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Residual Elements and Irradiation Embrittlement

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ABSTRACT

Past work on the role of residual elements (particularly copper and phosphorus) in the enhanced irradiation embrittlement observed in pressure-vessel steels irradiated at 550°F (288°C) is reviewed. Only three mechanisms for explaining the embrittlement are plausible—temper embrittlement, irradiation-enhanced diffusion to an interface, and enhanced nucleation of defect aggregates which produce hardening and embrittlement. Experiments employing scanning microscopy and Aüger spectroscopy show that the embrittlement is not produced by segregation of copper or phosphorus at an interface. Microhardness recovery experiments indicate that the embrittlement in copper-containing alloys is accompanied by greater irradiation hardening. Transmission electron micrographs of special iron alloys doped with 0.3 at-% copper show a microstructure indicative of a higher concentration of defect aggregates than pure iron irradiated under the same conditions. These aggregates are believed to be vacancy in nature because vacancies are mobile during irradiation at 550°F (288°C) and because no correlation between embrittlement and copper or phosphorus content are noted after irradiation at temperatures where vacancies are not mobile.

PROBLEM STATUS

This is an interim report on one phase of the program; work on this and other phases is continuing.

AUTHORIZATION

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RESIDUAL ELEMENTS AND IRRADIATION EMBRITTLEMENT

INTRODUCTION

From the initial identification of radiation embrittlement of pressure-vessel steels as a potentially significant problem, investigators began to consider factors which might minimize the problem. Studies were conducted on microstructure and composition as well as environmental factors, such as temperature and neutron spectrum, to find a way to minimize radiation embrittlement. In the USA, studies centered on composition control. At NRL a program jointly sponsored by the Office of Naval Research and the U.S. Atomic Energy Commission (USAEC) was carried out in which systematic investigations demonstrated the capacity to produce (and reproduce), through composition control, consistent low sensitivity to radiation embrittlement in laboratory-scale heats of steels meeting the American Society for Testing and Materials (ASTM) specification for A302-B. The laboratory findings were validated through procurement of a 30-ton heat of ASTM A533-B (higher nickel version of A302-B) which proved to be less than one-third as sensitive to radiation as a typical commercial steel of the same type.

Two elements, copper and phosphorus, were found to be particularly important in controlling the tolerance to neutron radiation at temperatures typical of water reactor service. These studies have been extended to the higher-strength ASTM A543 and to weld compositions used for joining the A533-B and the A543 steels with the same conclusion. Thus, while this observation may not be universally applicable, it holds for the steels and weld metals now being used in USA water reactors and for the higher-strength candidate A543.

Studies leading to the observation of specific composition effects on radiation sensitivity have been reported in detail and will only be highlighted in this report. However, initial results of fundamental studies, which are aimed at understanding the mechanisms by which residual elements affect steel embrittlement, are reported in more detail. These studies in concert are expected to provide important knowledge for projecting radiation damage and for assuring maximum radiation resistance in future reactor pressure-vessel steels.

STUDY HIGHLIGHTS OF THE COMPOSITION EFFECTS ON RADIATION-EMBRITTLEMENT SENSITIVITY

Early NRL irradiation-effect experiments conducted at 550°F (288°C) on several reactor pressure-vessel steels (or candidate steels) showed significant variability in the degree of transition temperature shift from steel-to-steel and even from heat-to-heat for the same steel. These observations instigated a series of experiments which were carried out in cooperation with the United States Steel Corporation (USS) which attempted to isolate factors affecting specific radiation resistance. Small laboratory heats of A302-B steel were prepared by USS to investigate the effect of the steelmaking practice: heat treatment history and residual element level. Initial irradiation experiments conducted at temperatures of 250°F (120°C) demonstrated that the embrittlement sensitivity of a steel could be altered significantly by heat treatment, thus suggesting sensitivity to microstructure (1). Metallurgical cleanliness also affected radiation sensitivity as evidenced by smaller transition temperature shifts for heats which had been prepared using a vacuum melting practice compared with shifts observed for conventional open hearth melted steels. These results were inconclusive without the results of irradiation experiments conducted at typical reactor service temperature of approximately 550°F (288°C).

Elevated-temperature irradiation of the experimental heats of A302-B produced striking differences as shown in Fig. 1 (2). Heats low in residual element content showed

