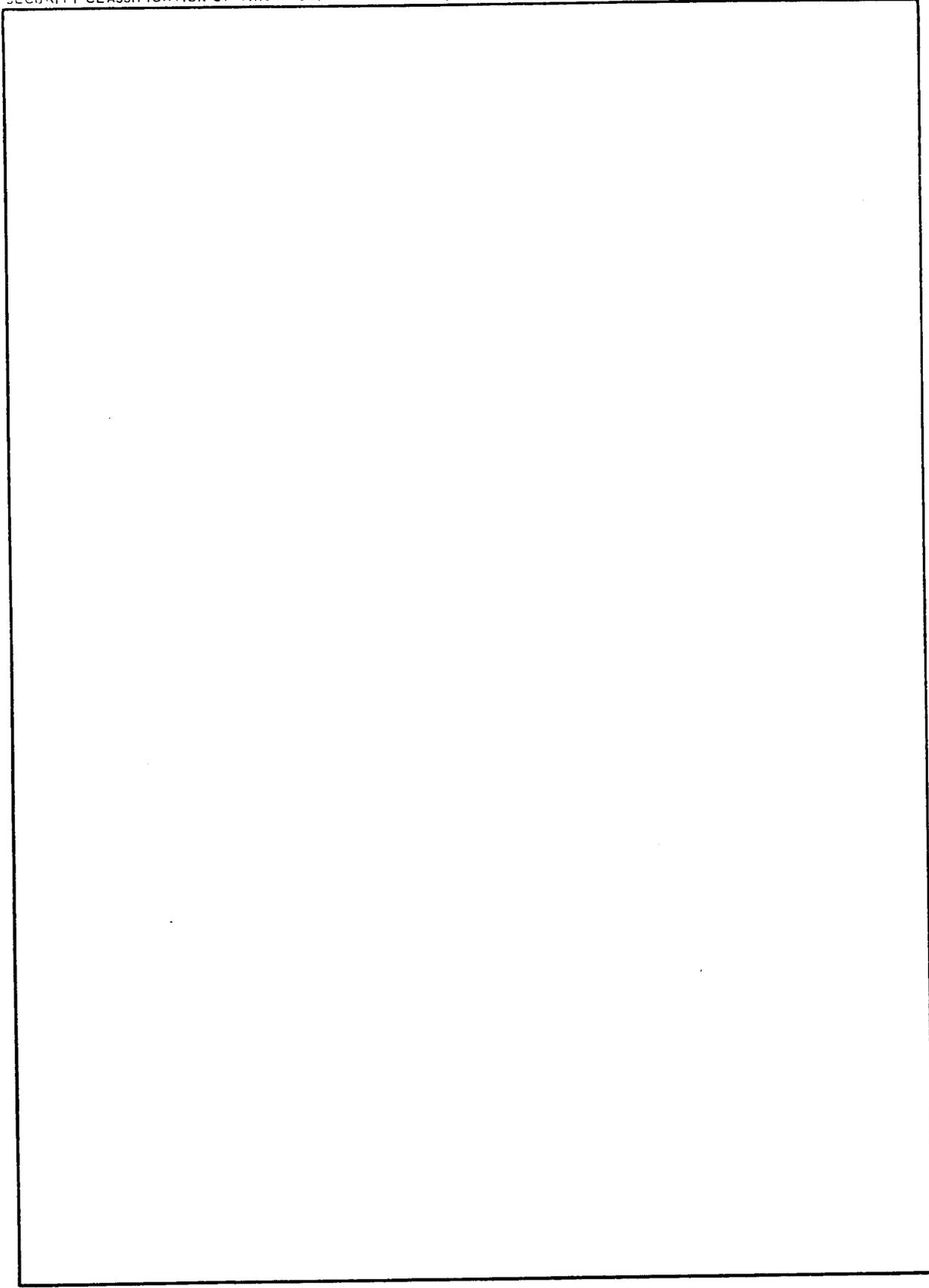


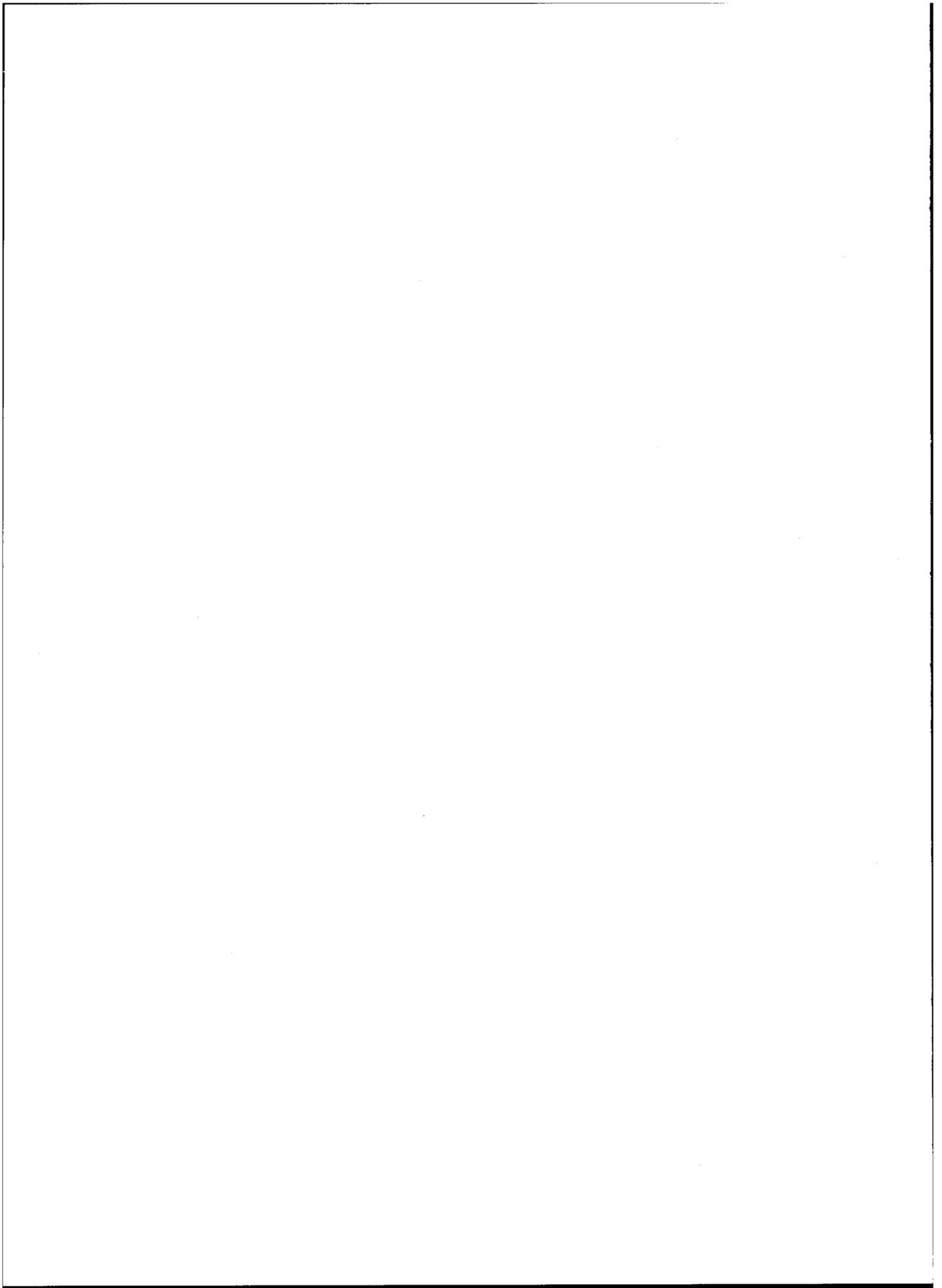
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Pressure-vessel steels and weldments containing the residual elements copper and phosphorus show a marked tendency toward embrittlement after irradiation at 290°C. Auger electron spectroscopy was used to analyze fracture surfaces of these materials to ascertain if segregation of copper and phosphorus during irradiation was responsible for the embrittlement. No evidence of segregation was found. An alternative mechanism is suggested in which the residual elements modify the defect microstructure, with attendant increases in yield strength and ductile-to-brittle transition temperature.		

