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Secondary precipitation within the cementite phase of reactor pressure vessel steels

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ABSTRACT

Solute clustering is known to play a significant role in the embrittlement of reactor pressure vessel (RPV) steels. In this study, previously unobserved manganese-, nickel-, and silicon-rich precipitates in the cementite phase of a thermally aged, low copper RPV steel are characterised at the atomic scale via atom probe tomography. Additionally, copper-rich precipitates are observed in the cementite phase of a thermally aged, high copper RPV steel. Due to their secluded nature, these secondary precipitates could be utilised as indicators of the time–temperature exposure of RPVs and assist in assessing remnant lifetime.

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In a light water reactor, the reactor pressure vessel (RPV) must withstand high temperatures, high pressures, and long-term exposure to high-energy neutrons. As they are prohibitively expensive to replace, RPVs are typically the limiting factor in reactor lifetime.

In order to improve the initial properties of RPV steels, solute is added to the iron. For example, Ni strengthens the steel at low temperatures; Si de-oxidises the steel; and Mn, via the formation of MnS, attenuates brittleness [1]. While these solutes are critically important to the structural integrity of the RPV, solute clustering is known to play a significant role in its embrittlement [2]. Copper-rich precipitates (CRPs) form in steels with greater than 0.1 at.% copper at typical RPV operating temperatures (on the order of 300 °C) [3]. Significant previous research has shown that CRPs are a key cause of hardening and the eventual degradation of RPVs [3–6]. Due to the formation of CRPs, new generation RPVs have been engineered to contain less than 0.1 at.% copper [4]. Although these steels are no longer subject to the detrimental effects of CRPs, attention has now turned to the potential hardening and embrittlement effects of manganese-, nickel-, and silicon-rich precipitates (MNPs). Therefore, it remains imperative to track how solute is distributed within the microstructure throughout the lifetime of the RPV.

Although CRPs within the matrix of RPV steels have been extensively studied [4–9], there is relatively little in the published literature regarding CRPs within carbides. Copper-rich solute clusters located within carbides were first reported by Khalid and Edmonds utilising TEM [10,11]. However, the material analysed in that study was a high-alloy hypereutectoid steel containing large amounts of Mn and thus significantly different from the model RPV steels investigated in this study. Through the use of scanning transmission electron microscopy-energy-dispersive spectrometry (STEM-EDS) they showed that these precipitates were high in copper. However, an extensive chemical characterisation was not conducted. MNPs located within the matrix of low copper steels have also been extensively studied [12–16], and although MNPs have been observed at heterogeneous nucleation sites after thermal ageing [4], previous work has not revealed any secondary MNPs located within carbides in the new generation RPV steels.

In this study, CRPs and MNPs were observed within the cementite phase of a high copper and low copper RPV steel, respectively, following long term thermal ageing. Atom probe tomography (APT) was used to characterise the precipitates and obtain more detailed chemical information. This was made possible through APT's unique combination of atomic sensitivity and sub-nanometer 3D spatial resolution [17].

The high and low copper model RPV steels analysed in this study were provided by Rolls-Royce Plc. (Table 1). After rolling, the steels were subjected to an initial heat treatment as 25 mm thick plates. The

Table 1
Nominal chemical compositions of high and low copper RPV steels in at.%.

	Cu	Ni	Mn	Si	Mo	C	Cr	P	Fe
High Cu steel	0.3	3.3	1.5	0.4	0.3	0.9	0.1	0.01	93.3
Low Cu steel	0.04	3.3	0.3	0.4	0.3	1.2	0.1	0.01	94.4

plates underwent austenitisation at approximately 920 °C for 1 h followed by an air cool. Carbides typically form during this step in the heat treatment [18]. The plates were then tempered at approximately 600 °C for 5 h followed by a final air cool.

Following this forging and processing, the steels were thermally aged for 11,700 h at 405 °C (high copper) or 365 °C (low copper). Although RPVs typically operate at 290 °C, higher temperatures were utilised in this study to expedite cluster formation. The steels were kept in vacuum during the thermal ageing treatment to avoid oxidation. Upon removal from the furnaces, the steels were quenched in water.

Specimens for TEM were prepared from 3 mm disks, which were ground down to a thickness of approximately 90 μm. The specimens were then electropolished using 90% perchloric acid with a TenuPol Electropolisher. The TEM was conducted on a Jeol 2100.

Specimens analysed using APT were prepared either by electropolishing or site-specific focused ion beam (FIB) lift-out. The former utilised 0.5 mm by 0.5 mm matchsticks, which were first-stage electropolished using 25% perchloric acid, then further sharpened (second-stage electropolished) using 2% perchloric acid

in butoxyethanol [19]. The latter was carried out on a Zeiss Auriga FIB-SEM. The site-specific FIB lift-out technique is described in detail by Thompson et al. [20]. Atom probe experiments were conducted using voltage mode with a pulse fraction of 20% on a LEAP 3000X HR. The 3D reconstruction of the data was created using IVAS™ 3.6.6, a software based on a standard reverse-projection algorithm [21].