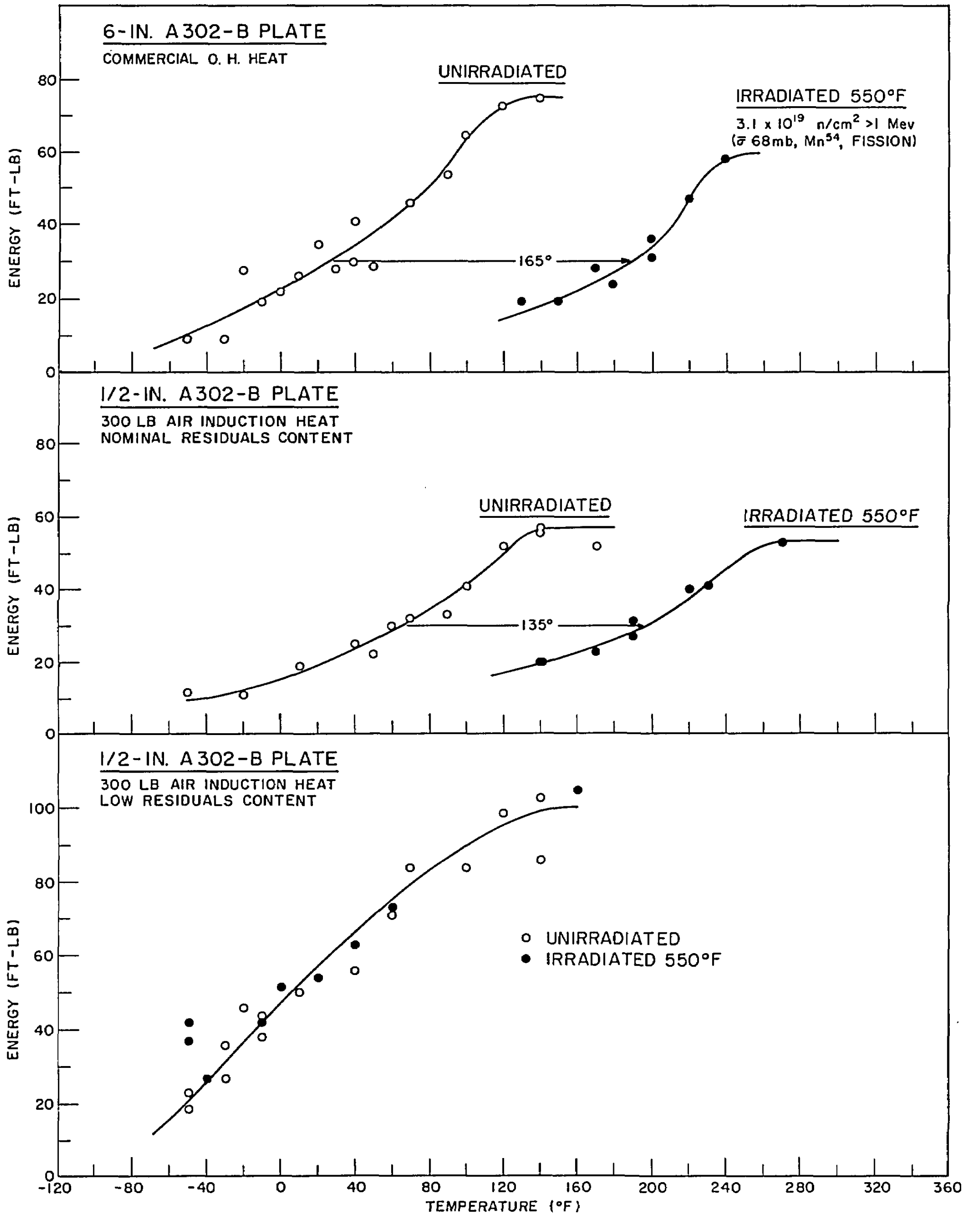

Fig. 1 - Comparison radiation embrittlement sensitivities of one large commercial heat and two air-induction heats of A302-B steel with nominal and low residual element contents based on Charpy V-notch ductility following 550°F (288°C) irradiation

essentially no transition temperature change or Charpy V-notch shelf drop, but those to which typical residual element levels had been added consistently showed significant changes. The most identifiable components for causing embrittlement were copper, phosphorus, and vanadium. The addition of sulfur caused a major preirradiation shelf reduction but no discernable neutron irradiation effect. Similar studies sought to identify the effects of copper, vanadium, and nitrogen on aluminum deoxidized A302-B laboratory heats. Copper was identified as the important factor.

Other studies sought to test the effects of variable nickel composition in a nickel-chromium-molybdenum base composition with no indication of any effect. Vanadium appears to have a secondary effect which is probably related to the modification of the carbide structure. Thus, copper and phosphorus were identified as major contributors to radiation embrittlement of A302-B steel at elevated irradiation temperatures. A summary review of these experimental results is provided in Ref. 3.

With the successful demonstration of reproducible embrittlement control on laboratory-scale heats, a scaleup demonstration to test these findings on a commercial-scale heat was undertaken based on NRL composition specifications. The composition specifications are summarized in Table 1, and a schematic view of the processing is provided in Fig. 2 (4). This heat was representative of current commercial steelmaking practice for nuclear applications with the exception of controls on residual element content as shown in Table 1. The plate was split as noted in Fig. 2 and heat-treated to two strength levels — 1/4-thickness yield strength, which is 67-68 ksi ($\approx$47 kg/mm^2) for class 1 and $\approx$80-84 ksi ($\approx$57 kg/mm^2) for class 2. Pure copper shot was added during the pouring of one ingot.

Irradiation to a neutron fluence of 2.8×10^{19} n/cm^2 > 1 MeV at 550°F (288°C) resulted in very different degrees of embrittlement as shown in Fig. 3. Both transition temperature increase (ΔTT) and shelf drop were exaggerated in the 0.13% copper ingot. Thus, the commercial heat confirmed the deleterious copper effect observed in laboratory studies.

In addition to the studies of pressure-vessel steels, companion work on weldments in pressure-vessel steels was carried on concurrently. Experimental welds low in copper content (<0.10%) were compared with commercial filler welds with typically high copper concentrations of 0.24 to 0.48%. Again, the experimental results of Charpy-V transition shifts after 550°F (288°C) irradiation dramatically illustrated the importance of low copper content in reducing the embrittlement. These results are illustrated in Fig. 4 (3). The low-copper experimental welds showed shifts of 45°F (25°C), but the commercial filler bearing 0.42% copper showed a shift of 535°F (297°C).

Additional studies of radiation-resistant weld metal design for providing guidelines to commercial weld practice were continued in

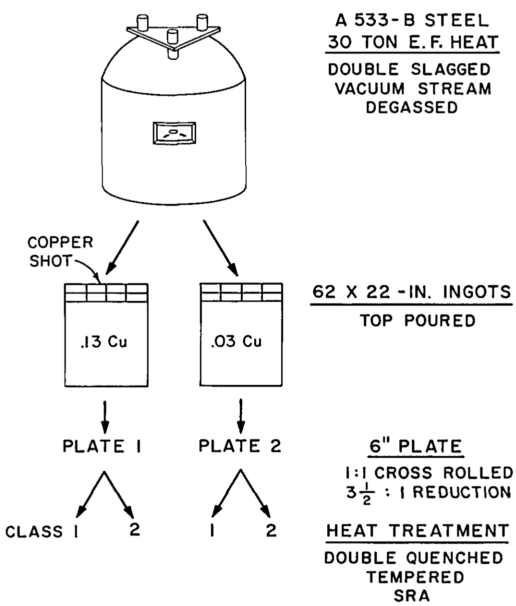

Fig. 2 - Schematic plan for processing a commercial heat of A533-B steel to study the radiation sensitivity