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AUGER ELECTRON SPECTROSCOPY ANALYSIS OF THE FRACTURE SURFACES OF IRRADIATED PRESSURE-VESSEL STEELS

INTRODUCTION

One of the major factors of concern in the reliability of pressure-vessel steels for nuclear service is the increase in ductile-to-brittle transition temperature, or embrittlement, which results from exposure to neutron irradiation (1). An extensive program over the past six years has been in progress at the Naval Research Laboratory to characterize the factors influencing embrittlement. This research led to the correlation of the residual elements copper and phosphorus with the degree of embrittlement of pressure-vessel steels (2) and weldments (3) irradiated at 288°C (550°F), a characteristic service temperature for reactor pressure vessels. This principle was successfully transferred to commercial practice with the demonstration that embrittlement in a 30-ton heat of A533-B pressure-vessel steel could be held to one-third that in typical commercial heats through close control of the residual-element specifications (4). In spite of these clear demonstrations of the importance of residual elements in embrittlement, the details of the mechanism were not evident, thus making it difficult to generalize the results to other steels and applications.

An analysis of available evidence (5) indicated that two mechanisms were consistent with the observed behavior:

- (1) embrittlement of an interface due to impurity segregation, which would be accelerated by the vacancy superstructure during irradiation, or
- (2) a modification of the defect microstructure resulting from impurity-defect interactions, which would increase the yield strength and hence shift the ductile-to-brittle transition temperature upward.

Auger electron spectroscopy, which has been successfully applied to the detection of temper embrittlement of steels (6 - 9), was used to examine the fracture surfaces of irradiated pressure-vessel steels for possible segregation using the methods developed by Stein, Joshi, and Laforce (6); the results of this work are presented in this report. Parallel investigations of irradiation hardening and of transmission electron microscopy to examine embrittlement by mechanism (2) have been reported elsewhere (10, 11).

EXPERIMENTAL TECHNIQUE

Auger electron spectroscopy is based on the analysis of the Auger electrons emitted in radiationless transitions from excited atoms. Atoms in the solid are typically excited by a 2-to-3-kV electron beam which creates vacant sites in the electronic structure of the atom. Such excited atoms return to the ground state when electrons from higher energy states drop into the vacant site and emit the excess energy as x rays or, in the case of interest, transfer it to other electrons in a higher energy level which may be ejected from

the solid. The energies of these Auger electrons are discrete since they are determined by the difference in energy levels, e.g., an Auger electron emitted from the L shell as a result of a transition from the L shell to the K shell would have an energy equal to $E_K - 2E_L$. Different elements have unique energy levels and permissible transitions, so Auger electron spectroscopy can be used to identify the elements present (12-14). Energies of the Auger electrons used in this study are in the range of a few eV to 1000 eV, so only those electrons ejected from atoms in the first atomic layers (10 to 15 Å) will have sufficient range to escape from the surface and be collected by the detector (15). Auger spectroscopy thus provides a sensitive tool for investigating surface segregation (6 - 9, 16).

The detection and energy-analyzing system has been described in detail elsewhere (6), and it will only be noted here that d^2N/dE^2 rather than dN/dE is measured as a function of retarding voltage E , where N is the number of electrons. This method provides a better resolution of the emission peaks from the background current. The sensitivity of the technique to surface contamination dictates the use of stringent high-vacuum conditions, which require a bakeout of the system at 180°C to obtain vacuums of 10^{-9} torr or better. A fresh surface is exposed in vacuum by breaking the specimens, which are in the form of 1/8-in.-diameter rods notched near the end to a minor diameter of 0.080 in. Specimens with transition temperatures below room temperature are cooled with liquid nitrogen. The specimen holder can accommodate six specimens during a run without opening the vacuum system (6).

