Summary of thesis entitled: “Nanoscale study of ageing and irradiation induced precipitates in the DIN 1.4970 alloy”

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Climate change is an ever pressing issue and needs to be addressed with any means at our disposal. Nuclear energy provides a safe, clean, reliable and compact way to generate power, and significant investments in nuclear infrastructure could substantially offset carbon emissions from fossil fuels. However, the dominant nuclear reactor technology of pressurized water reactors (PWR) faces two pressing issues: the public perception of safety and the accumulation of nuclear waste. Next generation liquid metal cooled reactors, especially lead or lead-bismuth cooled systems, could offer solutions to these problems. The MYRRHA reactor in development at SCK-CEN in Belgium is an advanced nuclear system with the primary goal of transmuting long-lived radioactive waste into waste with shorter half-life. Nuclear waste from PWRs may remain dangerously radioactive for over 100,000 years due to the presence of plutonium and americium; MYRRHA could reduce this time by a factor 100 by burning up the actinides thanks to its fast neutron spectrum. In addition, MYRRHA offers attractive safety features, such as passive cooling and low pressures, as well as sub-critical core operation by sustaining the nuclear chain reaction with an accelerator.

Of course the development of novel nuclear systems is not without its hurdles, and a large part of the challenges are materials related. Because the neutrons are not moderated in a metal cooled reactor, the structural materials in the core sustain much more severe radiation damage, which accelerates material degradation. A key component in the reactor core is nuclear fuel cladding; it is the tube that contains the fuel and fission products and therefore must operate under some of the harshest conditions, being a combination of elevated temperatures, high fast neutron flux, potentially corrosive fission products on the inside and potentially corrosive coolant on the outside. It must perform the dual function of efficient heat transfer and safety barrier, which places competing requirements on the tube thickness.

The material that was selected for the MYRRHA cladding was the DIN 1.4970 alloy. This is an austenitic stainless steel (iron based alloy) with 15% nickel and 15% chromium, as well as a small addition of titanium. Stainless steels have excellent mechanical properties, also at high temperature, and show excellent performance in nuclear applications. However, after substantial irradiation time with fast neutrons, a phenomena called “swelling” tends to be observed in these materials: nanoscale voids grow in the material, which causes macroscopic expansion of the material, and eventually catastrophic embrittlement and failure of the component. The mechanism by which this happens is the clustering of excess vacancies created during irradiation. The problem of swelling was discovered in the 60’s and decades of research went into how to mitigate this problem. It was discovered that by proper alloying and thermo-mechanical processing, catastrophic swelling could be substantially delayed. It is out of these research efforts that the DIN 1.4970 alloy evolved from more classical steels like 18/10 alloys. Three main features of the DIN 1.4970 alloy seemed to delay the onset of swelling: increased nickel content, cold-working of the material, and a small addition (< 1%) of titanium.

In my Ph.D. work, I focused on this small titanium addition in the DIN 1.4970 alloy. Research from the 70's and 80's reported that titanium could combine with carbon in the alloy to form nano-sized TiC precipitates. It was theorized that these particles contributed to the improved swelling resistance of the alloy by trapping point defects, thereby inhibiting their clustering and subsequently preventing void growth. However, this was never demonstrated. On the contrary, ageing the material could precipitate the TiC particles, but this aged material tended to perform worse in terms of radiation- and creep resistance compared to non-aged material without precipitates. Mechanisms to explain this behavior were never explored. But with the development of MYRRHA, interest in this behavior resurfaced. The DIN 1.4970 alloy was initially developed for a sodium cooled reactor (SNR-300) which would operate at much higher temperatures than MYRRHA. The low irradiation temperature regime was little explored in the SNR-300 research program. Hence, the question arose of how the material would behave under low irradiation temperatures, and what the role of Ti and TiC particles would be in the microstructural development. Some evidence seemed to suggest that at low irradiation temperatures, TiC might be unstable. In light of this possibility, I wanted to explore whether heat treatments could be tailored to make the material more radiation resistant.

