## The Evolution of Precipitates in High Cu and High Ni RPV Welds under Longterm Thermal Ageing

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Under neutron irradiation, solute-enriched clusters form in low alloy steels and welds that are used for manufacturing reactor pressure vessels (RPV) in light water reactor (LWR) systems. This can result in a significant increase in the yield strength of the steel and an increase in the ductile-to-brittle transition temperature (DBTT) compared to the non-irradiated steel. To date, the behavior of RPV materials is evaluated through extensive surveillance irradiation tests performed throughout the lifetime of the nuclear power plant. Thus, it is important to be able to predict and also understand the mechanism(s) by which this embrittlement occurs. Over the past 35 years, there have been significant efforts to identify and characterize these Cu-Mn-Ni-Si-enriched clusters, as RPV degradation can seriously limit the operating lifetime of a NPP. The analysis of neutron-irradiated 0.3 wt.% Cu RPV welds using atom probe field-ion microscopy first demonstrated that Cu-Mn-Ni-Si solute clusters, also known as Cu-enriched clusters (CEC), form, due to the combined effects of irradiation and the supersaturation of Cu in Fe. All RPV steels and welds now have strictly controlled Cu limits to avoid this degradation. However, several studies have shown that solute clusters are formed during neutron irradiation. These clusters were significantly enriched with Mn, Although the formation of a MnNi-phase in Fe is predicted by thermodynamics calculation [1,2], no evidence has been presented to date to demonstrate that a MnNi precipitate can form in low alloy steels during ageing at a temperature of 365°C.

In this work, precipitates that form in a high Cu-Mn-Ni low alloy steel under long-term thermal ageing at a temperature ~60C-deg higher than a pressurized water reactor has been studied using advanced electron microscopy and atom probe tomography (APT) techniques. Cu precipitates were observed in the early stage of ageing, i.e. 1000 hours [3]. These CRPs undergo a martensitic transformation from BCC-9R-3R-FCC structure as reported in [4]. One such thermally-aged Cu precipitate with a 9R structure was imaged and is shown in the high resolution TEM image in Figure 1. After prolonged ageing at 365°C, a Mn-Ni phase nucleated at the interface of the Cu precipitate and bcc Fe matrix as a "shell" surrounding the Cu as the core, as shown in Figure 2. Our studies also show that further ageing leads to the change in the morphology of these "core-shell" precipitates, as shown in Figure 3. EDX and EELS spectrum images have also demonstrated that a thicker MnNirich shell had formed at Cu precipitates associated with dislocations or grain boundaries due to preferential channeling of solutes along dislocations and grain boundaries. Further results obtained from TEM and APT will be compared and discussed in the presentation.

## References:

- [1] Liu, CL, et al, Mat. Sci. & Eng. A **238(1)** (1997), p. 202.
- [2] Xiong W, et al., (2014), MRS Comm.
- [3] Morley, A, Department of Materials. Oxford, University of Oxford. DPhil Thesis (2008).
- [4] Lim, JJH, Department of Materials. University of Oxford, UK. DPhil Thesis submitted (2014).

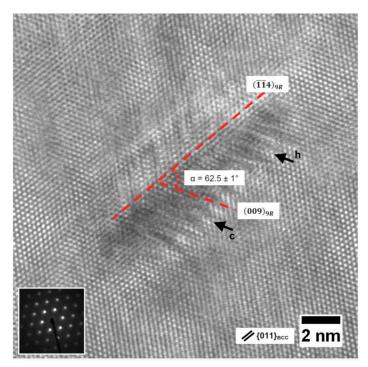
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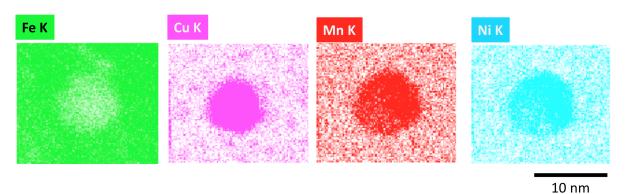
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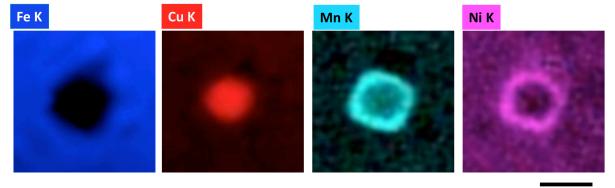
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**Figure 1**: High resolution transmission electron image taken along  $<111>_{Fe}$  showing a twinned 9R structure Cu precipitate (8 nm) in WV steel weld after thermal ageing for 49,800 hours at 365 °C. The angle  $\alpha$  between the  $(009)_{9R}$  basal and  $(\overline{114})_{9R}$  twin planes is  $62.5 \pm 1^{\circ}$ . The 2-layer fringe spacing at the position of a hexagonal-type stacking faults is indicated. Similarly, the 4-layer fringe spacing at the position of a cubic-type stacking fault is also indicated.



**Figure 2**: EDS spectrum images corresponding to a thermally-aged precipitate nucleated at the matrix of low alloy steel weld aged for 18,620 hours.



**Figure 3:** EELS multivariate statistical analysis reconstructed spectrum images corresponding to a thermally-aged precipitate nucleated at the matrix of low alloy steel weld aged for 49,800 hours.