Table 1
Chemical Composition: Specifications and NRL Check Analyses

Determination	Chemical Composition (wt-%)												
	C	Mn	Si	Ni	Mo	Cu	P	S	As	Sb	Sn	Bi	Other
Melt purchase Specifications													
Ladle	0.25/max	1.15/1.50	0.15/0.30	0.40/0.70	0.45/0.60	0.08/max	0.007/max	0.007/max	0.01*/max	0.01*/max	0.02*/max	0.02*/max	LAP/max
Check	—	1.10/1.55	0.13/0.32	0.37/0.73	0.41/0.64	0.10/max	0.010/max	†	0.01*/max	0.01*/max	0.02*/max	0.02*/max	—
Ingot 1 (Av of Plates A and B)	0.17	1.22	0.19	0.58	0.50	0.03	0.008	0.008	<0.03	<0.01	0.02	<0.005 (0.010-0.012 Al‡)	0.02 V 0.015 Al
Ingot 2 (Av of Plates A and B)	0.17	1.21	0.20	0.56	0.50	0.13§	0.008	0.007	<0.03	<0.01	<0.02	<0.005 (0.010-0.013 Al‡)	0.02 V 0.015 Al

*As + Sb + Sn + Bi $\leq$ 0.05 max.
†P + S $\leq$ 0.022 max.
‡Total aluminum by spectrographic analysis (Courtesy Lukens Steel).
§Copper added to ingot 1 during pour.

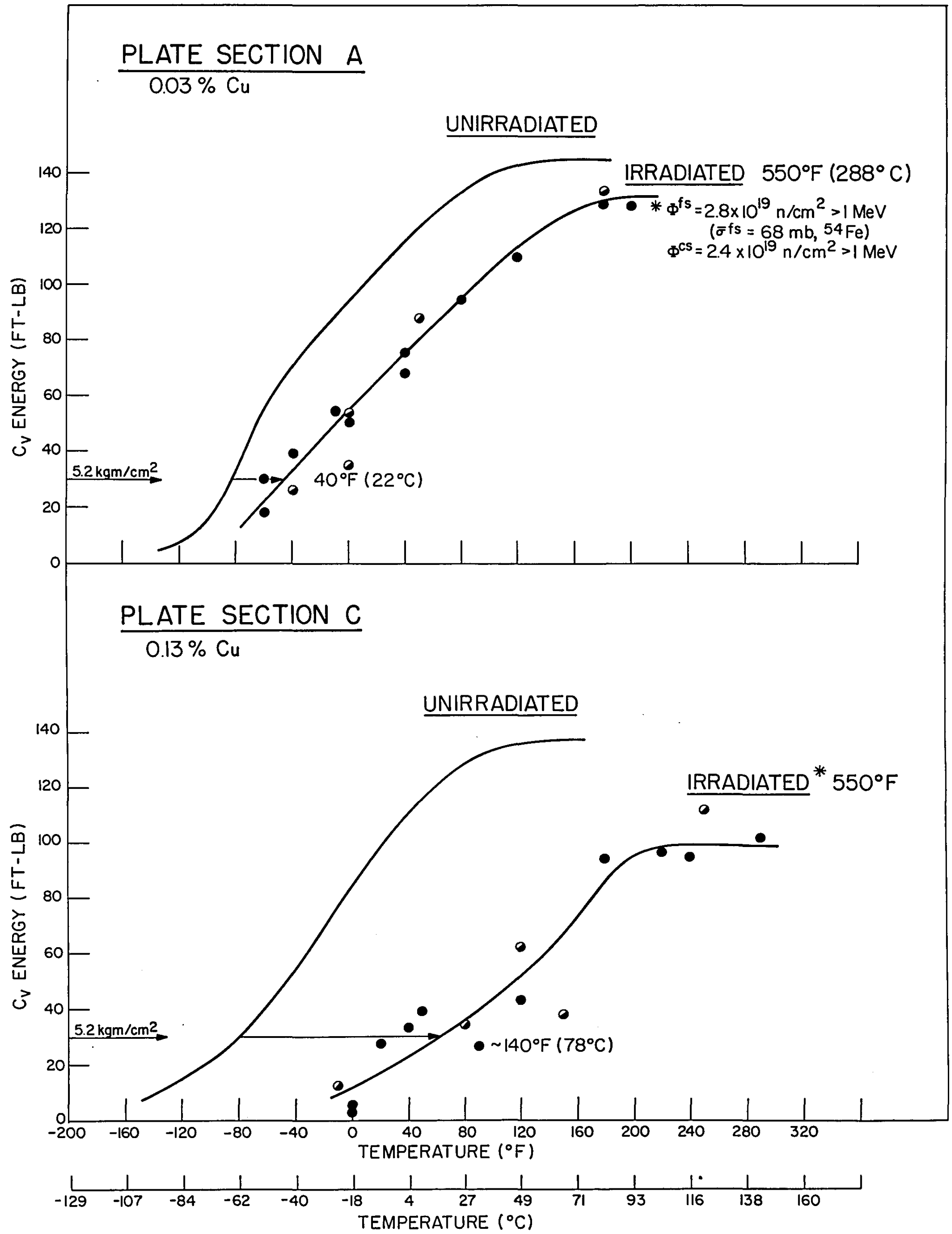

Fig. 3 - Transition temperature characteristics of A533-B demonstration heat in which the residual element content was controlled. The low sensitivity to radiation embrittlement exhibited by the low-copper (0.03 wt-%) plate is modified by increased copper (0.13 wt-%) content.