In the first stage of my Ph.D. (described in chapter 3 of the thesis) I fully characterized the material as received from the manufacturer and explored how I could modify the microstructure through ageing heat treatment. I quantified grain morphology and texture through optical microscopy (LOM) and electron backscatter diffraction (EBSD), characterized the dislocation structures with the weak beam dark field (WBDF) technique in transmission electron microscopy (TEM), and quantified the composition, size and weight fractions of secondary phase particles. I discovered relatively large (100 nm – 10 µm) TiC and TiN particles (primary precipitates) which comprised about 0.5 wt% of the total steel weight. While this seems small, this accounted for 2/3 of the total Ti and C present in the material. The leftover 1/3 was in solid solution. I explored an ageing heat treatment matrix between 500 – 1000 °C for ageing times up to 3000 hours and characterized the resulting microstructures quantitatively with TEM. In all heat treatments above 600 °C I found a large population of small TiC nanoprecipitates on the order of 1-10 nm in diameter. Lower heat treatment temperatures tended to correlate with slightly higher number densities and lower growth rates. However, the sizes of the particles were very resistant to coarsening, so called Ostwald ripening; even after very long ageing times, the growth of the particles was minimal. I ultimately attributed this to a possible competition for carbon effect between the TiC nanoprecipitates, and $M_{23}C_6$ particles which also formed during heat treatment and which could be found on grain boundaries. Lower ageing temperatures even seemed to cause a reversal in the TiC number density, indicating they are only metastable and $M_{23}C_6$ is thermodynamically preferred. Since I wanted to maximize the number of small intragranular TiC particles, I wanted to avoid the formation of $M_{23}C_6$. Therefore, I decided to continue our study solely on a short heat treatment at high temperature: 800 °C for 2 hours. These first results of my thesis were published in a paper entitled "Tailoring the Ti-C nanoprecipitate population and microstructure of titanium stabilized austenitic steels" in the Journal of Nuclear Materials.

Since I was interested in the mechanism by which these precipitates might interact with irradiation induced point defects, I also performed a detailed study on the nanoprecipitates themselves. I also thought this might shed additional light on the formation mechanism of the particles and their coarsening behavior. With atom probe tomography (APT) I discovered they contained a significant fraction of Cr, which is known to reduce the lattice parameter, thereby decreasing the strain energy at the particle-matrix interface. In addition, the particles were substantially depleted in carbon. I also investigated the shapes of the particles and discovered they were always terminated on {111} planes, forming small octahedra. I could explain this by referring to a simple interfacial energy model, and this model could also rationalize why the particles were depleted in carbon. Finally I was able to image the misfit dislocations on the interface with high resolution TEM (HRTEM) and calculate local strain fields. Using this I was able to propose a simple model for the semi-coherent TiC – austenite interface. Finally, I discovered that the precipitates preferentially grew on Shockley partial dislocations, which was previously unreported. Using these findings, I was able to disconfirm a number of formation mechanisms proposed in historical papers. These results were published as a paper entitled "Characterization of (Ti,Mo,Cr)C nanoprecipitates in an austenitic stainless steel on the atomic scale" in Acta Materialia.

