

## DISCUSSION

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*F.A. Smidt, Jr.*<sup>1</sup>—Mr. Powers has attempted to correlate the embrittlement sensitivity of pressure vessel steels irradiated at temperatures of 450 to 550 F (232 to 288 C) with two specific empirical factors, nitrogen and copper content. While an empirical approach such as this may have merit in attempting to establish trends in a relatively new and uncharted field, it must be modified as more definitive information becomes available. Such studies have been reported at this conference and in the open literature over the past 4 to 5 years. I should specifically like to cite the following examples where I believe the author's conclusions should be modified in the light of more recent knowledge.

1. The author has attempted to normalize his data to a fluence of  $1 \times 10^{19}$  n/cm<sup>2</sup> using the assumption that the transition temperature shift ( $\Delta TT$ ) is proportional to  $(\Phi t)^{1/2}$ . As pointed out by J.R. Hawthorne in an accompanying discussion, this is a questionable practice for copper-containing materials. In another paper in this symposium<sup>2</sup> it is shown that the mechanism of embrittlement sensitivity for copper-bearing pressure vessel steels is through enhanced nucleation of dislocation loops, a process which leads to a nonproportionality between radiation hardening (and  $\Delta TT$ ) and  $(\Phi t)^{1/2}$ .

2. The author concludes that the amount of interstitial nitrogen modifies the effectiveness of copper producing irradiation sensitivity and calls for additional work in defining the effect of strong nitride formers on the state of the nitrogen. Igata et al<sup>3</sup> in another paper in this symposium have examined the interaction of aluminum, molybdenum, chromium, copper, and nickel with nitrogen in solution during low-temperature irradiation and postirradiation anneals by internal friction. They find that (a) there is little interaction between copper and nitrogen, and (b) nitrogen, which is tied up in irradiation-produced defects during low-temperature irradiations, begins to go back into solution during

<sup>1</sup> Reactor Materials Branch, Metallurgy Division, Naval Research Laboratory, Washington, D.C. 20390.

<sup>2</sup> F.A. Smidt, Jr. and J.A. Sprague, "Property Changes Resulting from Impurity-Defect Interactions in Iron and Pressure Vessel Steel Alloys," *Effects of Radiation on Substructure and Mechanical Properties of Metals and Alloys*, ASTM STP 529, American Society for Testing and Materials, 1973, pp. 78-91.

<sup>3</sup> N. Igata, K. Watanabe, and S. Sato, "The Role of Some Containing Elements on Radiation Hardening in Pressure Vessel Steels," *Effects of Radiation on Substructure and Mechanical Properties of Metals and Alloys*, ASTM STP 529, American Society for Testing and Materials, 1973, pp. 63-74.

postirradiation anneals between 250 and 300 C (482 and 572 F). It would thus appear that if nitrogen is reducing the irradiation embrittlement it is acting independently of the copper.

The author further suggests that the effect of nitrogen in decreasing embrittlement is to influence the recovery mechanism by "facilitation of thermal instability of vacancy clusters." The effect of interstitial impurities on radiation hardening and embrittlement has been studied extensively in recent years and a consensus appears to have been reached (see documentation in discussion of Igata's paper by F.A. Smidt, Jr.) that the hardening and embrittlement caused by interstitial impurities are due to precipitation on dislocation loops formed during the irradiation that converts them from relatively soft barriers to dislocation motion to hard barriers. This mechanism is operative for irradiations at temperatures between the point where interstitial impurities can diffuse to the loops and temperatures where they go back into solution. Wuttig et al<sup>4</sup> have shown that for nitrogen in iron resolutioning occurs at 200 C (392 F). Thus if nitrogen were to influence the recovery process, increasing amounts in solution would cause greater embrittlement, not less.

The trend noted by Mr. Powers that interstitial impurities in solution reduce radiation damage for irradiations at temperatures near 550 F (290 C) does appear to be real however. In my work (footnote 2) an 0.1 atomic percent carbon alloy was found to have less radiation hardening than a pure zone-refined iron. It is suggested that a more plausible softening mechanism is the trapping of carbon (nitrogen) by vacancies. Wuttig et al (footnote 4) believed they had observed such a reaction in quenched iron. Such a defect could conceivably produce less hardening than carbon atoms and vacancies separately.