MATERIALS' HISTORY

The materials selected for Auger electron spectroscopy in this study were chosen on the basis of fracture behavior in previous tests where a correlation between copper content and radiation embrittlement was shown. Three classes of materials were examined in the irradiated and unirradiated conditions, an A302-B pressure-vessel steel, an A533-B pressure-vessel steel, and a weldment. Previous fracture testing (2 - 4) of these materials had shown that irradiation to fluences in the range of 3×10^{19} n/cm² > 1 MeV at 288°C produced the shifts in transition temperature presented in Table 1. Chemical analyses of these materials are given in Table 2.

Materials selected were the low-copper heat of A302-B, which showed no shift in transition temperature, and the high-copper modifications of A533-B plate and weldment, both of which showed large shifts in transition temperature. Auger specimens were machined from untested Charpy-V specimens cut from locations in the plate near fracture specimens previously tested (2 - 4). Auger specimens were irradiated at 288°C to a fluence of 3.2×10^{19} n/cm² > 1 MeV in the Union Carbide Research Reactor (UCRR) at Tuxedo, New York.

EXPERIMENTAL RESULTS

The Auger specimens were fractured at temperatures below the midpoint of the ductile-to-brittle transition temperature to expose a clean fracture surface for analysis. Optical examination showed the fracture surface to be mostly transgranular cleavage facets. Heat treatment of these materials produced a tempered bainite structure for the pressure-vessel steels and a tempered martensite structure for the weldments. Transmission electron microscopy of the pressure-vessel steels has shown about 40% of a planar section to be covered

by cementite and other precipitates, so that if segregation to these interfaces were to occur, it would be expected to cover about 40% of the surface. The weldments have fewer precipitates but are also finer grained, so the fracture surface probably includes some grain boundary.

A comparison of the Auger electron spectra from irradiated specimens of the three materials studied is shown in Fig. 1. The curves shown were all run with the same amplification factor and are displaced along the d^2N/dE^2 axis to facilitate comparison of the spectra. The major feature of interest in these results is the absence of any copper peak in the A533-B and weldment specimens which showed a large shift in transition temperature. The strongest Auger electron peaks in pure copper occur at 910 and 840 V, and, as can be seen in Fig. 1, there are no indications of peaks in that area in any of the samples.

The detection limit for copper in steel is estimated to be 1% to 5% in the surface layers analyzed. For those samples containing 0.2-wt-% Cu, a segregation of 5 to 25 times above the matrix concentration would be required to bring the concentration at embrittled interfaces, such as ferrite-cementite, to the limits of detectability. Phosphorus segregation was not detected either, although specimens were not specifically selected to investigate differences in phosphorus content. If present, a phosphorus peak should occur at 120 V. The sensitivity for phosphorus in the surface layers is approximately 0.1 wt %, which would require a segregation of 200 to 350 times to bring it within the range of detectability. Segregation of this extent is less than the 10^3 -times segregation observed for temper embrittlement by antimony (7). Phosphorus segregations of 220 times were detected in a temper-embrittled 3340 steel containing 0.016-wt-% P (8), of 300 times in a temper-embrittled 5140 steel containing 0.019-wt-% P (8), and of values ranging from 5 to 235 times in a Ni-Cr-C steel containing 0.02-wt-% P (9); a trace was even detected in a steel containing as little as 5 ppm P in the bulk concentration (9). It thus can be concluded that strong segregation of Cu or P does not take place in these irradiated alloys, but amounts less than 50 times for Cu and 350 times for phosphorus cannot be ruled out.

Table 1
Influence of 288°C Irradiation on the Shift in Transition
Temperature of Selected Pressure-Vessel Steels

Steel	ΔT_T (°C)	Fluence (10^{19} n/cm ² >1 MeV)
A302-B (2)		
38A (0.002-wt-% Cu)	0	2.3
38B (0.20-wt-% Cu)	30	2.3
A533-B (4)		
Ingot 1 (0.03-wt-% Cu)	22	2.8
Ingot 2 (0.13-wt-% Cu)	78	2.8
Weldment (3)		
N23 (0.03-wt-% Cu)	8	2.8
N42 (0.21-wt-% Cu)	108	2.8

Table 2
Composition of Auger Electron Spectroscopy Samples (wt %)