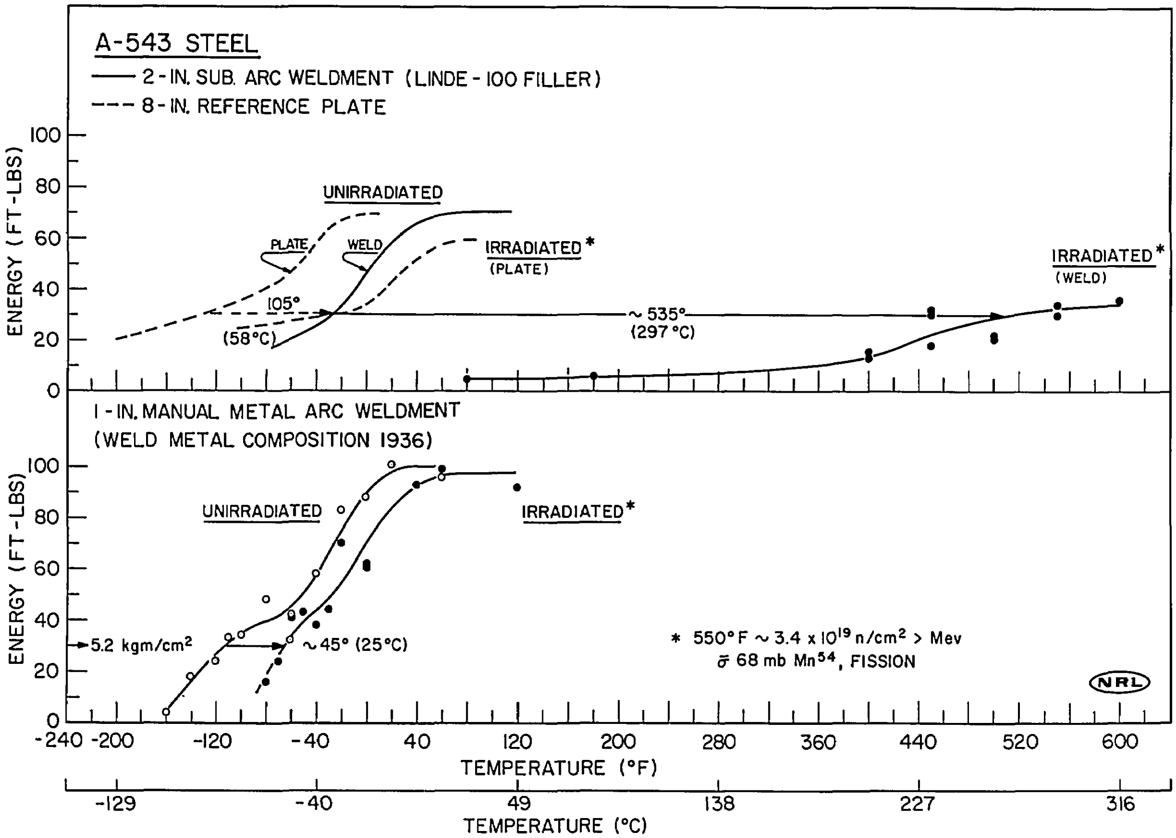

Fig. 4 - Relative radiation resistance of commercial versus experimental weld compositions and reference plate after irradiation at 550°F (288°C)

cooperation with The Babcock and Wilcox Company (5). Nine experimental welds were prepared with a base wire composition of 2-1/4 Cr - 1 Mo - 0.20 Si and 0.10 C. The copper content of these welds involved two ranges, <0.05% and 0.21 to 0.28%; all were low in phosphorus. Additional variations in weld composition included nickel and manganese. The results are summarized in Fig. 5. Analysis of the observed increases in transition temperature (ΔTT) following irradiation at 550°F permitted the establishment of the equation:

$$\Delta TT\ (^\circ F) = -118 + 14{,}800\%\ P + 990\%\ Cu. \tag{1}$$

Again, successful control of copper and phosphorus was the key to reduced radiation embrittlement in these materials. Weld studies are now in the stage of irradiation of full-scale weld samples to validate the laboratory-scale efforts described; initial results are favorable.

The attempt to isolate the mechanism by which copper and phosphorus cause increased embrittlement sensitivity emphasized the following facts. First, a comparison of the Charpy-V transition temperature shift after irradiation at 250°F (120°C) with the more important conditions observed at 550°F (288°C) (the usual service temperature) indicated that variations in residual element content produce no significant change in the response of these steels when irradiated at the lower temperature. This can be seen from an experimental investigation of phosphorus content effects (6), which shows a

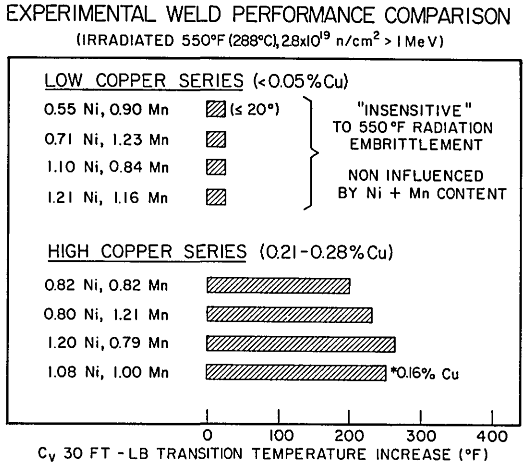

Fig. 5 - Summary of observed radiation embrittlement resistance of the weld series. Transition temperature behavior is divided by low versus high copper content.

comparable shift in transition temperature, 130°F (72°C) versus 160°F (89°C) for low phosphorus (<0.005%) and high phosphorus (0.030%) specimens irradiated at 250°F (120°C). After irradiation to the same fluence at 550°F (288°C), the low-phosphorus heat showed zero shift and the high-phosphorus heat showed a shift of 80°F (44°C).

Another feature of interest is the thermal aging stability of the heats containing residual elements. Potapovs and Hawthorne (2) aged the copper-bearing heats 75 days at 550°F (288°C) and observed no deleterious shift in the transition temperature. They also aged the phosphorus-bearing heats 45 days at 550°F with no shift in transition temperature.

Thus, the results of the applied research studies described briefly here have important implications to the planning of fundamental mechanism studies and to the modeling of projected mechanisms. The results of the fundamental studies are described below.

POSSIBLE MODELS FOR EMBRITTLEMENT MECHANISM

Since embrittlement is accentuated in steels containing relatively high levels of copper and phosphorus when exposed at 550°F (288°C), three models for the embrittlement mechanism deserve consideration. These three, temper embrittlement, irradiation-enhanced diffusivity, and enhanced nucleation of defect aggregates, are discussed below.

Restaino and McMahon (7) developed a model which has proven highly successful in explaining temper embrittlement in steels in the range 662° to 1112°F (350°-600°C). Since this model involves trace amounts of antimony, arsenic, tin, and phosphorus, its applicability to the present case can reasonably be considered. The model briefly suggests that trace elements segregate at austenite grain boundaries and are retained near the prior austenite boundaries during quenching. They segregate at the cementite-ferrite interface during tempering between 662° to 1112°F (350°-600°C), but diffuse away from the interface above 1112°F (600°C). Embrittlement results from lowering the cohesive energy of the cementite-ferrite interface to the point where the shear produced by slip bands impinging on the cementite particles causes the interface to rupture.

