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Evolution of manganese–nickel–silicon-dominated phases in highly irradiated reactor pressure vessel steels

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Abstract

Formation of a high density of Mn–Ni–Si nanoscale precipitates in irradiated Cu-free and Cu-bearing reactor pressure vessel steels could lead to severe unexpected embrittlement. Models long ago predicted that these precipitates, which are not treated in current embrittlement prediction models, would emerge only at high fluence. However, the mechanisms and variables that control Mn–Ni–Si precipitate formation, and their detailed characteristics, have not been well understood. High flux irradiations of six steels with systematic variations in Cu and Ni contents were carried out at ~295 °C to high and very high neutron fluences of $\sim 1.3 \times 10^{20}$ and $\sim 1.1 \times 10^{21}$ n cm^{-2}. Atom probe tomography shows that significant mole fractions of Mn–Ni–Si-dominated precipitates form in the Cu-bearing steels at $\sim 1.3 \times 10^{20}$ n cm^{-2}, while they are only beginning to develop in Cu-free steels. However, large mole fractions of these precipitates, far in excess of those found in previous studies, are observed at 1.1×10^{21} n cm^{-2} at all Cu contents. At the highest fluence, the precipitate mole fractions primarily depend on the alloy Ni, rather than Cu, content. The Mn–Ni–Si precipitates lead to very large increases in measured hardness, corresponding to yield strength elevations of up to almost 700 MPa.

Keywords: Radiation damage; Atom probe tomography; Precipitation; Irradiation embrittlement

1. Introduction

Light water reactor (LWR) plant life extension to 80 years is needed to sustain the largest US carbon-free energy resource [1]. The major permanent and safety-critical LWR component is the massive reactor pressure vessel (RPV). Neutron irradiation of RPV steels results in embrittlement, manifested as upward brittle-to-ductile transition temperature shifts (TTSs). TTSs are primarily caused by the precipitation and defect hardening that occur under irradiation. Life extension requires demonstration that RPVs operate within safety margins, including ensuring that the effects of long-term irradiation on fracture toughness can be predicted and safely managed. The major RPV challenge for life extension is to develop robust predictive models of TTS in neutron flux and fluence regimes for which data largely do not currently exist. Here we verify the existence of a potentially severe precipitation hardening and embrittlement mechanism that emerges only at high fluence. Notably, this mechanism is not accounted for in current embrittlement prediction models. We also report on a number of new insights and related details regarding the nature and potential impact of the responsible precipitation hardening phases.

Current US TTS regulations derive from physically motivated models fitted to the in-service power reactor, engineering (surveillance) database [2–4]. These models

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treat the accelerated formation of Cu-rich precipitates (CRPs), due to radiation-enhanced diffusion [5], as well as solute–defect cluster complexes, referred to here as matrix features, which form in steels both with and without significant Cu contents. Matrix features are believed to initially form in displacement cascades as defect–solute cluster complexes, or their defect-free remnants [2–4,6–9]. Both CRPs and matrix features also generally contain significant quantities of Mn, Ni and Si [6–27]. However, current models predict that the CRP contribution to hardening saturates when Cu is depleted from the matrix [2,3]. Additional hardening due to matrix features increases linearly with the square root of fluence at the same relatively slow rate in both the Cu-bearing and Cu-free steels, and does not saturate. The semi-empirical models were fitted to the surveillance database that contained little high fluence (>5 × 10^{19} n cm^{-2}) TTS, pertinent to extended life. Thus extrapolations of TTS to 80-year operation may not be reliable [4].

Most notably, the potential for large mole fractions of Mn–Ni–Si (MNS) precipitates to form at high fluence is not included in the existing embrittlement models. This deficiency may be one source of the large underpredictions of TTSs observed in higher flux and fluence test reactor irradiations [4]. MNS phases are also of interest in their own right, since they would not be observed at low temperatures, around 300 °C, absent radiation enhanced diffusion that greatly accelerates their otherwise sluggish thermal kinetics. Further, the MNS precipitates, and the role of Cu in their formation, may point to new directions for high-strength alloy development.

