increase is stronger in the SACW- and TTCW-Alloy 690 conditions (+15 and +6 %, respectively) than in the SA- and TT-Alloy 690 conditions (+6 and +2 %, respectively), suggesting that CW can promote SRO in the beginning of ageing or at lower temperatures. As ordering can be strain-driven as well as thermally activated, it is possible that high levels of deformation due to CW can promote SRO at lower temperatures. The combined effect of cold work and thermal ageing on the microstructure is difficult to characterize, as some studies point out that the formation of ordering is accelerated by cold work due to the increased diffusion rate of elements (Delabrouille et al. 2009) while others conclude that cold work delays the onset of ordering by destroying ordering (Young et al. 2013). The suggestion of the present work is that, while CW promotes an original disordered state, it favors the formation of SRO at lower temperatures by increasing vacancies and therefore diffusion of elements, and by increasing strain levels and therefore activating strain-induced SRO in addition to thermally-activated SRO.

The hardness increase is less strong in the heat-treated conditions than in the SA- and SACW-Alloy 690 conditions, as the presence of SRO prior to ageing makes further ordering reaction more difficult. The highest relative hardness increase is seen for all conditions aged at 420 °C, which is expected to be close to the critical temperature for the ordering of Alloy 690 with a 9.8 wt.% Fe content. It also correlates with the higher lattice contraction, observed in the TT-Alloy 690 condition (Table 7.2).

Upon ageing at 475 °C, hardness decreases significantly in all conditions as compared to the hardness observed upon ageing at 420 °C (Table 7.1), indicating that a disordering reaction occurs. This temperature is above the expected critical temperature for the ordering of Alloy 690 with 9.8 wt.% Fe content. The lattice parameter of the TT-Alloy 690 condition increases slightly as compared to that upon aging at 420 °C, but remains similar to that of the as-received TT-Alloy 690 condition, while the hardness remains higher in SA-, SACW- and TT-Alloy 690 conditions than in their as-received state (Table 7.1), showing that some SRO remains. Upon ageing at 550 °C, lattice expansion (Table 7.2) is clearly visible in the TT-Alloy 690 condition: the lattice parameter is similar to that of the as-received SA-Alloy 690 condition, showing that the disordering reaction counteracts the effects of the thermal treatment. In addition, the hard-
ness decrease from the hardness observed upon ageing at 475 °C levels off, especially in the TT- and TTCW-Alloy 690 conditions, indicating that the disordering reaction becomes saturated (Fig. 6.1.13). Hardness decreases more in the CW conditions than in the SA- and TT-Alloy 690 conditions at 475 and 550 °C, indicating that stress relaxation at higher temperatures occurs in parallel with the disordering reaction (Table 7.1). As a whole, ageing at 550 °C generates little change in hardness as compared to the as-received state in all conditions. The most significant change occurring at 550 °C is the extensive precipitation of \( \alpha \)-Cr in both CW conditions, which is worth noting as \( \alpha \)-Cr usually precipitates at temperatures higher than 600 °C. No \( \alpha \)-Cr was detected in non-CW conditions, and in all conditions Cr-rich M\(_{23}C_6\) carbides precipitate at GBs or within the migrated zone between original GBs and their migrated position. 

The study was expanded further to consider the effect of IG carbide precipitation and SRO on the strain localization at GBs. The use of HR EBSD and AFM did not reveal a noticeable influence of SRO on the properties of GBs, or on general strain levels. However, the effect of IG carbides is more visible, as strain localized around IG carbides even after the GB had migrated. In addition, AFM results clearly show that IG carbides are the hardest part of GBs, while softer and harder regions exist on both sides of a same GB. 