3. Finally, although it is possible that interstitial impurities in solution may produce some irradiation softening, as noted by Igata et al (footnote 3), it is highly unlikely that the effect would be enough to produce the changes in embrittlement the author ascribes to it. In my study of embrittlement mechanisms for the same temperature regime (footnote 2), I found that enhanced nucleation of vacancy loops occurred on copper atoms or clusters of copper atoms. The origin of the copper-vacancy interaction appeared to be an electronic interaction between the excess charge near the copper atom and the charge deficiency near the vacancy. Other elements with extensive solubility where a similar electronic interaction might occur include aluminum. In fact, Potapovs and Hawthorne<sup>5</sup> found that additions of 0.2 weight percent aluminum caused an ~70 F (39 C) shift in transition temperature as compared with an otherwise identical heat of 3½Ni-Cr-Mo steel (40 ppm N) under identical irradiation conditions [ $2.2 \times 10^{19}$  n/cm<sup>2</sup> at 550 F (288 C)]. I therefore suggest

<sup>4</sup> M. Wuttig, J.T. Stanley, and H.K. Birnbaum, *Physica Status Solidi*, Vol. 27, 1968, p. 701.

<sup>5</sup> U. Potapovs and J.R. Hawthorne, "The Effect of Residual Elements on 550 F Irradiation Response of Selected Pressure Vessel Steels and Weldments," NRL Report 6803, Naval Research Laboratory, Nov. 22, 1968; *Nuclear Applications*, Vol. 6, No. 1 Jan. 1969, p. 27.

that the correlation between embrittlement and an absence of free nitrogen may in fact be a correlation between embrittlement and uncombined aluminum.

*J.R. Hawthorne*<sup>6</sup>—The argument has been given that free (uncombined) nitrogen can be beneficial to radiation embrittlement resistance and, further, that the effect is manifested through a modification of the detrimental effect of copper content on radiation resistance.

I feel that, in the development of the argument, certain factors which may modify the conclusion should have been discussed and others treated more rigorously. In addition, I disagree with the interpretation of certain experimental data critical to the conclusions. (Several data generated by NRL were used in formulating the argument.)

It has been established that phosphorus content, as well as copper content, has a highly detrimental effect on radiation embrittlement resistance at elevated temperature (Fig. 3).<sup>7</sup> It has also been determined that the separate influences are generally additive.<sup>8,9</sup> Accordingly, variable phosphorus contents as well as variable copper contents lead to observations of variable radiation embrittlement resistance. The paper, however, has not discussed (or allowed for) the effects of variable phosphorus contents in making the analysis. As a result, it is possible that the reason(s) for sensitive or insensitive steel behavior could have been misjudged or overlooked. For example, the A350-LF steels supplied by NRL have phosphorus contents ranging from 0.027 to 0.031 percent but less than 0.15 percent copper. In a second case, the paper compares commercial melts and special laboratory melts without making a distinction as to total impurities content. It is unrealistic to compare a high-purity laboratory melt containing a special addition of 0.2 percent copper but only a trace amount of phosphorus with a commercial melt containing both 0.2 percent copper and a nominal amount of phosphorus.

I have reservations about the joint treatment of data from irradiations encompassing 450 F to 550 F (232 to 288 C) exposure temperatures. For most steels, exposure temperature in this range has a more marked effect on irradiation response than implied in the report. For example, the ASTM A302-B reference plate exhibited Charpy-V 30 ft · lb transition temperature increases of 130 and 140 F (72 to 78 C) when irradiated at 400 and 450 F (204 to 232 C), respectively, but only 65 F (36 C) when irradiated at 550 F (288 C) ( $5 \times 10^{18}$  n/cm<sup>2</sup> > 1 MeV).<sup>10</sup> Depending on the data distribution, however, I recognize

<sup>6</sup> Reactor Materials Branch, Metallurgy Division, Naval Research Laboratory, Washington, D.C. 20390.

<sup>7</sup> See footnote 5, pp. 27-46.

<sup>8</sup> Hawthorne, J. R., Fortner, E., and Grant, S. P., "Radiation Resistant Experimental Weld Metals for Advanced Reactor Vessel Steels," *Welding Journal Research Supplement*, Vol. 49, No. 1, Oct. 1970, p. 453.