In the final chapter of the thesis I describe the work which concerned the main research question: how do the nanoprecipitates of TiC respond to irradiation. To investigate this I went to the ion irradiation facility of the University of Michigan to irradiate my material with iron ions. While ion irradiation does not substitute for neutron irradiation in a quantitative sense, the accelerated damage rate makes it ideal for parameter studies and investigation of mechanisms. The DIN 1.4970 steel was irradiated at three different temperatures (300 °C, 450 °C, 600 °C) up to a medium-high dose of 40 dpa (a measure of damage). At each irradiation condition, two thermo-mechanical states were irradiated: the pristine material as received from the manufacturer (without nanoprecipitates), and the material that was aged at 800 °C for 2 hours (with nanoprecipitates). This gave us a matrix of 6 different conditions to investigate. The resulting materials were investigated quantitatively with TEM and APT. First, the various phases were identified. At 300 °C, both the aged and as-received material showed no more signs of TiC nanoprecipitates, indicating the irradiation had destroyed them in the aged material. At 450 °C and 600 °C, there were TiC nanoprecipitates in all the samples, indicating that they formed during irradiation in the as-received material and were stable in the aged material. Additionally, in all irradiation conditions, the clustering the Ni and Si was observed, which conforms to the known phenomenon of radiation induced segregation. At the two highest temperatures, the clusters were large enough to also form G-phase, a nickel silicide enriched in multiple metals such as Mn. Typically, radiation induced segregation and the formation of radiation induced phases such as G-phase are undesirable effects which correlate with onset of swelling. G-phase formation was more severe in the aged materials, which aligns with earlier reports that aged DIN 1.4970 has a worse performance in the reactor. With APT, it was shown that the TiC precipitate interfaces are important point defect sinks, since they were always decorated with an enriched shell of Ni and Si. Additionally, and somewhat counterintuitively, the aged material showed fewer TiC nanoprecipitates compared to the as-received material after irradiation. This could be attributed to an increased nucleation potential at lower temperatures combined with higher point defect concentrations. There was a clear inverse correlation between the number density of TiC precipitates, and the volume fraction of G-phase, which supported the original hypothesis. The quantitative information about the microstructure was also consistent with a basic rate theory model. Correlation does not imply causation however, so to exclude the possibility that other differences in the microstructure were responsible, the Frank loop dislocation structures were also quantified. While there were some differences to be found in the sizes of these populations, the overall dislocation density was comparable in all conditions, suggesting that differences in dislocation networks were not responsible. The nano-hardness of the aged and as-received materials after irradiation at the same temperature was also comparable. All these factors combined yielded confidence that a high TiC precipitate number density was largely responsible for the improved irradiation resistance (as measured by the reduced G-phase fraction). Unfortunately, I also demonstrated that ageing heat treatments were not a promising avenue for improving the radiation resistance, since the number density of new TiC precipitates that can potentially form under irradiation is reduced. For the ion irradiations and APT experiments, I was funded by the US department of Energy through the competitive NSUF RTE scheme by submitting proposals I wrote. The main results of the last chapter were published in a paper entitled “The role of Ti and TiC nanoprecipitates in radiation resistant austenitic steel: A nanoscale study” published in Acta Materialia.

In summary, in my Ph.D. I performed a detailed and extensive investigation if TiC nanoprecipitates in a DIN 1.4970 stainless steel. I contributed to the understanding of the structure, shape, and formation mechanisms of these particles, both after annealing and after irradiation. I showed that the TiC precipitates are important point defect sinks, which help to mitigate the negative effects of irradiation, such as radiation induced segregation, G-phase formation, and possibly swelling. While the microstructure could not be improved via ageing heat treatment, the newfound understanding of the underlying mechanisms lead to real suggestions for material improvement. For example, the radiation resistance of the alloy might be further improved by increasing the annealing temperature during manufacturing to bring more primary TiC in solid solution, which would enhance the nucleation potential of TiC during irradiation.

Side projects to my Ph.D. which I was also involved in were investigating the mechanical properties of the steel, the recrystallization behavior, and the corrosion resistance in liquid lead-bismuth. The first two were spun out into two master thesis projects which I mentored, and the second was published as a paper in Scripta Materialia entitled: “Orientation relationship of the austenite-to-ferrite transformation in austenitic stainless steels due to dissolution corrosion in contact with liquid Pb-Bi eutectic”. Finally, I also developed a software tool to facilitate TEM operation, which was extremely handy to accelerate my own microscopy work. This tool is described in chapter 4 of my thesis, as well as in a paper in the Journal of Microscopy entitled: “ALPHABETA: a dedicated open-source tool for calculating TEM stage tilt angles”. Finally, I also published a paper in the Journal of Nuclear materials where I analyzed data from a historical creep database. It is entitled: “Thermal creep properties of Ti-stabilized DIN 1.4970 (15-15Ti) austenitic stainless steel pressurized cladding tubes”.

My thesis is now open access, and can be downloaded from:

https://repository.uantwerpen.be/docman/irua/83a6dc/14999.pdf.