The use of TEM was not able to observe SRO directly, neither by imaging nor by the analysis of diffraction patterns. However, IG precipitates forming upon ageing are clearly identified as Cr-rich M\(_{23}C_6\) carbides, while a special form of M\(_{23}C_6\) carbide plates is present on twin boundaries. TEM imaging also revealed the presence of dislocation tangles at GBs and in grain interiors, with the highest number observed upon ageing at 420 °C. LRO is known to promote dislocation pile-up in the absence of visible barriers in Alloy 690, so a first hypothesis was that the dislocation tangles were due to SRO upon ageing at 420 °C. However, a precipitate, usually M\(_{23}C_6\) carbide, was identified systematically at the center of the tangles. The hypothesis is therefore that the dislocation tangles are the result of a recovery during thermal ageing. At 420 °C, the temperature is low enough so that grain boundaries and particles can act as barrier for the dislocation motion, explaining the tangles. At 550 °C, dislocations can move more easily and are not stopped by GBs and carbides anymore. A side consequence of the effort put to observe SRO via electron diffraction is the realization that both M\(_{23}C_6\) carbides and thin oxide films on the surface of the TEM samples can generate artifacts of interlattice reflections that can be attributed to ordering. Atom probe tomography is therefore probably the only way to observe SRO directly instead of using indirect measurements such as hardness and lattice contraction.
7.2. **Alloy 52 weld metal and weld interface**

Concerning Alloy 52 weld metal and its interface with LAS, there is a clear correlation between the microstructural characterization and the results of the microhardness and nanoindentation measurements. PWHT promotes carbon diffusion from the high-C/low-Cr LAS side of the weld interface to the low-C/high-Cr Alloy 52 weld metal side. It results in a CDZ in the LAS adjacent to the fusion line, while the carbon that has diffused piles up in the planar growth zone in the weld metal, directly adjacent to the fusion line. It leads to a significant hardness peak in Alloy 52 weld metal (840 HVIT), which is harder than the PMZ found at the fusion line (667 HVIT). Associated to the low hardness of the LAS CDZ, it creates a strong hardness mismatch at the DMW interface (see Fig. 7.1).

In the LAS HAZ, the dominant factor influencing the hardness is the grain size variation related to the amount of the heat input during the welding process (see Fig. 7.2). The hardness increases from 200-220 HVIT in the LAS base metal to 280 HVIT in the grain-refined zone about 400-600 μm away from the fusion line. The hardness goes back to the levels similar to that of the LAS base metal in the grain coarsening zone and CDZ, corresponding to a grain size similar to that of the base metal (2.5 μm). Thermal ageing at 400 °C for up to 10 000 h does not influence the grain size, carbide morphology or hardness level in the LAS HAZ. In addition, thermal ageing does not influence the microstructure of Alloy 52 weld metal or the hardness level from the weld crown to the weld root. It is expected, since the effect of thermal ageing for up to 10 000 h on the microstructure of Alloy 690 becomes significant only at 475 and 550 °C. Thermal ageing of Alloy 52 with a similar composition at 400 °C for 10 000 h is therefore not enough to produce visible changes.

![Fig. 7.1. Comparison of the nanoindentation hardness profiles of SINI-AW and SINI-PWHT at the LAS/Alloy 52 weld metal interface.](image-url)
Table 7.3. Summary of the main hardness results and their locations at the LAS/Alloy 52 weld metal for SINI-AW and SINI-PWHT.

<table>
<thead>
<tr>
<th>SINI</th>
<th>HVIT (1.5 mN)</th>
<th>Location</th>
<th>Distance from fusion line (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-welded</td>
<td>667</td>
<td>PMZ</td>
<td>0</td>
</tr>
<tr>
<td>PWHT</td>
<td>840</td>
<td>Weld metal</td>
<td>0-5</td>
</tr>
</tbody>
</table>

Fig. 7.2. Comparison of the hardness and grain size profiles in the LAS HAZ of NIWEL-5000 h DMW.

Fig. 7.3. Comparison of the microhardness profiles of NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h at the LAS/Alloy 52 weld metal interface.

The LAS/Alloy 52 weld metal interface is greatly affected, however, by thermal ageing (see Fig. 7.3 and Table 7.4). While PWHT promotes a hardness mismatch at the weld interface, thermal ageing clearly reduces this mismatch. The hardness peak in Alloy 52 weld metal decreases from 536 HVIT before ageing to 377 HVIT after 5000 h at 400 °C and to 331 HVIT after 10 000 h. A similar trend is
observed in the nanoindentation measurements, while it is visible that the position of the hardness peak in Alloy 52 weld metal moves further away from the fusion line.

The hardness peak in Alloy 52 weld metal after PWHT is related to the formation of a CDZ in the LAS side and carbon diffusion to the weld metal. It leads to the hypothesis that thermal ageing reduces the hardness peak in the weld metal side by allowing carbon to diffuse further away into the weld metal (lowering the peak and moving it further away). As a concluding remark, it is important to note that thermal ageing lowers the hardness peak to levels similar to that of the PMZ, between 600-650 HV\text{IT} as measured with nanoindentation at the SINI and NIWEL DMW interfaces.