Unfortunately, with regard to RPV embrittlement, there are no in-service, low flux-high fluence data for 80-year in-service vessel conditions. Previous research first predicted, and subsequently confirmed, that MNS precipitates can form in low-Cu steels and that they likely emerge from the matrix feature solute–defect cluster complexes, cited above that begin forming at low fluence [6–9,13,25]. More recent studies by others have also observed MNS precipitates in other low-Cu, high-Ni content steels, including in surveillance programs [17,26,27]. Large mole fractions of MNS precipitates are enhanced at higher Ni content and fluence as well as by lower irradiation temperatures and flux [4,7,8,15].

Here we focus on atom probe tomography (APT) studies of precipitates formed at two very high flux and high to very high fluence irradiation conditions. The experiments were carried out in the Belgian Reactor 2 (BR2) and the US Advanced Test Reactor (ATR), respectively. The test reactor fluxes range from 2500 (BR2) to 5800 (ATR) times higher than those in a vessel that reaches an end-of-life fluence of ∼10^{20} n cm^{-2} in 80 years. The corresponding BR2 and ATR fluence levels range from ∼1.3 × 10^{20} n cm^{-2} to a previously unexplored ∼11 × 10^{20} n cm^{-2}.

As shown below, and for the first time, the very high fluence condition in this study produces extremely large mole fractions of MNS phases in six steels with systematic variations in their Cu and Ni contents. The effects of high flux will be discussed in detail in future publications. We note, however, that it is well known that higher flux affects hardening and embrittlement, primarily by delaying precipitation to higher fluence [2,6–8,14,28,29]. This is illustrated in Fig. 1a and b for irradiation hardening, represented by an equivalent change in yield stress ($\Delta\sigma_y$) and precipitate volume fractions (f_v) in a high-Cu, medium-Ni content steel (LC), plotted as a function of the square root of fluence (ϕt), for low-flux (ϕ) irradiations in the previous UCSB Irradiation Variables (IVAR) Program and high-flux BR2 irradiations [29]. The increasing delay in both precipitation and hardening with increasing flux is obvious. These results are presented here simply to show that the precipitation hardening in these high to very high fluence test reactor irradiation conditions would likely occur at much lower fluence under low-flux power reactor conditions. The flux-adjusted power reactor equivalent fluences for these irradiations are yet to be verified, but based on our current best estimates, the BR2 irradiation would likely have an equivalent fluence that occurs before an 80-year end of vessel service life, while the corresponding ATR irradiation equivalent fluence would require more than 80 years [29]. However, the data from the ATR irradiation permit interpolation to an 80-year condition, and provide insight about

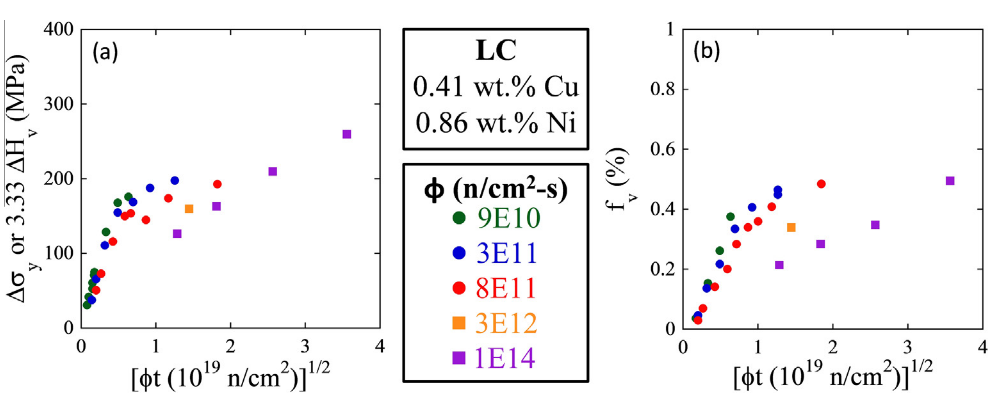

Fig. 1. (a) $\Delta\sigma_y$ and (b) f_v in a high-Cu, medium-Ni content steel (LC) for various irradiation conditions as a function of square root of the fluence showing a delay in both hardening and precipitate f_v with increasing flux.