Sample Heat	Cu	P	C	Mn	S	Si	Mo	V	Al	N	O	Ni	Cr
A302-B													
38A	0.002	0.003	0.24	1.34	0.004	0.27	0.54	0.010	0.027	0.009	0.0057	—	—
38B	0.20	0.003	0.24	1.34	0.004	0.28	0.54	0.010	0.021	0.008	0.0032	—	—
A533-B													
Ingot 1	0.03	0.008	0.17	1.22	0.008	0.19	0.50	0.02	0.015	—	—	0.58	—
Ingot 2	0.13	0.008	0.17	1.21	0.007	0.20	0.50	0.02	0.015	—	—	0.56	—
Weldment													
N23	0.03	0.006	0.06	0.90	0.005	0.49	0.87	—	—	—	—	0.55	1.95
N42	0.21	0.007	0.07	0.82	0.005	0.45	0.93	0.05	—	—	—	0.82	2.04

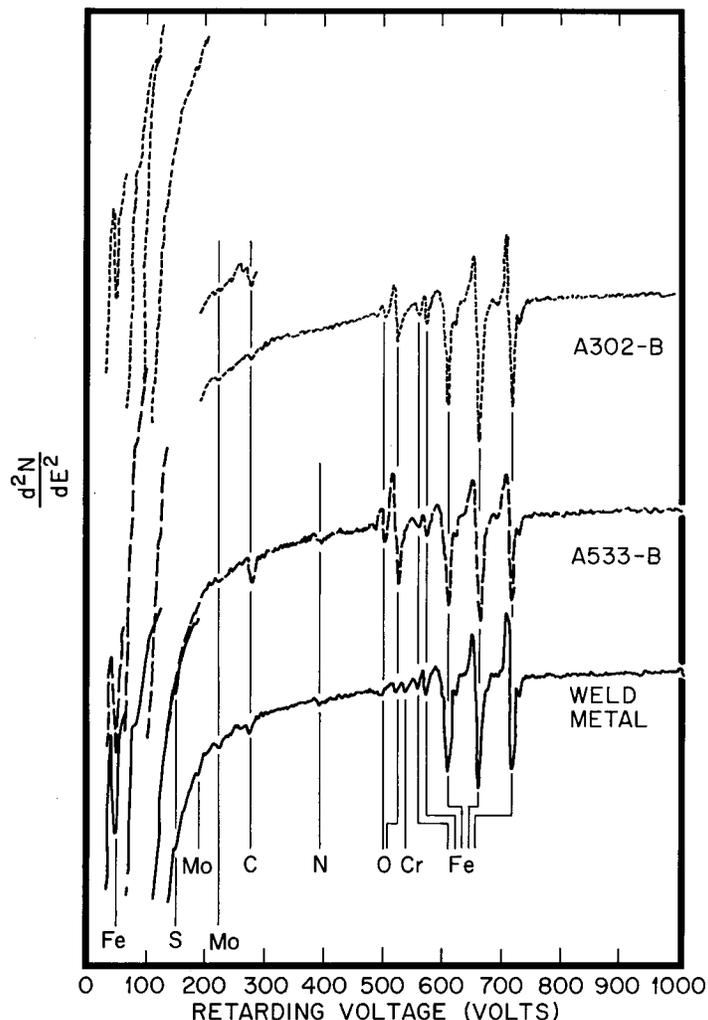


Fig. 1 — Auger electron spectra, with the second derivative of the number of electrons with respect to voltage as a function of the retarding voltage, for fracture surfaces of irradiated specimens of A302-B (0.002-wt-% Cu and 0.003-wt-% P), A533-B (0.13-wt-% Cu and 0.008-wt-% P), and an experimental weldment (0.21-wt-% Cu and 0.007-wt-% P). The positions of the major peaks are compared.

Trace elements detected on the fracture surface included carbon and oxygen on all specimens, irradiated and unirradiated, and nitrogen and sulfur in A533-B and the weldment, irradiated and unirradiated. The weldment material also showed an enrichment of chromium on the fracture surface of approximately 2.5 times (about 5%) as compared to 2% in the matrix in both irradiated and unirradiated samples. The unirradiated sample was sputtered to a depth of about 30 atomic layers in an attempt to verify chromium segregation, but interference with the adjacent oxygen peak made it impossible to determine small differences in concentration of chromium, and such a low degree of segregation could not be determined.