\textbf{Table 7.4.} Summary of the main microhardness results and their locations at the LAS/Alloy 52 weld metal for NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h.

<table>
<thead>
<tr>
<th>NIWEL</th>
<th>HV\text{IT} (350 mN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>536</td>
</tr>
<tr>
<td>5000 h</td>
<td>377</td>
</tr>
<tr>
<td>10 000 h</td>
<td>331</td>
</tr>
</tbody>
</table>

\textbf{Fig. 7.4.} Comparison of the nanoindentation hardness profiles of NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h at the LAS/Alloy 52 weld metal interface.

\textbf{Table 7.5.} Summary of the main nanoindentation hardness results and their locations at the LAS/Alloy 52 weld metal for NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h

<table>
<thead>
<tr>
<th>NIWEL</th>
<th>HV\text{IT} (1.5 mN)</th>
<th>Location</th>
<th>Distance from fusion line (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>858</td>
<td>Weld metal</td>
<td>0-2</td>
</tr>
<tr>
<td>5000 h</td>
<td>733</td>
<td>Weld metal</td>
<td>10</td>
</tr>
<tr>
<td>10 000 h</td>
<td>637</td>
<td>Weld metal</td>
<td>20</td>
</tr>
</tbody>
</table>
7.3. Potential consequences on SCC resistance

When considering the effect of thermal ageing of Alloys 690 and 52 on their SCC resistance, it is necessary to go back to the definition of SCC as it was detailed in the literature review in the beginning of the thesis. SCC is a particular form of EAC, which produces a brittle fracture in alloys with minimal uniform corrosion. SCC leads to delayed fracture, occurs at low stress levels and is difficult to detect. The main impact of SCC in nuclear power systems has been its role in the failure of many Alloy 600, 82 and 182 components in earlier reactor pressure vessel penetrations, steam lines, steam generator tubes and DMW. These failures occurred after a long incubation time during which no problems were reported, and therefore this research effort on the long-term behavior of Alloy 690 and 52 aims at avoiding the same situation.

Stress has to exceed a threshold to produce SCC, and although stress raisers usually increase SCC initiation, internal stresses such as residual stresses can be enough for SCC to occur. For that reason, DMWs can be particularly sensitive to SCC. Sensitive microstructures playing a key role in SCC susceptibility can be found in the HAZ of base metals, at weld interfaces and within the weld metals. Notably, the transition regions of weld interfaces are critical and have been a focus point of the research work in this thesis.

Among all the proposed mechanisms of EAC, the SCC mechanism based on the slip-dissolution model and HIC involving hydrogen embrittlement are the most used for Ni-base alloys in nuclear systems for intergranular and transgranular fracture, respectively. The results of the thesis will be discussed accordingly. In the slip-dissolution model, local plastic deformation produces a slip step in the protective film, and the strain rate at the crack tip is critical. In HIC, hydrogen embrittlement occurs first by reducing the mechanical properties of alloys to a high degree, increasing cracking susceptibility. Notably, hydrogen has played an important role in the PWSCC susceptibility of Alloy 600. A commonly accepted mechanism is that hydrogen accumulates ahead of the crack tip or at internal interfaces between the metal matrix and particles, where it can weaken atomic bond and promote dislocation emission or promote bond rupture.

For both weld metals and base metals, metallurgical factors such as alloy composition, cold work, intermetallic phases, GB segregation and residual stresses can enhance the localization of plastic deformation by favoring planar deformation, therefore favoring the brittle cracking of protective films in the slip-dissolution model. They can also increase the stress triaxiality at the crack tip and favor the role of hydrogen, or act as hydrogen traps increasing the amount of
internal hydrogen in the material. In Ni-base alloys, the formation of LRO can lead to increased residual stresses and decreased resistance to EAC, most notably to hydrogen embrittlement, and LRO can greatly reduce the mechanical properties of Ni-base alloys in general. SRO has been showed to cause lattice contraction around 0.03 % while LRO can lead to contractions up to 0.3 %. Notably, LRO is known to increase the level of internal stresses and leads to a significant hardness increase, an increase in the yield stress, and to change of the fracture mode from ductile micro-void coalescence to brittle intergranular fracture (Young et al. 2013; Kim et al. 2013). In addition, ordering can promote planar slip and heterogeneous deformation. It produces widely spaced coarse slip steps that constitute preferential point of film rupture (Young et al. 2013).

