CONF-950804--3

THERMAL EMBRITTLEMENT OF REACTOR VESSEL STEELS[1]

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ABSTRACT: As a result of observations of possible thermal embrittlement from recent studies with welds removed from retired steam generators of the Palisades Nuclear Plant (PNP), an assessment was made of thermal aging of reactor pressure vessel (RPV) steels under nominal reactor operating conditions. Discussions are presented on (1) data from the literature regarding relatively low-temperature thermal embrittlement of RPV steels; (2) relevant data from the U.S. power reactor-embrittlement data base (PR-EDB); and (3) potential mechanisms of thermal embrittlement in low-alloy steels.

1 LITERATURE SURVEY

The survey concentrated on effects of long-term aging at temperatures up to 350°C on the ductile-to-brittle transition temperature (DBTT) of RPV steels, for base metal, weld metal, and heat-affected zone (HAZ). The results of the literature survey are summarized in Figs. 1 and 2, which include marks on the aging time scale indicating the approximate time of exposure for the Palisades steam generators [10.8 effective full-power years (EFPY)] and the approximate design life of a commercial RPV (32 EFPY). Unless otherwise stated, the shift in DBTT was determined at an energy level of 30 ft-lb (41 J).

The most commonly used steels for U.S. nuclear RPVs are Mn-Mo-Ni steels. Data are available on A 212 grade B, A 302 grade B, A 533 grade B, and A508 class 2 and 3 steels. Work[1] on A 212 grade B showed that aging at 260°C for 16,000 h decreased the DBTT [calculated at 15 ft-lb (20 J)] by 2°C. Ten heats[2] of A 302 grade B alloys aged at 288°C for 1800 h showed the DBTT decreased by 5 to 14°C. Tests of unirradiated surveillance A 302 grade B specimens from the Big Rock Point[3,4] and Dresden 1 reactors[5] showed increases in the DBTT of up to 14°C after up to 26,105 h at 301°C, whereas similar aged material from the Oconee 1 reactor[6] showed no effect.

Several studies of A 533 grade B alloy have been performed. Early studies of thermal aging[7] included four heats aged at 300°C for times up to 1000 h. These data are very alarming at first sight, showing increases in the DBTT of as much as 62°C. However, these alloys were not given a postweld heat treatment (PWHT) after the quench-and-temper heat treatment. Therefore, this particular set of data must be viewed with caution, but the results do provide strong evidence of the sensitivity of these steels. Aging at 300 to 305°C for up to 20,000 h showed either "no change"[8] or a decrease[6] in

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[1] Research sponsored by the Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission, under Interagency Agreement DOE 1886-8109-8L with the U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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the DBTT of 5°C. The DBTT of materials from the Arkansas 1 reactor[9] shifted –4 to 10°C after aging at 280°C for 93,000 h.

A 508 class 2 material from the Oconee 3 reactor[9] increased 1°C after exposure at 282°C for 103,000 h. Three A 508 class 3 materials were aged[10] at 300°C for up to 20,000 h. Half-thickness impact specimens taken near the surface showed an increase in the DBTT of 35°C after aging for 2,000 h, with no further increase with continued aging to 20,000 h. The unique behavior of the near-surface material from the first alloy was tentatively attributed to a strain-aging effect. Another study with A 508 class 3 material[11] showed that aging at 350°C for up to 10,000 h had "little effect" on the DBTT. Material from the Doel reactor, called Soudotenax 56, apparently similar to A 508 class 3,[12] was aged at 287°C for 63,000 h, indicating little effect of aging. Material from the Gundremmingen reactor[13] (alloy 20NiMoCr 2 6) showed an increase in the DBTT of 40°C after exposure for 37,560 h at about 284°C.

