Effect of Phosphorous (P) on precipitation and segregation behavior in neutron irradiated Reactor Pressure Vessel steels in the Advanced Test Reactor (ATR-2): An Atom Probe study.

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1. Objective:

The reactor pressure vessel (RPV) in a light-water reactor (LWR) provides primary shielding from the release of radiation in the case of a severe accident. Thus, precise knowledge on their fracture toughness, both during normal operation and under accident scenarios is extremely important. Under normal condition, the RPV has sufficient fracture toughness however, in the irradiated condition, the fracture toughness of the RPV may be severely degraded [1-2]. Degradation in performance of RPV steel under irradiation is currently evaluated according to U.S. Nuclear Regulatory Commission (NRC) Regulatory Guide [3], which presents methods (based on data correlations) for estimating the Charpy transition temperature shift (TTS). The sequence of embrittlement mechanisms is:

Irradiation and metallurgical variables → Evolution of hardening features → $\Delta\sigma_y$ (increase in the yield) → TTS

Systematic modeling efforts and experiments are required to link various mechanisms to the TTS and are governed by a combination of metallurgical and irradiation variables [4]. However, accurate TTS predictions need simplified analytical representations of models that are fitted to existing TTS databases (or other embrittlement databases). The main objective of this proposal is to cover one such aspect of TTS database by providing data on role of Phosphorous (P) in segregation and precipitation behavior in irradiated RPV steels.

2. Background and Significance:

At RPV operating temperatures and irradiation conditions, migrating vacancies, interstitials, and small interstitial clusters recombine during long-range diffusion, or are absorbed at sinks. The matrix features (MFs) formed from the cascades are known to produce hardening in RPV steels containing both low and high Cu content. The excess concentration of vacancies under irradiation also accelerates precipitation of Cu, along with Ni, Mn, P and Si which results in formation of copper rich precipitates (CRPs) and manganese-nickel rich precipitates (MNPs) [5]. The causes, character, and consequences of the MFs are not as well understood as are those of CRPs and MNPs, and improved treatments of their contributions to TTS are the subject of continuing study by the research community.

At low P levels and typical low to intermediate flux irradiation conditions, the dominant MFs are believed to be Mn-Ni-Si-P-Cu vacancy solute complexes or their remnants. However, at higher P levels alloy phosphide precipitates are observed. The effects of P and role of phosphide phases are relatively poorly understood for irradiated RPV steels. Previous studies have shown that role of P in mediating hardening and embrittlement is greatly enhanced at higher Mn, due to formation of Mn_3P precipitates. Although, the amount of impurity P in RPV alloys is generally very small, (< 0.05 wt %), it is very insoluble, and remains supersaturated following typical stress-relief heat treatments [3]. Thus, P can undergo accelerated precipitation due to radiation enhanced diffusion (RED) to form phosphide phases [6]. This is illustrated in Fig. 1 (a-b) where the tomographic atom probe map shows phosphide precipitates in a Fe- 0.025 wt % P binary model alloy irradiated at ~ 290°C and high flux to $\varphi t \sim 1.8 \times 10^{23}$ n/m^2 [7]. In this case, the P clusters appear to be more diffuse, and significant segregation of both P and Mn to dislocations is observed. Notably, Mn does not appear to be associated with the P clusters in this case (not shown here), which is a puzzling observation and needs further examination.

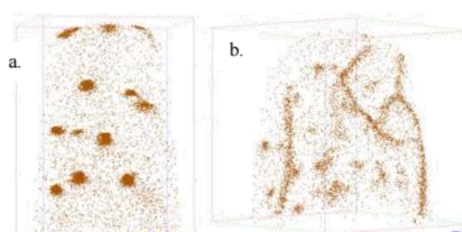

Fig. 1: Three-dimensional APT data on for model alloys irradiated to 1.77×10^{19} n/cm2 at 290°C and high flux. (a) Fe-0.025 wt % P alloy & (b) Fe-0.025 wt % P-1.6 wt % Mn alloy.