It is clear from the results of this thesis and the other studies on the subject that the main microstructural changes caused by thermal ageing of Alloy 690 are IG carbide precipitation and ordering, which both affect the SCC resistance. SRO was indirectly suggested in the present thesis by hardness and lattice parameter measurements, but clear evidence of LRO can be found in model Ni-30Cr-10Fe alloys, while neutron diffraction and atom probe tomography are used to assess more precisely the presence of ordering. In addition, although no SCC initiation or propagation tests were carried within the frame of this doctoral thesis, the work presented correlates well to a series of recent studies on the effect of thermal ageing on the SCC resistance of Alloy 690, carried out on the SA-, TT-, SACW- and TTCW-Alloy 690 materials.

A study of Kim et al. concluded that lattice contraction due to SRO is actually the leading factor in Alloy 600 PWSCC (Y. S. Kim et al. 2015). SRO was directly observed during slow strain rate testing of Alloy 600 in water at 360 °C, and a direct correlation between SRO level and PWSCC susceptibility was drawn as FC-Alloy 600 with lower ordering level was more PWSCC resistant than WQ-Alloy 600 showing higher lattice contraction (Kim et al. 2013). Especially, the hypothesis behind these studies is that SRO is first thermally activated, generates a crack due to the accommodation of lattice contraction between two grains, and that SRO is further strain-induced in the plastic zone of the crack tip, therefore acting in both SCC initiation and propagation (Kim et al. 2013). It originates from the evidence that intergranular cracking can occur by lattice contraction arising from ordering, as for example a tricrystal of CuAu fails by intergranular cracking in 35 seconds after an ordering reaction at 350 °C without corrosion. In that sense, this mechanism is not exactly a SCC mechanism as it explains also cracking without corrosion reactions.
In a similar fashion, a following communication of Kim et al. highlighted a direct correlation between the enhanced resistance to SCC of TT-Alloy 690 over SA-Alloy 690 during slow strain rate testing (SSRT) in 360 °C primary water. It was linked to the lower lattice contraction of TTCW-Alloy 690 over SACW-Alloy 690 upon ageing at 350 and 420 °C, indicating that the higher level of SCC resistance of TTCW-Alloy 690 correlates with a lower degree of SRO forming at 360 °C during SSRT. In addition, a lower strain rate led to a higher SCC susceptibility, leading to the conclusion that lower strain rates enable SRO to develop further and promote SCC (Kim & Kim 2016).

In contrast, a study from Kuang et al. on the SCC initiation susceptibility of the same SACW- and TTCW-Alloy 690 concluded that the enhanced SCC resistance of TTCW-Alloy 690 during the SSRT was due to the beneficial role of IG carbides in mitigating SCC. The effect of a slower strain rate, for a given uniform strain applied, resulting in greater SCC degradation, was explained by the enhancement of the corrosion process (Kuang & Was 2015). On the contrary, another study from Kuang et al. pointed out the detrimental effect of IG carbides promoted during thermal ageing. Indeed, thermal ageing at 350 °C has little effect on the IG carbide precipitation of SA- and SACW-Alloy 690, as it has been seen in the present thesis. Thermal ageing at 475 °C, however, promotes semi-continuous IG carbides on random high-angle GBs. In addition, the thermal ageing of SACW-Alloy 690 resulted in lower yield strength and larger uniform elongation compared to the as-received SACW-Alloy 690. The increasing softening of SACW-Alloy 690 upon thermal ageing with increasing ageing temperature was concluded to be mainly due to the restructuring of the dislocation structure. In this study, thermal ageing at 350 and 475 °C had little effect on the SCC initiation susceptibility of SA-Alloy 690, but thermal ageing at 475 °C reduced the SCC resistance of SACW-Alloy 690 despite the lower residual strain. The major difference in microstructure between the samples aged at 350 and 475 °C is IG carbide precipitation. It was speculated to be the primary cause of reduction of SCC resistance in SACW-Alloy 690 (Kuang et al. 2015). It is also to be noted these studies carried out on the exactly same alloy conditions than that in the present thesis, did not consider the role of SRO.