There are very few data available for weld metals. Data from the Big Rock Point, Dresden 1, and Oconee 1 reactors[4-6] show small changes, both plus and minus, up to a maximum increase in the DBTT of 8°C after exposure for times ranging up to 26,114 h. Specimens from the Arkansas 1 and Oconee 3 reactors[9] showed changes in the DBTT of –8 to 0°C after exposure up to 103,000 h at about 280°C. Data from the Gundremmingen reactor[13] show no change in the DBTT for weld metal exposed for 37,500 h. Material from the Doel reactor showed an increase in DBTT of 30°C after exposure for 63,000 h at 287°C.[12] However, much of the data was generated with reconstituted specimens, and effects of the reconstitution process must be considered. Data from only unreconstituted specimens yield a much smaller shift of only 9°C. Druce[10] observed no effect of aging at 300°C for up to 10,000 h. Similar work (as reported by Vatter[14]) for aging at 300 or 325°C showed only a "gradual increase" in the DBTT. Data for the Palisades, Indian Point, and H. B. Robinson reactors surveillance weld metal[15] show increases in the DBTT of 16 to 17°C for aging of up to 70,128 h at 260 to 279°C. However, this comparison is for two different weld wires and locations.

2 REVIEW OF POWER REACTOR-EMBRITTLEMENT DATA BASE

The PR-EDB was examined for indications of thermal aging in the surveillance data. Currently, the PR-EDB contains over 700 data points for transition temperature shift. However, the predictive methodology contained in Nuclear Regulatory Commision *Regulatory Guide 1.99*, Rev. 2 (RG 1.99) was based on two sets of data (177 data points in one set and 228 in the other). The current review also compared the data in the current PR-EDB and the previous data set containing 177 data. The number of shift data points versus the time in EFPY for which the tested specimens were exposed under operating conditions in the reactor was examined. For the PR-EDB, the peak in the distribution is at 2 years, but there are over 100 data points available with over 6 years exposure. For the RG 1.99 data, the bulk of the exposures are also for two EFPY with only about 10% of the data beyond 6 years and no data beyond 11 years. Figures 3 and 4 provide plots of the residual versus EFPY for base materials and weld materials, respectively, in the PR-EDB data base, where residual is defined as measured shift minus RG 1.99 prediction. The data appear to be centered about the residual value of zero. For the PR-EDB, the RG 1.99 predictive equations are clearly valid out to about 9 to 10 years and appear valid out to about 15 EFPY.

The dependence of the 30-ft-lb transition temperature shift (DTT30) on EFPY and fluence was examined for data sets with fluence less than 1×10^{17} neutrons/cm^2 (E >1 MeV) where the irradiation-induced shift would likely be very small. Only four of the 40 points showed a shift greater than 11°C; one is for an HAZ, while three are for welds, one with 0.35% Cu and 0.73% Ni, and the other two with 0.18% Cu and 0.20% Ni. It is felt that the DTT30 results from these three capsules do not provide real evidence of large shifts at low fluence due to extremely large data scatter. For 8 thermal capsules, with exposure times ranging from about 10,000 to 43,000 h, the DTT30 values range from –16 to 11°C with a mean value of about 0°C. The mean and standard deviation for all the low-fluence DTT30 data shown are 1°C. Thus, the data indicate no trend for a measurable shift for times up to 43,000 h.

3 MECHANISMS OF THERMAL EMBRITTLEMENT

It has long been recognized that a number of processes could lead to the embrittlement of RPV steels subject to long-term service at elevated temperatures. These processes include: formation of hardening phases, such as copper-rich precipitates (CRP); segregation of phosphorus to grain boundaries leading to a lower intergranular fracture stress; and segregation of impurities to dislocations leading to strain aging. These phenomena could be accelerated or enhanced under irradiation. Pure thermal aging represents a zero-flux limit of damage rate-dependent effects.