The NRL irradiations were conducted at 550°F (288°C), just below the range for the temper embrittlement phenomena, so in view of the long times involved, the effect of phosphorus may be explained by this mechanism. However, as previously noted, thermal aging studies for periods up to 45 days cause no degradation in the fracture properties of the experimental alloys containing either phosphorus or copper. This is considered sufficient evidence to rule out the possibility that the temper embrittlement mechanism is likely in the present situation.

The second model is based on an enhancement of diffusivity of the trace elements as a result of the increased vacancy concentration during irradiation. The increased diffusivity would permit the trace elements to migrate to grain boundaries or precipitate at interfaces where they could cause embrittlement. As was previously noted, the irradiation temperature is important in the interpretation of this phenomenon because the effect of residual elements is obvious only in experiments with irradiation temperatures around 550°F (288°C). This temperature is near the point where a major recovery stage occurs during postirradiation annealing of irradiated iron (8). Recent quenching experiments on iron (9) show that long-range vacancy migration can take place below 550°F (288°C), thus providing conditions for vacancy migration to the solute atoms.

The feasibility of the irradiation-enhanced diffusivity mechanism was qualitatively examined by comparing the diffusivity of copper in iron at 288°C with the distance such a copper atom could migrate by random walk migration. Rothman et al. (10), using tracer diffusion methods to study the diffusion of copper in iron, found the diffusivity to be very close to that for the self-diffusion of iron near the α-γ transformation. Extrapolation of the data to 288°C indicates a diffusivity of about 1.5×10^{-22} cm^1/sec. A calculation of the diffusivity from self-diffusion values for iron using an activation energy of 47.1 kcal per mole and a D_0 of 0.02 yields a diffusivity of 1.3×10^{-20} at the same temperature. Assuming an irradiation time of 6 weeks, random walk migration distances of about 5 to 50 Å are calculated for these diffusivities. Assuming diffusion over a distance of approximately 1000 Å would be required for copper atoms randomly distributed in the matrix to reach a close sink, an increase in diffusivity by a factor of 10^3 or 10^4 would be needed to make the mechanism feasible. The vacancy concentration may be increased enough during irradiation to supply this enhanced diffusivity, so that to eliminate the possibility of this mechanism the fracture surface had to be experimentally examined to determine if segregation of copper or phosphorus had produced an embrittled interface.

A third model, and the one considered most likely, is the formation of a stable copper-vacancy defect which modifies the nucleation of defect aggregates so as to increase the yield strength of the material containing residual elements and thus, in turn, increase the transition temperature. It is a well-known fact (11) that the defect aggregates in the form of clusters of interstitials or vacancies, or dislocation loops of interstitials or vacancies, form barriers to the motion of dislocations, thus hardening the irradiated material in a manner analogous to the precipitation hardening mechanism proposed by Orowan (12). The increase in the yield strength resulting from the presence of defect aggregates has been shown to be temperature independent in an irradiated iron (13). This temperature-independent increase in yield stress can in turn be used to explain the shift in transition temperature as shown schematically in Fig. 6. If the fracture stress is assumed to be roughly temperature independent and the intersection of the fracture stress curve and the flow stress curve is taken as the ductile-to-brittle transition temperature for the unflawed condition, an increase in flow stress produced by irradiation can be shown to shift the point at which the fracture stress and flow stress curves intersect and increase the ductile-to-brittle transition temperature.

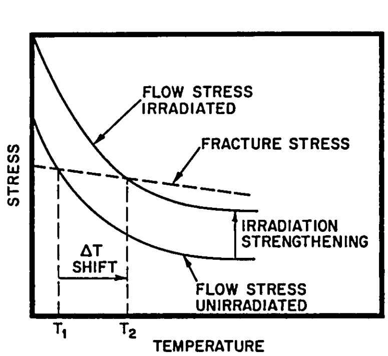

Fig. 6 - Schematic diagram illustrating how irradiation strengthening produces a shift in transition temperature

By increasing the irradiation temperature, radiation strengthening becomes less as dynamic recovery begins to take place, i.e., some damage anneals out while more is formed. At an irradiation temperature of 550°F (288°C), almost all damage anneals out in the materials low in residual elements; hence, very little shift in transition temperature occurs in these materials. The steels high in copper and phosphorus do not show complete dynamic recovery so it is postulated that the copper or phosphorus atoms are interacting with the defects produced during irradiation to form some type of stable defect.

Irradiations at 250°F (120°C) or lower, where only interstitials are mobile, do not show any transition temperature variations related to the presence of residual elements, so interstitials are not the species interacting with the residual elements. Vacancies, on the other hand, are known to undergo long-range migration at 392°F (200°C) and up (9). The interaction of copper and phosphorus with vacancies to form stable defects which do not undergo dynamic recovery during irradiation at 550°F (288°C) emerges as the most likely model for explaining the effect of these elements on enhanced irradiation sensitivity.

The confirmation of this model depends on the verification of several experimental facts. First, it must be shown that fracture is not occurring by intergranular failure which might result from segregation of these impurities at an interface. A very sensitive technique must be used to scan the fracture surface and confirm that no segregation has occurred. Another point which should be verified is that the yield strength in the specimens containing residual elements was higher than the yield strength in the low residual samples after irradiation at 550°F (288°C). Finally, a difference should be shown to exist in the defect aggregates of samples containing residual elements and those low in residual elements. This is a difficult problem in that even pure iron irradiated at 140°F (60°C) is known to show visible defects only above fluences of about 8×10^{19} (14). Therefore, irradiation to much higher fluences would be necessary to be able to observe changes in defect microstructure after irradiation at 550°F (288°C).

EXPERIMENTAL INVESTIGATION OF MECHANISM OF RESIDUAL ELEMENT EMBRITTLEMENT

A number of experimental techniques have been used to investigate various aspects of the proposed models. The first such study, which actually predates the formulation of the models, was an examination of the fracture surfaces of rebroken Charpy-V specimens using scanning microscopy to characterize the fracture mode. This effort was a cooperative program between NRL and the Battelle-Northwest Laboratory conducted under the auspices of the USAEC. In the program, NRL supplied broken Charpy specimens, which had previously demonstrated residual element sensitivity, to Battelle-Northwest where selected specimens were rebroken and the fracture surface examined by scanning electron microscopy. A complete analysis of the program has been published by Hellerich and Hunter (15), and a summary of the significant points is provided in Ref. 16.