<sup>9</sup> Hawthorne, J. R. and Fortner, E., "Radiation and Temper Embrittlement Processes in Advanced Reactor Weld Metals," *Transactions, Journal of Engineering for Industry*, American Society of Mechanical Engineers, Aug. 1972.

<sup>10</sup> Steele, L. E. and Hawthorne, J. R., "Effects of Irradiation Temperature on Neutron-Induced Changes in Notch Ductility of Pressure-Vessel Steels," NRL Report 5629, June 28, 1961.

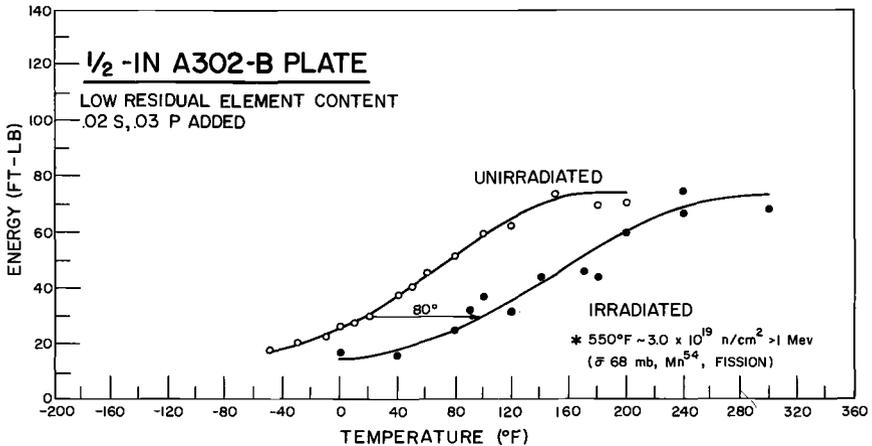
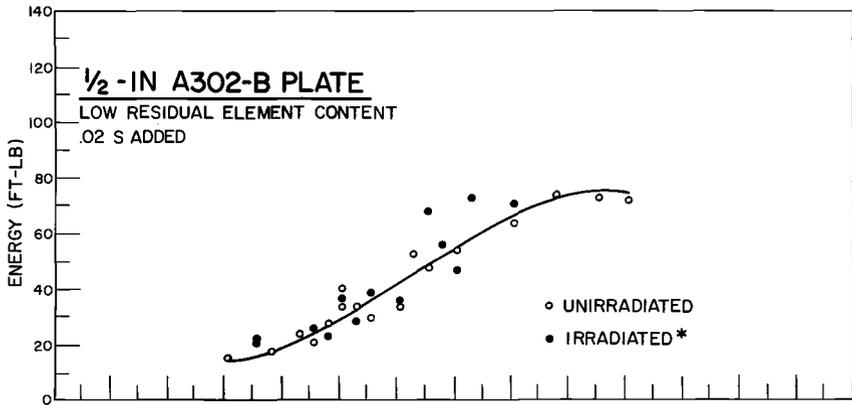
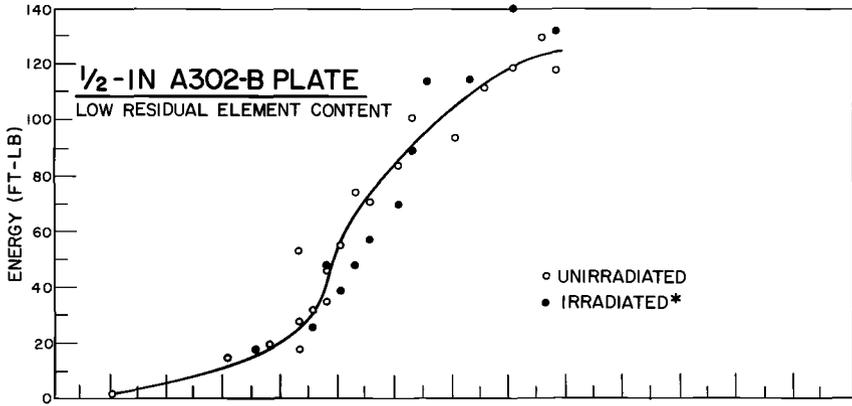


FIG. 3—Notch ductility behavior of A302-B test plates (sulfur-phosphorus series) from a 3-way split laboratory melt before and after irradiation at 550 F (288 C) [Potapovs and Hawthorne (Footnote 5)].

that this factor may or may not be critical to the author's analysis.