In the late 1970s, Odette et al. proposed that an undefined thermal aging mechanism might be responsible for accelerated low-øt (ø = flux, t = time) embrittlement in surveillance (low-ø) versus test reactor (high-ø) irradiations.[17] In the mid 1980s, Fisher et al. developed a model of embrittlement due to copper precipitation accelerated by irradiation. It was initially applied to mild C-Mn Magnox steels[18] but later extended to Mn-Mo-Ni RPV steels.[19] Fisher proposed that at very low ø, an independent aging effect due to thermal copper precipitation would become significant, leading to peak hardening in periods of "25 years" at 290°C for copper contents of 0.1%. Odette et al.[20] also carried out an analysis of the peak aging time (t_p) to better quantify the effect of the (nominal) copper content. For nominal copper contents of 0.4% at 288°C, $t_p \approx 350{,}000$ h or about 40 years, similar to Fisher's results. However, due to a lower assumed effective activation energy, Odette et al. also found that precipitation kinetics at lower copper levels resulted in predicted t_p values that are very large, viz., more than 70,000 years at 0.2% Cu at 290°C. Unfortunately, these predictions represent extreme extrapolations.

The focus of work on aging mechanisms shifted to the potential for embrittlement associated with phosphorus segregation-induced weakening of grain boundaries. The key conclusion of this work[10,14] was that while some phosphorus segregation would occur, end-of-life thermal embrittlement would be minimal at temperatures of around 290°C, primarily due to sluggish diffusion kinetics. Work on temper embrittlement has recently shifted to radiation enhanced or induced segregation. A major motivation was the observation of an increasing incidence of intergranular fracture in fine-grained mild steel welds in U.K. Magnox reactors. Jones et al.[21] developed a simple but powerful model, providing a unified treatment of the combined effects of radiation hardening and radiation enhanced temper (segregation) embrittlement (RETE) mechanisms, accounting for the effects of temperature, flux (or time), and copper content. While there is also a possibility that RETE occurs in Mn-Mo-Ni RPV steels, most data for these alloys do not support this concern.

Thermal aging effects are very sensitive to both composition (e.g., copper on the hardening embrittlement mechanism) and microstructure (e.g., heat treatment on the temper embrittlement mechanism). Therefore, some caution should be exercised in making conclusions regarding aging effects outside the existing data base. To evaluate a broader range of compositions and aging mechanisms, a small study was initiated at the University of California, Santa Barbara (UCSB) involving five simple model Fe-Cu-Mn-N alloys and 12 commercial split-melt A 533 grade B-type steels aged at 290 and 350°C for periods up to 7200 h. Preliminary data[16] for the simple model Fe-Cu-X steels show that the alloys without copper experience a small degree of softening, while those with a large copper content of 0.9% show substantial hardening at both 290 and 350°C. The overall effect of manganese and nitrogen appears to be minimal. Based on $t^{1/3}$ kinetics, extrapolation using the t_p hardening in the 0.9% Cu alloys at 290°C is also reasonably consistent with earlier work. Almost all the commercial steel alloys show at least a slight increase in yield strength (s_y)[16] but generally within the overall data scatter of about ±20 MPa. Applying a criteria that there is a minimum of 20 MPa yield stress increase in the s_y at 8000 h and that Δs_y increases systematically with increasing t and temperature, four alloys show a significant effect of aging at 350°C and three out of these four at 290°C. Notably, most hardening is restricted to high-copper (0.4 and 0.8%) and nickel (0.8 and 1.6% at 290°C) alloys and increases with higher concentrations of these elements. While these preliminary short-term results cannot be directly used to address the question of long-term thermal embrittlement, they demonstrate that purely kinetic limits do not preclude thermally induced hardening at temperatures as low as 290°C. There is a significant sensitivity to copper and nickel content and, by implication, to heat treatment, since this affects the effective copper in solution.

Recently, Odette and co-workers have developed a self-consistent assessment of the effect of ø at intermediate to high levels which is able to rationalize complex, and in some cases, seemingly contradictory observations.[22] The primary effect of radiation is to greatly accelerate the formation of CRP as a consequence of radiation-enhanced diffusion (RED) produced by excess vacancies and interstitials, $D^* \approx K(\phi)\phi$. The RED factor, K, is ø-independent at low rates and varies as $1/\phi$ at high rates due to vacancy-interstitial recombination at thermally unstable defect clusters. The predictions of an embrittlement model developed by Stoller[23] lead to a similar conclusion. While requiring additional verification, these results suggest that ø effects vanish below a minimum value in the range of about 5×10^{11} neutrons/cm^2-s at 290°C.