Of the irradiated specimens examined one was a specimen of A302-B from an ASTM reference heat which had shown a substantial shift in transition temperature after irradiation at 550°F (288°C). The sample was rebroken at a temperature which was below the transition temperature after irradiation but which would have been just at the beginning of the shelf in the unirradiated specimen. Appearance of the fracture surface is shown in Fig. 7 and shows that the fracture has typical brittle cleavage facets separated by a few tear ridges. Its appearance is entirely similar to the fracture surface observed in unirradiated A302-B specimens fractured in the brittle region. Of significance is the fact that the fracture surface does not appear to follow any grain boundary or

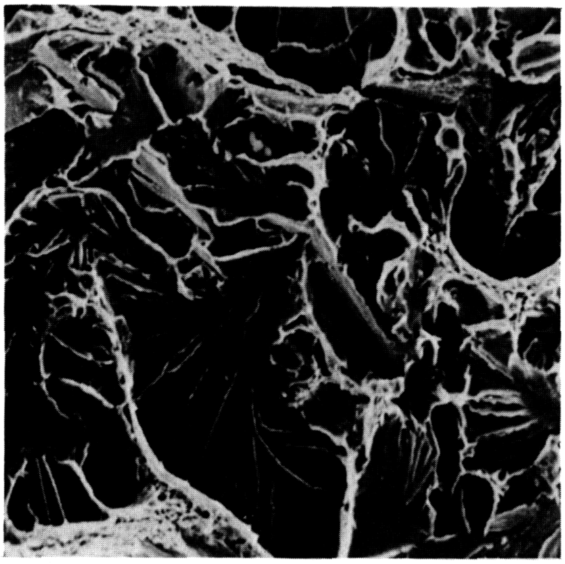

Fig. 7 - A scanning electron micrograph typical of impact fracture in A302-B steel irradiated at 550°F (288°C) to a fluence of 3.1×10^{19} n/cm^2 > 1 MeV. The well-defined cleavage facets separated by regions of plastic tearing are very similar to those of unirradiated samples fractured in the brittle region.

precipitate-matrix interface as would be the case if segregation and weakening had occurred at such interfaces.

Another irradiated specimen of a weldment severely embrittled by copper was examined after rebreaking the specimen at a point on the upper shelf after irradiation. This particular specimen had undergone a shift in transition temperature of 390°F (200°C), which was accompanied by a drop in shelf energy from 80 ft-lb to 40 ft-lb. The fracture surface of this sample was characteristic of that found in high-strength materials which fail by low-energy tear processes. The important fact to note in this instance again is that there was no evidence that the fracture had propagated along a weakened interface, thus confirming the belief that no segregation was occurring in these materials. Hawthorne (17) has dealt with the problem of changes in shelf energy as a result of radiation hardening, and the phenomena is well explained within the general trend of lower shelf energies as the yield strength increases. These changes are most easily characterized on the RAD diagram developed by Pellini (18).

Another examination of the fracture surfaces using Aüger electron spectroscopy was conducted in a cooperative effort with D. F. Stein, University of Minnesota. The Aüger spectroscopy technique has been shown to be a very sensitive technique for detecting segregation of trace elements at surfaces (19). The Aüger electrons are produced when the metal surface is bombarded with an electron beam; K-shell electrons are displaced by the incident electrons. Subsequent rearrangements occur as electrons from higher levels drop into the vacant K-shell hole, resulting finally in the ejection of an electron from one of the upper energy levels with a discrete energy characteristic of the difference in electron energy levels of the atoms of the elements from which it was ejected. This energy is characteristically in the range of 2 to 3000 kilovolts so that only electrons within about 10 Å of the surface are capable of escaping from the surface. The technique thus provides a very sensitive probe for the analysis of segregation of trace elements to a surface. Sensitivity to the elements varies but is estimated to be about 0.1 to 0.01% for phosphorus and 1 to 5% for copper in the surface layers. Absorption of even a monolayer of gas is sufficient to absorb all ejected electrons so a fresh surface must be exposed in a high vacuum either by cleaving the samples in the vacuum or by sputtering a few layers of atoms off the surface.

In the first experiment, shown in Fig. 8, irradiated samples of a low-copper heat of A302-B (0.002 wt-% copper, 0.003 wt-% phosphorus), a high-copper sample from the A533-B demonstration heat (0.13 wt-% copper and 0.008 wt-% phosphorus), and an experimental weld (0.21 wt-% copper and 0.007 wt-% phosphorus) were examined using the Aüger technique. No copper or phosphorus segregation was detected in any of the samples, thus indicating that segregation of these elements is not a major concern. Of the elements that were detected on the fracture surface, carbon and oxygen were found in all three, and nitrogen and sulfur were found in the A533-B and weld metal. Among the results which were somewhat unique was the observation of a chromium segregation to the amount of about 5% in the weld metal as compared to a nominal 2% in the base material. Also unusual was the observation of argon in all the samples and of a trace of chloride in the weld metal. Melting histories of the samples show that the low-copper A302-B heat had been melted under an argon atmosphere while the weld metal deposit had been laid down under an argon cover gas, so the presence of argon in these materials is not surprising. However, the A533-B heat had not been exposed to argon and thus posed a question as to the origin of this element at the fracture surface.

Duplicate samples of these materials in the unirradiated condition have been supplied to Professor Stein for additional analyses to resolve the origin of the argon, i.e., absorption during melting or as a transmutation product, and to further investigate the origin of the chloride and the chromium segregation in the weld metal deposit. A second series of experiments also indicated traces of argon and chlorine in A533-B samples which were