The most interesting result involved the identification of the two peaks at 185 and 200 V, which are labeled Mo in Fig. 1. These peaks were originally identified as chlorine or

boron at 185 V and argon at 220 V after the first run on irradiated samples. Both peaks appeared in A533-B and the weldment, but only the one at 220 V was distinguishable in A302-B. The observation of argon in the A533-B, which had been prepared by commercial air-melting practice and never exposed to argon, was surprising but conceivably could have arisen from transmutation of one of the trace impurities. Analysis of unirradiated A533-B specimens showed the same peak as well, so it was concluded the identification of the peak as argon was erroneous. A search then was made of tables of Auger transitions for other possible elements having transitions at these energies. Of the other possible elements, the most likely candidate was molybdenum, since peaks in the Auger spectra of molybdenum occur at 185 and 220 V, but the relative intensities in pure molybdenum were reversed from those observed in the present experiments. An Auger spectrum was run on a 316 stainless-steel specimen containing 2.33-wt-% molybdenum to compare the relative peak heights in this alloy with those observed in the pressure-vessel steels. A comparison of the spectra of pure molybdenum, 316 stainless steel containing 2.33-wt-% molybdenum, and the weldment containing 0.93-wt-% molybdenum is shown in Fig. 2. These results substantiate the identification of the peaks at 185 and 220 V in the pressure-vessel steels as due to molybdenum but do not eliminate the possibility that another element is also contributing to the peak at 220 V.

DISCUSSION

As previously noted in the introduction, certain residual elements in pressure-vessel steels are known to increase the sensitivity of these materials to embrittlement in nuclear environments at service temperatures around 290°C. The mechanism of embrittlement, however, has not been identified, and the present experiments are part of the effort to determine the mechanism. Analysis of the experimental evidence from fracture tests of irradiated materials (5) indicated that two mechanisms were consistent with the experimental data, one based on segregation at the fracture surface and the other based on uniform strengthening of the matrix through radiation damage. The salient experimental facts are (a) the greater shift in transition temperature for specimens irradiated at 288°C containing small amounts of copper (summarized in Table 1), and (b) the observation that a greater shift in transition temperature occurs after a 120°C irradiation, but one which is independent of the residual-element content (17). Since vacancies are mobile only at irradiation above 200°C (18), whereas self-interstitials are mobile at both irradiation temperatures, it seems likely that a vacancy interaction with the impurities is involved in the embrittlement mechanism.

The first mechanism for embrittlement would involve an enhancement of the diffusivity of copper (or phosphorus) as a result of the increase in vacancy concentration during irradiation. Copper atoms interacting with vacancies would be carried to a nearby interface, such as a grain boundary or second-phase precipitate particle acting as a vacancy sink; these atoms then would be deposited at the interface. This interface then would become embrittled and serve as a nucleation site and propagation path for the crack during failure.

The second mechanism is based on the fact that defect aggregates, such as prismatic dislocation loops or small three-dimensional clusters which form during irradiation, produce an increase in the yield stress. Such an increase in yield stress in a bcc metal will in turn raise the ductile-to-brittle transition temperature. The role of copper impurities in changing the yield strength is probably through a vacancy-copper interaction which modifies the defect microstructure. This interaction might be through heterogeneous nucleation on