Considering the role of IG carbides, it is generally accepted that IG carbides can increase the SCC resistance of Alloy 690. As detailed in the literature review of the thesis on IG carbides in Alloy 690, it was proposed, however, that IG carbides can enhance localized strains near GBs, and have therefore detrimental effect on the SCC growth. It should be noted, however, that the IG carbides are
usually considered to form during heat treatment at around 700 °C. These car-
bides were indeed considered beneficial in the results from Kuang et al. on
TTCW-Alloy 690. On the contrary, IG carbides resulting from thermal ageing at
475 °C arguably increased the SCC susceptibility of SACW-Alloy 690 signifi-
cantly. The conclusion is therefore that IG carbides forming upon thermal age-
ing promote a different behavior than the carbides forming upon heat treat-
ment, and that the role of SRO forming upon thermal ageing should also be
taken into account.

Following the proposal from Kim et al. that the dominant mechanism leading
to IG cracking is lattice contraction by SRO, SRO can explain the increased SCC
susceptibility of SACW-Alloy 690 upon ageing at 475 °C, while also explaining
the increased SCC resistance of TTCW-Alloy 690 over SACW-Alloy 690 in SSRT
at 360 °C.

Other studies from Young et al., however, tend to limit the role of SRO in favor
of LRO. A study evaluating varying degrees of LRO on the PWSCC resistance of
a model Ni-30.7 Cr wt.% alloy showed a CGR of 1.2×10⁻⁷ mm/s after 2000 h at
475 °C, similar to CGR of Alloy 690 with more than 20% CW. The study refuted,
however, the hypothesis from Kim et al. that SRO is an intrinsic force driving
the crack propagation in Alloy 600 and 690. The conclusion was that the ther-
mal ageing was detrimental to IGSCC resistance only with the development of
LRO. In that way, ordering will act in a way similar to cold work, decreasing SCC
resistance by increasing the crack tip strength and decreasing the toughness of
the ordered alloy. More work was, however, deemed necessary to understand
the effects of varying degrees of ordering on the susceptibility of Alloy 690 to
EAC (Young 2017).

The results from the present thesis are somewhat intermediate between the
observations from these three series of studies. Similar observations concerning
IG carbide precipitation and stress relaxation in CW samples upon thermal age-
ing were made as in Kuang et al., while Vickers hardness did not reveal a signif-
icant influence of ordering. Nevertheless, SRO was studied with careful charac-
terization and both nanohardness measurements and lattice contraction
strongly suggest the formation of SRO with a peak at 420 °C, as in studies from
Kim et al. However, as the idea that SRO acts as a driving force for cracking was
further investigated by characterizing strain localization at GBs with HR EBSD
and AFM, results show that strain localization is mostly related to IG carbide
precipitation forming upon ageing, which relates to observations from Kuang et
al. Finally, the amplitude of hardness variation and lattice contraction is char-
acteristic of SRO and not LRO, but results show that TT-Alloy 690 aged at 420
°C for 10 000 h reaches hardness higher (544 HV1) than that of TTCW-Alloy 690 (with 20% CW) prior to ageing (507 HV1), which relates to observations from Young et al. However, the macrohardness of TT-Alloy 690 remains much lower (150 HV1) than that of TTCW-Alloy 690 (307 HV1) and grain growth promotes hardness decrease in TT-Alloy 690 upon ageing, which can be seen as beneficial. Results from this thesis suggest therefore that SRO can act as LRO in reducing mechanical properties of Alloy 690 with 9.8 wt.% Fe to levels similar to Alloy 690 with 20% CW, but in a localized way that can easily be overlapped by the opposing effects of other factors, such as IG carbide precipitation or grain growth. However, due to the local nature of SCC, the local effect of SRO cannot be overlooked. Especially, local hardness increase of this nature can favor hydrogen embrittlement or strain localization ahead of a crack tip. However, no evidence was found with the available characterization methods of increased GB strain localization due to SRO, while a clear effect of IG carbide precipitation was seen, especially at 475 and 550 °C. Current observations do not support, therefore, the hypothesis that SRO acts as a sole driving force for IG cracking by increasing IG strains, but they do support the fact that SRO can be locally as detrimental as LRO and cannot be disregarded by considering only the effect of IG carbides.