3. Approach

A variety of mechanisms may lead to increases in hardening by P from both enhanced MF (phosphide precipitates, vacancy-solute complexes and dislocations) and CRP (larger volume fractions and higher number densities) contributions. Significant P interactions with Ni, Cu and Mn are supported by both thermodynamic considerations and experimental observations. It is speculated that P forms bonds with vacancies, hence it is expected to increase the thermal stability and hardening efficiency of MF vacancy solute (Cu-Ni-Mn-P) cluster complexes. Other possible complications to treating P effects includes segregation of P to grain boundaries [7], as well as dislocations. Grain boundary P segregation reduces the amount of P available for precipitation under irradiation. However, accelerated grain boundary P segregation due to RED can also cause irradiation enhanced temper embrittlement, typically associated with brittle intergranular fracture [7].

In order to investigate role of P in precipitation and segregation behavior, a series of RPV steels with varying solute contents were irradiated to a fluence of $1.4\text{x}10^{20}$ n/cm^2 at T_{irr} of 290°C with flux of $3.6\text{x}10^{12}$ n/cm^2 in the UCSB ATR-2 experiment at a typical LWR operating temperature of 290°. This proposal aims to use atom probe tomography (APT) to quantify the P enriched precipitates that formed under irradiation in this series of steels with wide ranges of Cu and Ni content (shown in Table 1).

***Table 1**: Composition (wt.%) of materials to be investigated under proposal. (Med-Medium)*

Code	Description	Cu%	Ni%	Mn%	Cr%	Mo%	P%	C%	S%	Si%
C3	Cu-free Med Ni	0.02	0.85	1.60	0.00	0.49	0.006	0.13	0.000	0.16
C4	Cu-free Med Ni	0.02	0.86	1.53	0.05	0.55	0.031	0.16	0.003	0.16
C5	Cu-free Med Ni	0.02	0.86	1.61	0.04	0.53	0.050	0.15	0.000	0.16
C6	Cu-free High Ni	0.02	1.68	1.50	0.05	0.54	0.007	0.15	0.003	0.17
C7	Cu-free High Ni	0.00	1.70	1.55	0.05	0.56	0.047	0.16	0.003	0.17
C13	Low Cu Med Ni	0.11	0.83	1.61	0.00	0.51	0.004	0.15	0.000	0.16
C14	Low Cu Med Ni	0.11	0.83	1.62	0.00	0.52	0.040	0.16	0.000	0.17

APT is known to be powerful technique for elucidating precipitates and segregation behavior at nano-scales for irradiated materials. This proposal plans to utilize the APT facility (4000X HR Local Electrode) in the Microscopy and Characterization Suite (MaCS) at the Center for Advanced Energy Studies (CAES) to characterize the RPV steels (Table 1). The selected samples are aimed at gaining a better general understanding of the role of P for a range of Ni contents up to 1.7 % and for range of Cu content up to 0.11 %. The APT experiments are aimed at address following issues:

- Measure precipitate composition, their size, shape, number density as function of P content.
- Examine and quantify segregation of P microstructural features such as grain boundaries and dislocations as a function of Cu and Ni content.

4. Time requested on instruments:

Specimens for APT analysis would be prepared from matrix and grain boundary using dual beam FIB. Considering scope of this proposal, 7 set of samples (Table 1) are planned for APT analysis in this RTE call. Requested time on the instruments:

- FEI Quanta 3D Focused Ion Beam – 6 days (~5 hours per sample)
- Cameca LEAP 4000X – 10 days (~1-1.5 days per sample)

PI has extensive experience in sample preparation for APT using dual beam SEM. Average time required for PI to prepare APT specimens from one set of sample (usually 6-7 tips per lift-out) ranges from 4.5 to 5 hours. Considering 7 sets of samples for given scope of work, 6 days of FIB time would be sufficient.

5. Harvest strategy and impact:

An irradiation experiment has been performed as part of the Idaho National Laboratory (INL) Advanced Test Reactor (ATR) National Scientific User Facility (NSUF). The experiment was awarded to University of California, Santa Barbara (UCSB) several years ago with full funding for the irradiation experiment in the ATR provided by DOE through the NSUF. A detailed description of the UCSB ATR-2 experiment and materials provided in previous progress reports [8]. Irradiation embrittlement of reactor pressure vessel beltline materials is currently evaluated using U.S. Nuclear Regulatory Commission Regulatory Guide 1.99 Revision 2 (RG1.99/2), which presents methods for estimating the shift in Charpy transition temperature (TTS) and the drop in Charpy upper shelf energy (ΔUSE). The purpose of the work reported here is to improve on the TTS correlation in RG1.99/2 using the broader database now available and current understanding of embrittlement mechanisms.

6. References:

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