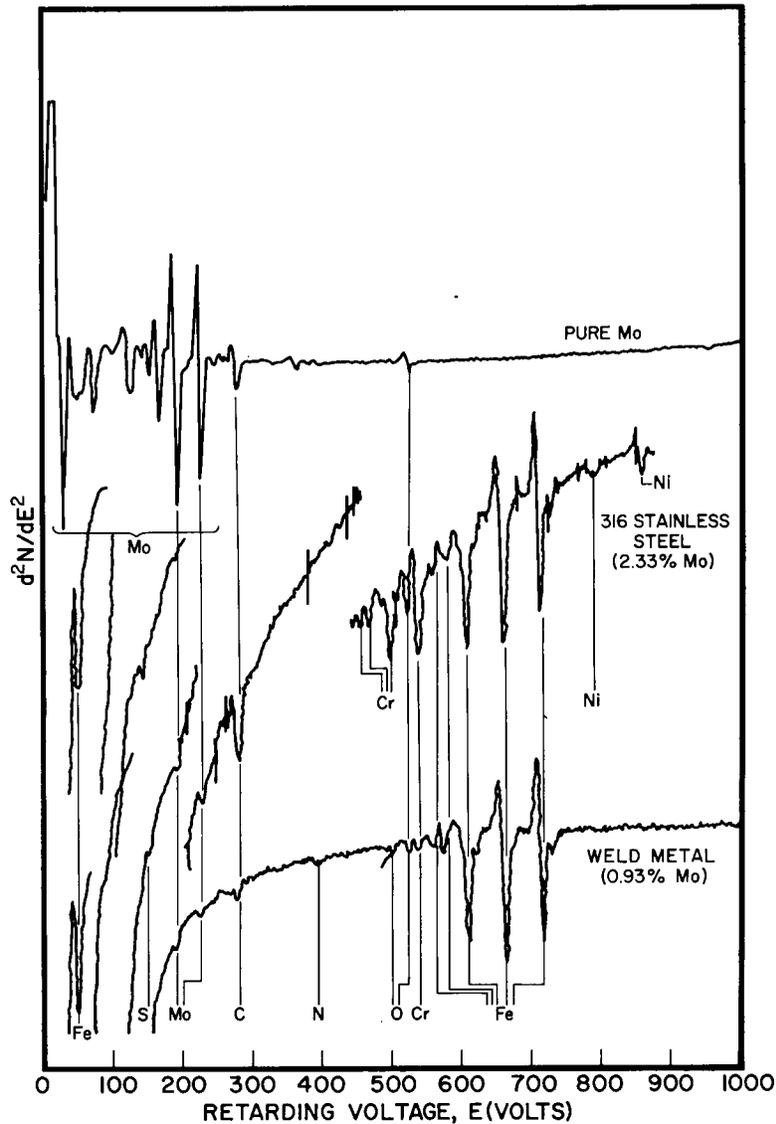


Fig. 2 — Comparison of Auger electron spectra from fracture surfaces of pure molybdenum, 316 stainless steel containing 2.33-wt-% Mo, and a weldment, showing that peaks at 185 and 220 V in the weldment are due to molybdenum content.

copper atoms or by a change in the vacancy supersaturation by vacancy trapping which could modify the homogeneous nucleation rate.

The failure to detect copper or phosphorus segregation on the fracture surface of these irradiated pressure-vessel steels is strong evidence against the first mechanism and a necessary although not sufficient support of the second mechanism. Since previous studies (6 — 9, 16) have shown that a substantial segregation of impurities or alloying elements is necessary to markedly change the transition temperature, it is most unlikely that segregation to the entire fracture path is responsible for the observed embrittlement. It might be possible that nucleation would be enhanced by segregation to a restricted region, such as

precipitate interfaces, but there is no evidence that the nucleation sites have changed during embrittlement or that the fracture is nucleation controlled. Therefore, there is no evidence in the study to support the position that embrittlement is associated with segregation, at least not for these impurity levels.

The present results are also supported by a previous study reported by Hellerich and Hunter (19) using scanning electron microscopy to examine the fracture surfaces of irradiated specimens. Their results on A302-B specimens high in residual elements and on an embrittled weldment showed the fracture surface of irradiated specimens to have the same features as unirradiated specimens broken in the brittle region. There was no evidence of grain-boundary embrittlement or failure along a precipitate-matrix interface.

Demonstration that the shift in transition temperature is correlated with an increase in yield strength has recently been confirmed in compression tests of these materials and of an iron alloy doped with 0.3-at-% copper in another study (10). Results of electron-microscopy studies also show a higher density of dislocation loops in iron doped with 0.3-at-% copper than in pure zone-refined iron after irradiation to a fluence of 4.5×10^{20} n/cm² > 1 MeV at 280°C (11).

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