4 SUMMARY AND CONCLUSIONS

Most of the data from the literature suggest that there is no embrittlement in typical RPV steels at these temperatures for times as great as 100,000 h. Only three base and two weld metals show any significant effects of aging. The data from Hasegawa[7] are suspect because these materials did not receive a PWHT. The results from the near-surface material of one forging reported by Druce were not observed with material taken from the middle of the same forging or other similar forgings, suggesting that these results are atypical. The results from the Gundremmingen reactor are difficult to interpret due to the uncertainties associated with the archive material. The data from the Doel reactor are suspect since the results of the reconstituted specimens are significantly different than those from the monolithic specimens. The Palisades data involve comparisons between welds made with different weld wires. The few data available[16] also indicate no evidence for embrittlement of HAZ materials up to 20,000 h. However, none of the data from the literature represents steels with the combination of high copper and high nickel that may increase sensitivity to thermal aging at these temperatures.

Review of the PR-EDB has not revealed convincing evidence of thermal embrittlement. The low-fluence surveillance data show DTT30 results less than 11°C. For surveillance exposures to about 15 EFPY, the DTT30 results are in good agreement with the predictions of the current RG 1.99 predictive equations. Although there are a few instances of relatively high DTT30 values at low fluences, the excessive scatter in the data and level of uncertainty in the DTT30 measurements render those results inconclusive.

While it is difficult to demonstrate that there are no significant effects of thermal aging, current understanding of both hardening and segregation mechanisms suggests that any thermal embrittlement is naturally incorporated in the effects observed following irradiation. That is, independent thermal aging and irradiation shifts should not be added if ø effects are not important or are properly accounted for. It seems likely that low lead-factor surveillance data provide a reasonable basis for embrittlement predictions. Indeed, theoretical considerations suggest that by creating alternative trapping and segregation sites, radiation may suppress embrittlement associated with phosphorus segregation.

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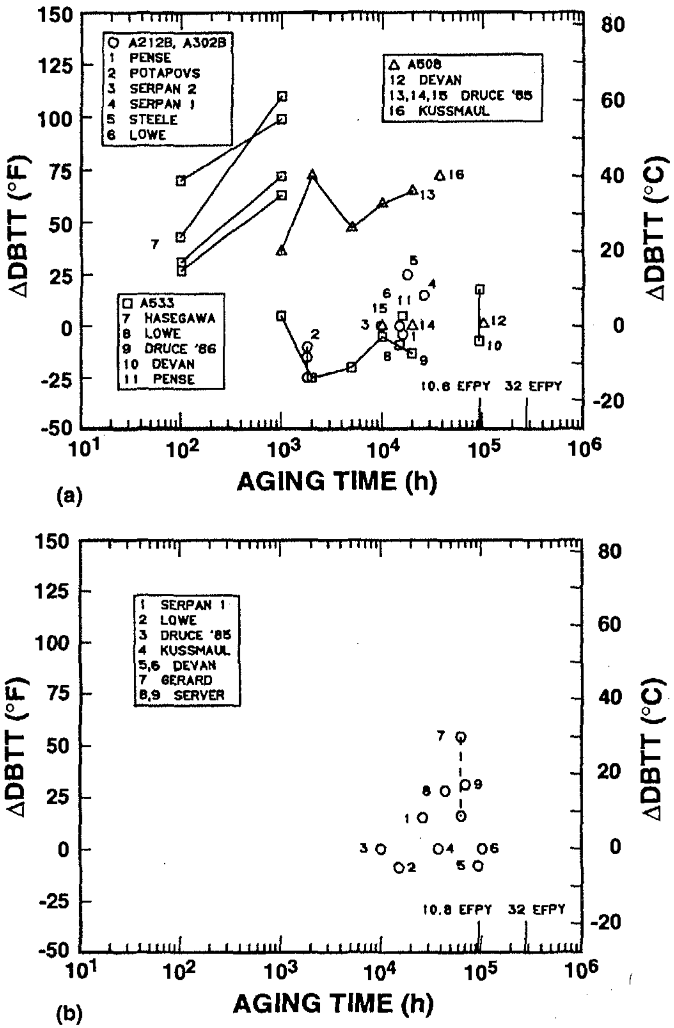