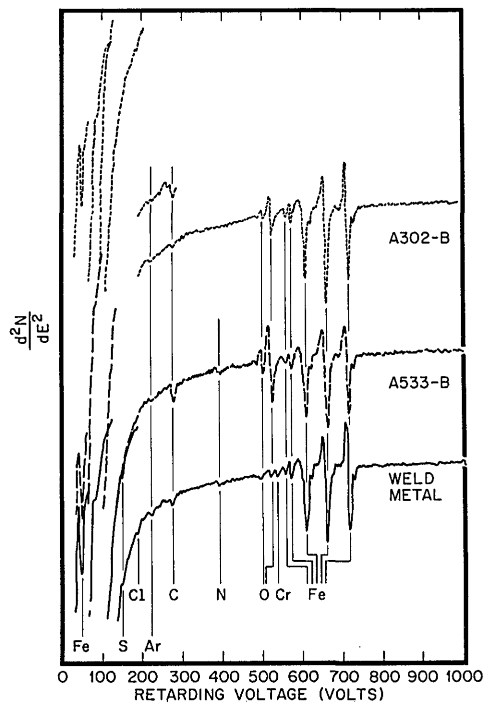

Fig. 8 - Aüger electron spectra—second derivative of number of electrons with respect to energy as a function of energy expressed as retarding voltage—for irradiated samples of A302-B (0.002 wt-% copper and 0.003 wt-% phosphorus), A533-B (0.13 wt-% copper and 0.008 wt-% phosphorus) and an experimental weld (0.21 wt-% copper and 0.007 wt-% phosphorus). Position of the major peaks are marked.

air melted by commercial steelmaking practice and in a laboratory heat of A302-B which was air melted. This established that the argon was not a transmutation product but still left questions as to the source. Reanalysis of possible interference elements showed that molybdenum normally shows two peaks at 190 volts and 220 volts, exactly the positions noted for the chlorine and argon peaks, although the intensity in pure molybdenum is reversed from that observed in these steel samples and no theoretical reason is known why such a reversal should occur. Since 0.5 wt-% molybdenum was present in both these steels but argon was not, this interpretation of the results is probably most consistent with the material's history. The weld metal which showed even stronger chlorine and argon peaks contained 1.0 wt-% molybdenum.

There was also some possibility that boron might give a peak at the same position as the chlorine peak. A spectrographic analysis of the sample detected no boron with a detection limit of 1 ppm. Chlorine cannot be determined by spectrographic analysis so its absence cannot be established. Chromium segregation was also checked by sputtering down 30 atomic layers and no changes greater than a factor-of-three change were noted in the chromium content, and due to interference from a nearby oxygen peak this cannot be considered significant.

Hardness recovery experiments were also run on samples from the special A533-B heat to ascertain if the difference in copper content could be correlated with the difference in strength and/or recovery characteristics (20). Results are shown in Fig. 9 (on material tempered at 1150°F, 620°C). Although a certain amount of scatter is present, as would be expected in hardness measurements, it is quite clear that the increase in hardness of the high-copper material is greater than that of the low-copper material after irradiation at 550°F (288°C). The shape of the recovery curves is somewhat obscured by the data scatter but does show that recovery in both materials continues after the annealing temperature exceeds the irradiation temperature. Both materials tend to recover their preirradiation value at approximately the same temperature, around 1025°F (550°C). Thus, these hardness measurements support the model, showing a greater increase in strength in the copper-containing samples. The recovery behavior is not appreciably modified, however, so the difference in behavior is more likely one of magnitude of dynamic recovery than formation of a new type of defect aggregate such as voids.

The final piece of experimental evidence pertaining to the mechanism of embrittlement by residual elements in these materials has not yet been completed. This experiment involves examination of the irradiated specimens by transmission electron microscopy. An early attempt to detect defect aggregates in irradiated pressure-vessel steels gave negative results on A302-B specimens irradiated in the foil form to a fluence of

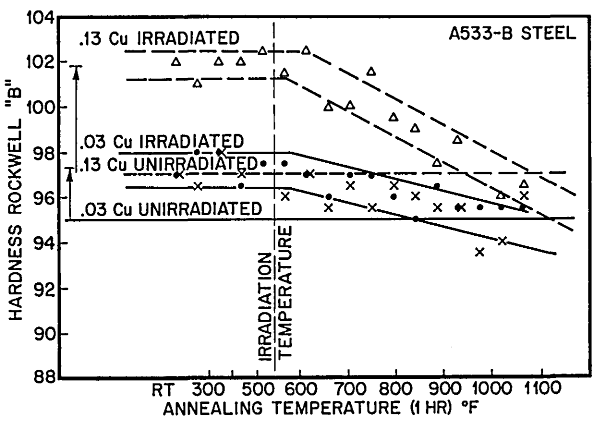

Fig. 9 - Hardness recovery curves for high and low copper heats of A533-B steel irradiated at 550°F (288°C) showing hardness trend bands in Rockwell B hardness as a function of postirradiation annealing temperature. Also shown as reference lines are hardness of unirradiated specimens and (arrows) the increase in hardness resulting from irradiation. Values for duplicate samples of irradiated 0.03 wt-% copper material are indicated by solid points and x's.

3×10^{19} n/cm^2. These specimens had been prepared in cooperation with NRL by J. V. Alger of the USS, Applied Research Laboratory. A sample of one heat containing 0.21 wt-% copper was examined after irradiation to a fluence of 3×10^{19} n/cm^2 > 1 MeV. The microstructure of this sample was typical of that expected in a tempered bainite microstructure. Dislocation density was appreciable, and carbides, probably cementite, were observed in the grain boundary along with smaller carbides, presumably aluminum carbide, dispersed through the center of the grains. No defect aggregates were observed at magnifications up to 245,000X. This result was not unexpected since, even in pure iron, defects are not observed below fluences of about 8×10^{19} n/cm^2 > 1 MeV.

After this initial experiment, it was obvious that special experiments would be needed to detect changes in the defect microstructure resulting from the presence of residual elements. Two paths were pursued. In one, pure iron specimens were doped with 0.3 at-% of selected impurities including copper and phosphorus. Compression specimens and microscopy foils were prepared from these materials for a series of irradiation experiments covering three fluences, 1×10^{19}, 8×10^{19}, and 4×10^{20} n/cm^2 > 1 MeV, at 550°F (288°C), plus two additional experiments to 8×10^{19} at temperatures of 150°F (65°C) and 650°F to 700°F (343°-390°C). In addition to these specially prepared samples, specimens representative of pressure-vessel steels were included in the same irradiation capsules. At the present time the experiment irradiated to 4×10^{20} at a temperature of 535°F (280°C) has been received from the reactor. Preliminary examinations of a foil of pure iron and a foil containing 0.3 at-% copper have been completed. Microstructural characteristics of these materials are shown in Figs. 10 and 11. The high density of defects observed in these materials is greater than any previously observed in iron. Bryner (14), for example, has reported only a low density of defects in the as-irradiated condition for fluences up to 2×10^{20} in Ferrova E iron irradiated at 140°F (60°C).