Finally, I must disagree with the assumption that transition temperature increase data can be normalized in all cases by the relation: transition temperature increase ( $\Delta T$ )  $\propto$  (fluence,  $\Phi$ )<sup>1/2</sup> where fluence is n/cm<sup>2</sup> >1 MeV. This assumption and the extrapolation (or interpolation) of data to a fluence of  $1 \times 10^{19}$  n/cm<sup>2</sup> have provided a misleading picture of steel performance in some critical cases. It has been determined that the sensitizing influence of copper content on the irradiation-induced transition temperature shift is related to the yield strength elevation. Smidt and Sprague in another paper in this symposium (footnote 2) report that the radiation elevation of yield strength is not linearly related to (fluence)<sup>1/2</sup> for either iron-copper or copper-containing low-alloy steel plates and welds. Separately, it is noted in Fig. 4<sup>11</sup> that the data trend for 550 F (288 C) irradiation of the ASTM A302-B reference steel plate indicates a transition temperature increase of approximately 125 F (70 C) for a fluence of  $1 \times 10^{19}$  n/cm<sup>2</sup>. On the other hand, the formula projection was 100 F (56 C) or

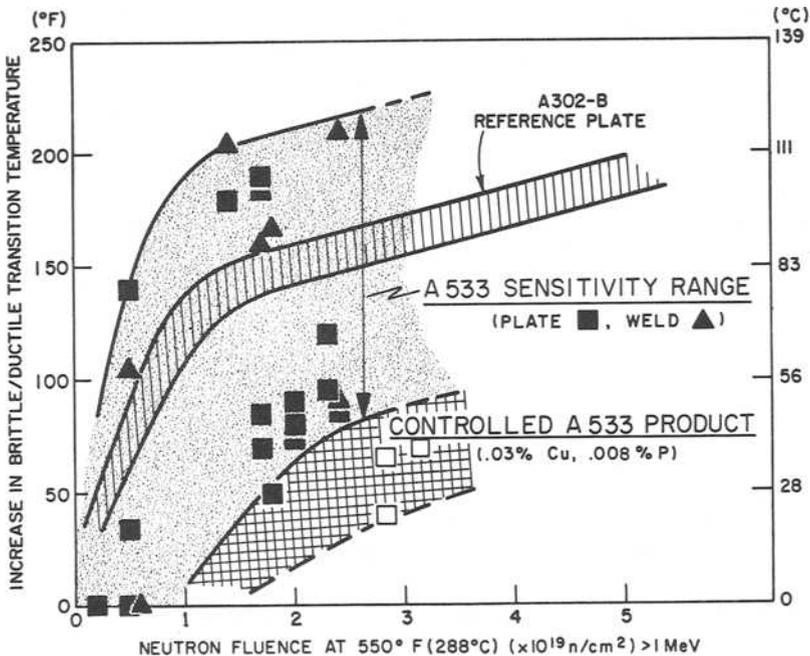


FIG. 4—Increase in Charpy-V 30 ft · lb transition temperature with neutron exposure at 550 F (288 C). The performance of plate from a controlled A533-B steel melt is compared with the performance of the ASTM A302-B reference plate and conventional A533 materials representative of current reactor vessel construction. The benefit of controlled copper and phosphorus contents is readily apparent [Hawthorne (footnote 11)].

<sup>11</sup> Hawthorne, J. R., "Demonstration of Improved Radiation Embrittlement Resistance of A533B Steel Through Control of Selected Residual Elements," NRL Report 7121, May 21, 1970; *Irradiation Effects on Structural Alloys for Nuclear Reactor Applications*, ASTM STP 484, American Society for Testing and Materials, 1971, pp. 96-126.

less, whereupon this steel was judged "insensitive," and subsequently offered as an outstanding example of an insensitive steel containing 0.2 percent copper. Similar citations for at least two other steels also appear questionable.

The preceding discussion is not meant to disqualify the possibility of nitrogen effects on radiation embrittlement resistance, but merely to point out that certain points require critical review or clarification.