Figure 1. Shift in transition temperature (ΔDBTT) as a function of aging time for (a) base metals and (b) weld metals.

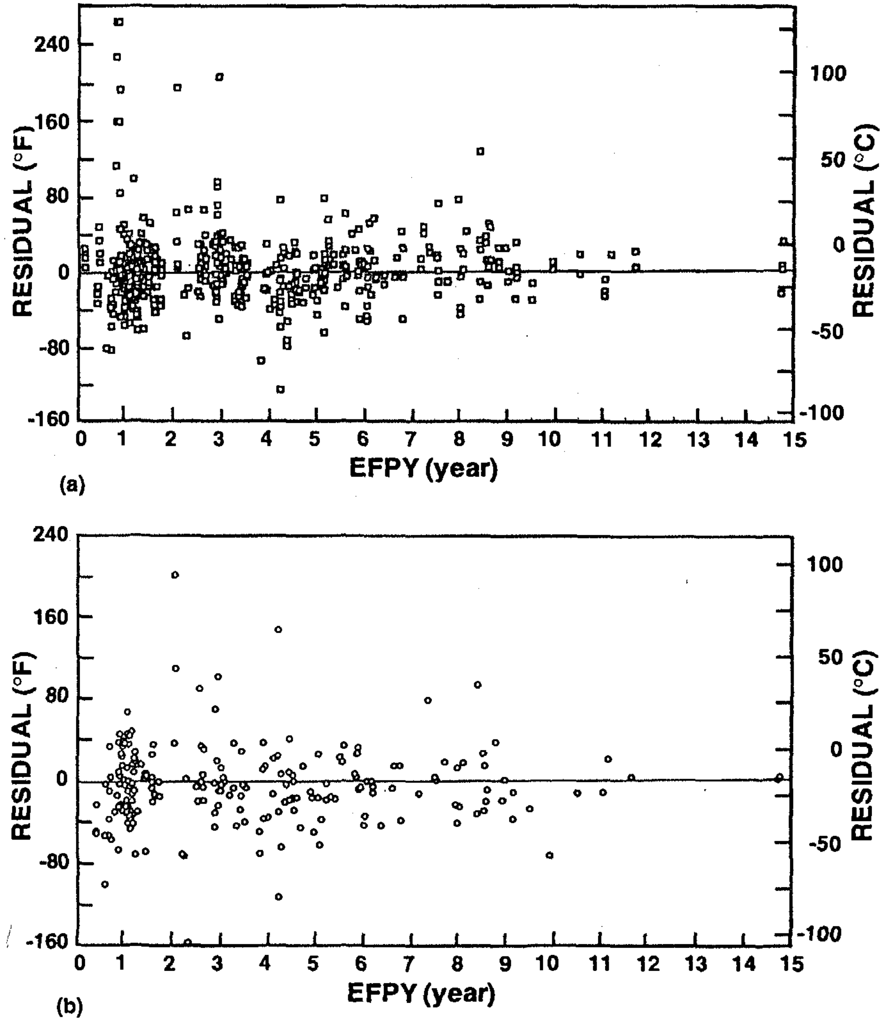

Figure 2. Plots of residual shift (measured shift – RG 1.99 prediction) versus EFPY for (a) base materials and (b) weld metals from PR-EDB.