There is actually a sort of transition point between thermal ageing at 420 and 475 °C, between a situation where SRO has a clear effect on hardness level while IG carbide precipitation remains limited, and a situation where SRO has less effect and IG carbide precipitation becomes significant. The conclusion of the thesis in that regard is that SSRT should be conducted also after ageing at 420 °C and compared to the results of Kuang et al. and Kim et al. for SACW-Alloy 690 aged at 350 and 475 °C. Further, considering the evolution of this transition with time, the critical temperature for ordering in Alloy 690 with 9.8 wt.% is set around 420 °C, but it is possible that IG carbide precipitation levels similar to that found upon ageing at 475 °C for 10 000 h can form at 420 °C after longer ageing times. Indeed, plant operation for 60 years and more represents more than 500 000 h. In that situation, a combination of IG strains due to IG carbides and local degradation of mechanical properties due to SRO can become very detrimental to the SCC resistance of Alloy 690.

Considering Alloy 52 weld metal, the effect of PWHT on the strength mismatch in a RPV safe-end DMW has been a concern for new PWRs and has been studied over several projects of Finnish and Swedish power companies, especially the behavior of SINI-AW and SINI-PWHT. It has been found that the conventional way to calculate the mismatch, as a ratio between the yield strengths
of the weld metal and the base metal, is difficult to apply in the case of DMWs due to narrow transition zones with steep gradients of mechanical properties. Moreover, the crack tip stress and the elastic-plastic fracture behavior in the different DMW zones are important from both mechanical and EAC point of view. Related to the formation of the CDZ in SA 508 and the hard layer in Alloy 52 weld metal upon PWHT, the fusion boundary in SINI-PWHT was seen to have the lowest fracture resistance of all the DMW zones, while PWHT increased the fracture resistance of Alloy 52 weld metal. In addition, cracks tended to propagate only along the soft CDZ in SA 508 in SINI-PWHT, while they were jumping also in Alloy 52 weld metal in SINI-AW. The behaviors of SINI-AW and SINI-PWHT serve as a model for the study of the effect of thermal ageing in NIWEL-AR, NIWEL-5000 h and NIWEL-10 000 h. Since no differences were noted in Alloy 52 weld metal or SA 508 base metal between NIWEL-AR and NIWEL-10 000 h, it can only be assumed so far that thermal ageing at 400 °C does not have detrimental effects on Alloy 52 weld metal. Although, following the study of Alloy 690 with a similar composition, the formation of SRO and LRO in Alloy 52 weld metal upon thermal ageing is a possibility, but it was not revealed by microhardness testing with 350 mN. Although the use of nanoindentation as for Alloy 690 was considered, the heterogeneous nature of the weld metal microstructure made the interpretation of the measurements too difficult. Instead, as the main change in behavior observed between SINI-AW and SINI-PWHT occurred at the weld interface, more attention was paid to the characterization of the transition regions (CDZ, PMZ, hard layer) of the weld. The CDZ in SA 508 was found to remain stable upon ageing, while the hard layer in Alloy 52 weld metal was found to soften significantly and move further away from the fusion line. Thermal ageing at 400 °C for 5000 and 10 000 h is therefore considered to be beneficial in the case of the RPV safe end NG-DMW with Alloy 52 weld metal as it reduces the strength mismatch at the weld interface. It is expected that cracks will not be confined to the SA 508 CDZ but able to go back and forth over the fusion line to the weld metal, which increases the fracture resistance of the interface. Questions remain concerning the formation of SRO or extensive IG precipitation in Alloy 52 weld metal at higher temperatures or over longer ageing times, that could be detrimental to the SCC resistance. Further characterization is ongoing on the fracture resistance of NIWEL-10 000 h, and more work is needed concerning the development of SRO in Alloy 52, notably by the measurement of lattice parameters before and after ageing.
8. Conclusions

The thermal ageing of Alloy 690 and Alloy 52 weld metal and its interface with a ferritic LAS were studied in this doctoral thesis. For Alloy 690, a special focus was put on the influence of ageing temperature and prior condition of the alloy (cold work and heat treatment) on the formation of SRO and IG precipitation. The visible microstructural changes induced by thermal ageing were characterized and the formation of SRO was studied mainly via indirect methods: hardness and lattice parameter measurements. For Alloy 52 weld metal, the influence of thermal ageing on the microstructures and hardness levels was characterized, and a special focus was put on the LAS/Alloy 52 weld metal interface, which represents a critical location. The main conclusions based on the work carried out during the thesis are summarized as follows.