The most significant difference between the microstructures apparent in the preliminary investigation was the beginning of network formation in the copper-containing material. Network formation such as this results from the interaction of dislocation loops at high fluences and has previously been reported in molybdenum by Mastel and Brimhall (21) after fluences of 1×10^{20}. The pure iron does not contain these networks although there appears to be some clumping of defects, perhaps due to the interaction of the defect aggregate stress fields. It would thus appear that the copper-containing material has a higher density of defect aggregates. This increased density of defects could result if the binding energy between copper atoms and vacancies were sufficient to form a stable complex which would serve as the nucleus for loop formation and, in turn, lead to a higher density of defect aggregates than would be found in pure iron. An example of an analogous situation has been reported by Brown, Kelly, and Mayer (22) in the case of boron impurities in graphite. In that investigation the boron interaction with interstitials nucleated more loops with smaller radii.

The origin of an interaction between copper atoms and vacancies is not readily apparent. Although vacancies are attracted to regions of compression in the lattice such as might exist around oversize solute atoms, copper and iron atoms are approximately the same size, so such a size effect is probably not the origin of the interaction. Iron is not the only case where trace amounts of copper have been observed to modify the defect microstructure. Siegel (23) has reported that trace amounts of copper in gold, where again the size effect is negligible, increase the number of tetrahedra formed in quenched gold. Perhaps the interaction has its origin in some undetermined electronic interactions. Experimental evidence at any rate points to an interesting problem.

Although the microscopy evidence on differences in microstructure in irradiated iron containing traces of copper should be considered as tentative at this point, more detailed experiments to quantitatively analyze the microstructure and determine the

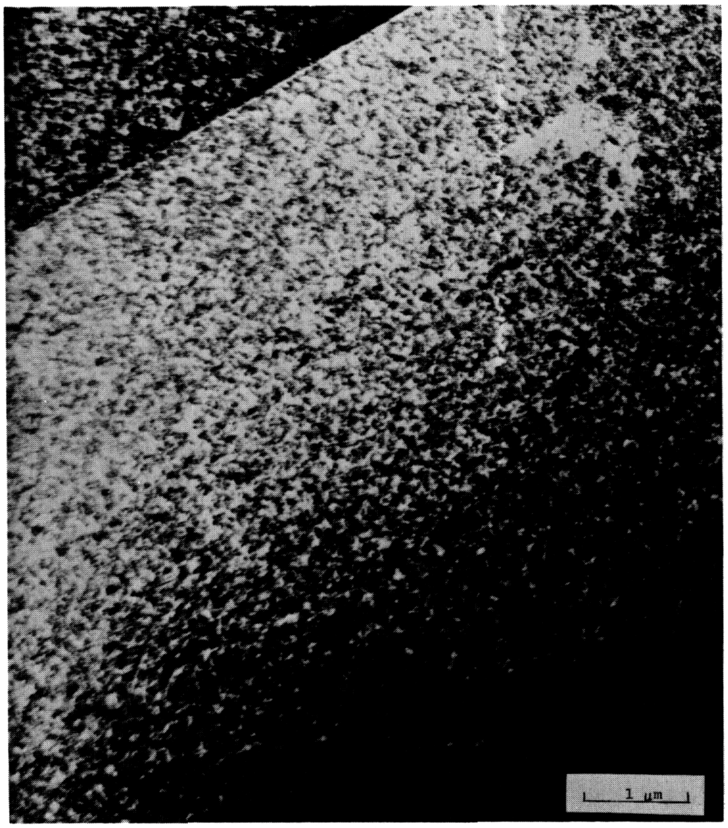

Fig. 10 - Transmission electron micrograph of defect aggregates in pure iron irradiated to a fluence of 4×10^{20} n/cm^2 > 1 MeV at 535°F (280°C). Aggregates appear as small spots which can be individually resolved at higher magnifications in thin sections. The magnification is 29,000X.

Fig. 11 - Transmission electron micrograph of microstructures in iron sample doped with 0.3 at-% copper irradiated to a fluence of 4×10^{20} n/cm^2 > 1 MeV at 535°F (280°C). Dislocation segments indicate interactions among loops have occurred in regions of very high loop density. A stigmatism inherent in magnetic materials and apparent in this 70,000X photograph makes high-resolution work difficult.

character of the loops should be completed within the next 6 months. At the present time, however, the bulk of the evidence of scanning electron fractography, Aüger electron spectroscopy, and hardness recovery and electron microscopy experiments points toward a model in which vacancies interact with the copper to form a defect aggregate which is more stable and more numerous than those ordinarily observed in the absence of copper. The increase in the number of defects and the retardation of the dynamic recovery processes, in turn, cause greater increase in irradiation hardening and hence a greater shift in transition temperature. As already demonstrated in commercial practice (4), the problem can be controlled by carefully specifying limits on the amounts of residual elements tolerable in heats for nuclear materials. It is also possible that operation of the reactor vessel at slightly higher temperatures where the extent of dynamic recovery would be greater could alleviate the problem, assuming other difficulties are not encountered.

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13. ABSTRACT

Past work on the role of residual elements (particularly copper and phosphorus) in the enhanced irradiation embrittlement observed in pressure-vessel steels irradiated at 550°F (288°C) is reviewed. Only three mechanisms for explaining the embrittlement are plausible—temper embrittlement, irradiation-enhanced diffusion to an interface, and enhanced nucleation of defect aggregates which produce hardening and embrittlement. Experiments employing scanning microscopy and Aüger spectroscopy show that the embrittlement is not produced by segregation of copper or phosphorus at an interface. Microhardness recovery experiments indicate that the embrittlement in copper-containing alloys is accompanied by greater irradiation hardening. Transmission electron micrographs of special iron alloys doped with 0.3 at-% copper show a microstructure indicative of a higher concentration of defect aggregates than pure iron irradiated under the same conditions. These aggregates are believed to be vacancy in nature because vacancies are mobile during irradiation at 550°F (288°C) and because no correlation between embrittlement and copper or phosphorus content are noted after irradiation at temperatures where vacancies are not mobile.

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