*A. E. Powers (author's closure)*—First of all, there seems to be doubt by discussers Smidt and Hawthorne that the relation,  $\Delta TT = A(\Phi t)^{1/2}$  is a reasonably good relation for normalizing the irradiation embrittlement to  $1 \times 10^{19}$  n/cm<sup>2</sup> (> 1 MeV). They cite data from the paper by Smidt and Sprague in this symposium where various iron alloys are irradiated at fluences of  $2.5 \times 10^{19}$  and  $4.5 \times 10^{20}$  n/cm<sup>2</sup>. The square-root relation seems to hold for all alloys up to fluences as high as  $4.5 \times 10^{20}$  n/cm<sup>2</sup> except the Fe-0.3Cu alloy. Since there are no data points below  $2.5 \times 10^{19}$  n/cm<sup>2</sup>, the discussers have no basis to claim that the irradiation embrittlement of the iron-copper alloy is not a straight-line function of  $(\Phi t)^{1/2}$  at least up to  $2.5 \times 10^{19}$  n/cm<sup>2</sup>. In none of the items in Table 1 were interpolations made from data points higher than  $3 \times 10^{19}$  n/cm<sup>2</sup>.

I have attempted to make clear in my paper that the major reason for differences in irradiation hardening and embrittlement at irradiation temperatures of about 500 F (260 C) is the variation in concurrent annealing of the irradiation damage that may occur during irradiation. The sensitive steels do not anneal during irradiation at 500 F (260 C); whereas the insensitive steels do undergo considerable annealing during irradiation.

It would appear that copper, being a precipitation-hardening element in iron, inhibits annealing of irradiation defects during irradiation at 500 F (260 C) and that uncombined nitrogen counteracts or reduces the effect of copper in stabilizing irradiation defects against thermal dissipation.

The conclusions of this paper are not contrary to the findings of others (Little and Harries; Columbo, Rossi, and Sebille; Smidt and Hawthorne) that nitrogen directly increases the irradiation hardening of iron. I do not doubt that this effect does occur at temperatures as high as 500 F (260 C), but I believe this direct hardening effect of nitrogen in commercial steels is minor compared with the effect of uncombined nitrogen in reducing the resistance to co-irradiation annealing of copper-containing steels.

The annealing effect is more prominent in long-time service applications than in short-time test irradiations. For example, Ref  $\bar{10}$  postulates that a typical reactor pressure vessel operating at 500 F (260 C) and constructed of insensitive steel will probably not undergo a  $\Delta TT$  of more than 25 F (14 C) no matter how long the service life. We have recent data from a moderately sensitive steel which showed a  $\Delta TT$  of 160 F (89 C) at  $1 \times 10^{19}$  n/cm<sup>2</sup> by a 6-week irradiation and a  $\Delta TT$  of 120 F (67 C) after a 5½-year irradiation to the same fluence and at the same approximate temperature of 470 to 500 F (243 to 260 C).

With regard to phosphorus, NRL work indicates that phosphorus conveys some irradiation embrittlement in the 500 F (260 C) range, but the effect is minor compared with that of copper, and I believe it is minor compared with the

influence of uncombined nitrogen in promoting co-irradiation annealing in this reactor temperature region.

J. R. Hawthorne's comment about arranging Table 1 in groups of smaller temperature ranges than the 450 to 550 F (232 to 288 C) range is appreciated. A better scheme would be to normalize the temperatures to one temperature, for example, 500 F (260 C), if it were possible to do so. Highly sensitive steels appear to have little or no temperature dependence at least up to 550 F (288 C), whereas insensitive steels appear to have appreciable temperature dependence. Table 1 contains the estimated irradiation temperatures, and the reader can make his own judgments.

The suggestion by F. A. Smidt that aluminum, rather than the absence of interstitial nitrogen, is responsible for an increment of irradiation sensitivity appears to have no foundation in view of the data in Table 1 where aluminum contents are presented. Compare, for example, Items 7 and 8, 10 and 11, 19 and 20, 20 and 21. These items do not show a correlation between aluminum content and  $\Delta TT$ , but do show a correlation between interstitial nitrogen and  $\Delta TT$  values.