- IG carbide precipitation in Alloy 690 increased with ageing temperature, with precipitates identified mostly as IG Cr-rich M$_{23}$C$_6$ carbides in non-cold-worked conditions. DIGM was promoted at 475 and 550 °C, resulting in a typical wavy appearance of GBs and bulged zones. Carbides were observed to grow from original GBs within the migrated zone.

- Formation of SRO was deduced from indirect measurements in all conditions 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. It is consistent with the shift of the critical temperature for ordering at around 420 °C for 9 wt.% Fe reported in the other studies. The occurrence of SRO was inferred by nanoindentation in all conditions and by lattice parameter measurements for TT-Alloy 690. It was not possible to observe interlattice reflections associated with ordering in TEM electron diffraction patterns.

- Heat treatment of Alloy 690 promoted ordering prior to ageing, in relation to a lower carbon content after IG carbide precipitation favoring the nucleation of SRO. At higher temperatures, disordering affected these conditions more than the water-quenched conditions.
- Cold work promoted high strain levels in Alloy 690 prior to ageing. As a result, recrystallization and stress relaxation occurred in CW samples at higher temperatures and accentuated the effect of the disordering reaction. In addition, high levels of deformation due to CW promoted the extensive precipitation of α-Cr in recrystallized areas upon ageing at 550 °C.

- Thermal ageing of Alloy 52 at 400 °C up to 10 000 h did not produce any visible changes in the microstructure of the weld metal or in the hardness level from the weld crown (lower hardness) to the weld root (harder).

- Thermal ageing of the LAS side of the DMW at 400 °C up to 10 000 h did not produce visible changes. The microstructure of the LAS HAZ was still determined by the grain-refined, grain-coarsened and CDZ related to the welding process. A clear correlation was seen between grain size and hardness variation in the LAS HAZ.

- The LAS/Alloy 52 weld metal interface was found, however, to be greatly affected by thermal ageing. A hardness mismatch results from the diffusion of carbon from the LAS to the weld metal upon PWHT, with carbon pile-up next to the interface, leading to a significant hardness peak in the weld metal. Thermal ageing after PWHT reduced dramatically the hardness peak in the weld metal side, while shifting it further away from the fusion line. Carbon diffusion further into the weld metal is the main mechanism to explain the phenomenon.

The results on the effect of thermal ageing on Alloy 690, although not including SCC tests, are a good complement to the other recent studies. The conclusion is that SRO develops in Alloy 690 with 9.8 wt.% Fe upon thermal ageing with a peak at 420 °C and can, just as LRO, locally affect the material to levels similar to that of 20% CW. It was linked based on other studies to a decrease of SCC resistance. In addition, IG carbide precipitation developing upon ageing has been seen as detrimental to the SCC resistance in the other studies and was therefore thoroughly investigated in this thesis. The potential combination of a high levels of SRO and extensive IG carbide precipitation over long ageing times is seen as a concern for the SCC resistance of Alloy 690 in PWRs. Concerning the thermal ageing at 400 °C of Alloy 52 weld metal, no detrimental effect was noticed, while thermal ageing clearly reduces the strength mismatch caused by PWHT at the
weld interface, which is seen beneficial for both the mechanical properties and EAC resistance of the DMW.


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In modern pressurized water reactors, the substitution of nickel-base Alloy 600 and its associated filler metals Alloy 82 and 182 by Alloys 690, 52 and 152 with higher chromium content has improved the integrity of the main components in the primary circuit, such as the steam generator tubes and the reactor pressure vessel safe-end dissimilar metal weld. However, metallurgical changes during thermal ageing of Ni-base alloys, notably intergranular carbide precipitation and short-range ordering, can affect the long-term primary water stress corrosion cracking resistance of components. In addition, there is little or no data on the effect of thermal ageing on the narrow transition zones present at the typical interfaces between structural ferritic low alloy steel and Alloy 52 weld metal in dissimilar metal welds. Several conditions of Alloy 690 and two sets of narrow-gap dissimilar metal weld mock-ups using Alloy 52 weld metal were aged for up to 10 000 h, and the effect of thermal ageing on the microstructure, hardness level, lattice parameter and strain localization in the materials were characterized.