APT analysis is complicated by the fact that the mass spectra of RPV steels can contain several peak overlaps, the most notable of which is the [58]Ni and [58]Fe peak overlap. Typically, the relative contributions to these peaks are deconvolved using known natural isotopic abundances. Generally, this calculation is applied to the entire dataset. However, in this study the peak deconvolution depended heavily on local chemistry and was therefore carried out separately for the precipitates, carbide matrix, and iron matrix.

Another potential peak overlap is Si^{28} and N^{14}. However, the nitrogen content in these model RPV steels is very low. Furthermore, the limited amount of nitrogen that is present in these steels is largely tied up in aluminum nitride particles and molybdenum carbo-nitrides. Regardless, it is possible to calculate the expected Si contributions to the relevant overlapping peaks (14 Da and 15 Da) using isotope abundances. From these calculations it was determined that the nitrogen content was negligible in the three atom probe samples presented.

In this study, CRPs were observed within the cementite phase of thermally aged high copper RPV steels. In order to confirm that these particles were located within the cementite, rather than above or below, a series of under-, in-, and, over-focus TEM images were
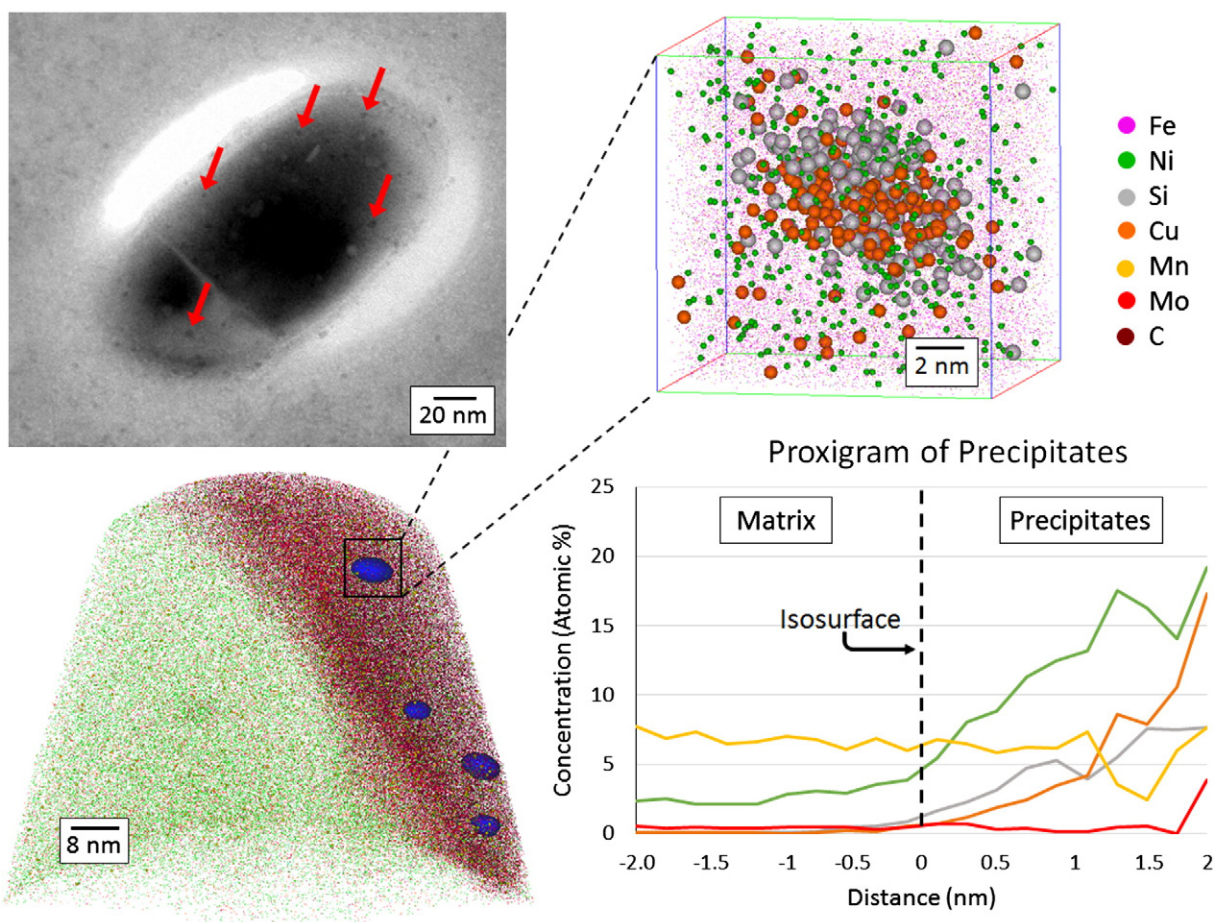

Proxigram of Precipitates

Fig. 1. The TEM image shows the copper-rich precipitates (highlighted by red arrows) randomly dispersed within the cementite phase of the high copper RPV steel after thermal ageing. The atom probe tomography reconstruction is of the same material and contains four CRPs within the cementite phase. An isosurface is used to emphasise the precipitates (blue — Cu, Ni, and Si). A proxigram of a single cluster is used to highlight how its composition varies as a function of distance from the cementite/precipitate interface.