NRL Report 6803

The Effect of Residual Elements on 550°F Irradiation Response of Selected Pressure Vessel Steels and Weldments

ULDIS POTAPOVS AND J. RUSSELL HAWTHORNE

Reactor Materials Branch
Metallurgy Division

November 22, 1968

NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

The effect of variable residual element contents on 550°F radiation embrittlement sensitivity of pressure vessel steels has been examined in a continuing cooperative program between the Naval Research Laboratory (NRL) and the U. S. Steel Corporation (USS), Applied Research Laboratory. Results indicate that phosphorus and copper can contribute significantly to the 550°F radiation embrittlement sensitivity of Type A302-B steel. The results also show that vanadium may have a slight adverse effect and that sulfur is neutral, although it serves to decrease the full shear energy absorption level of the steel. Nitrogen variations from ≈0.008% to 0.015% in aluminum deoxidized steel have no significant effect, while the addition of aluminum to Ni-Cr-Mo steel with a given nitrogen content may slightly promote irradiation embrittlement. The program results demonstrate that apparent insensitivity to 550°F irradiation embrittlement can be consistently achieved with laboratory heats of a nominal A302-B steel composition by maintaining the total residual element contents at a low level.

Radiation embrittlement sensitivity of weldments has been investigated in a cooperative program, between NRL and the Babcock and Wilcox Company, aimed at the development of low sensitivity weld fillers for joining Ni-Cr-Mo steel. Data from this new program again point to copper as a dominating factor in determining radiation embrittlement sensitivity, further verifying the results obtained in the NRL-USS A302-B steel investigation. Two experimental weld wire compositions with low copper contents (<0.1%) are shown to possess resistance to 550°F irradiation embrittlement equal or superior to that of A543 base plate.

PROBLEM STATUS

This is a final report on one phase of the problem; work continues on other phases.

AUTHORIZATION

NRL Prob. M01-14
Projects RR 007-01-46-5409,
USA-ERG-3-67; AEC-AT(49-5)-2110

Manuscript submitted September 9, 1968.

THE EFFECT OF RESIDUAL ELEMENTS ON 550°F IRRADIATION RESPONSE OF SELECTED PRESSURE VESSEL STEELS AND WELDMENTS

INTRODUCTION

Variable resistance to radiation embrittlement observed among different pressure vessel steels and weldments (1, 2), and even among different heats of the same steel (3, 4), has suggested that chemical composition or steel processing may be significantly influencing the material performance in nuclear service. To identify and to isolate those particular factors responsible for variable irradiation response, NRL has developed cooperative research programs with steel producers and with pressure vessel fabricators.

One investigation by NRL and the U. S. Steel Corporation (USS), Applied Research Laboratory, is examining variable sensitivity among different pressure vessel and structural steel compositions in plate form. Initial findings of this program have been reported (5). Subsequent to the first publication of findings, it was revealed (6) that residual element content can be a dominant factor determining the 550°F radiation embrittlement sensitivity of A302-B steel. In Fig. 1, a minimum content of residual elements, such as P, S, As, Sn, Sb, Cu, is seen to markedly improve the resistance of this pressure vessel steel to radiation embrittlement at a typical service temperature (≈550°F). Encouraged by these results, a second-round effort by the NRL-USS Cooperative Program was formulated and aimed at isolating those residual elements having particularly strong contributions to increased radiation sensitivity. Information generated by this second-round effort is presented in this report.

As a direct result of progress made by plate embrittlement studies, it was possible to establish a meaningful program for investigating variable radiation embrittlement sensitivity among weld metals. Initial findings of this very recent undertaking, formally identified as the NRL-Babcock and Wilcox Company Cooperative Program, are also presented in this report. Major progress toward the development of a low radiation embrittlement sensitivity weld metal for joining heavy section Ni-Cr-Mo (A543) steels is indicated.

PLATE INVESTIGATIONS: NRL-USS COOPERATIVE PROGRAM

The first objective of the continuing NRL-USS program was to determine if low sensitivity to 550°F irradiation embrittlement could be reproduced at will in a typical pressure vessel steel (A302-B) by maintaining the total residual element content at a low level. Other objectives included specific assessments of individual element contributions to embrittlement behavior, in order that steel procurement specifications could be developed limiting the contents of these elements to below some critical level.

Sulfur and phosphorus were selected for investigation because of their traditional association with steel embrittlement. Copper and vanadium, on the other hand, were chosen through metallurgical reanalysis of Ni-Cr-Mo plate and weldments having high radiation embrittlement sensitivities. For example, a 4-in. A543 steel weldment, originally prepared for ASME Code Case studies, showed a marked variation in embrittlement sensitivity between its weld metal and base plate (Fig. 2). Differences in

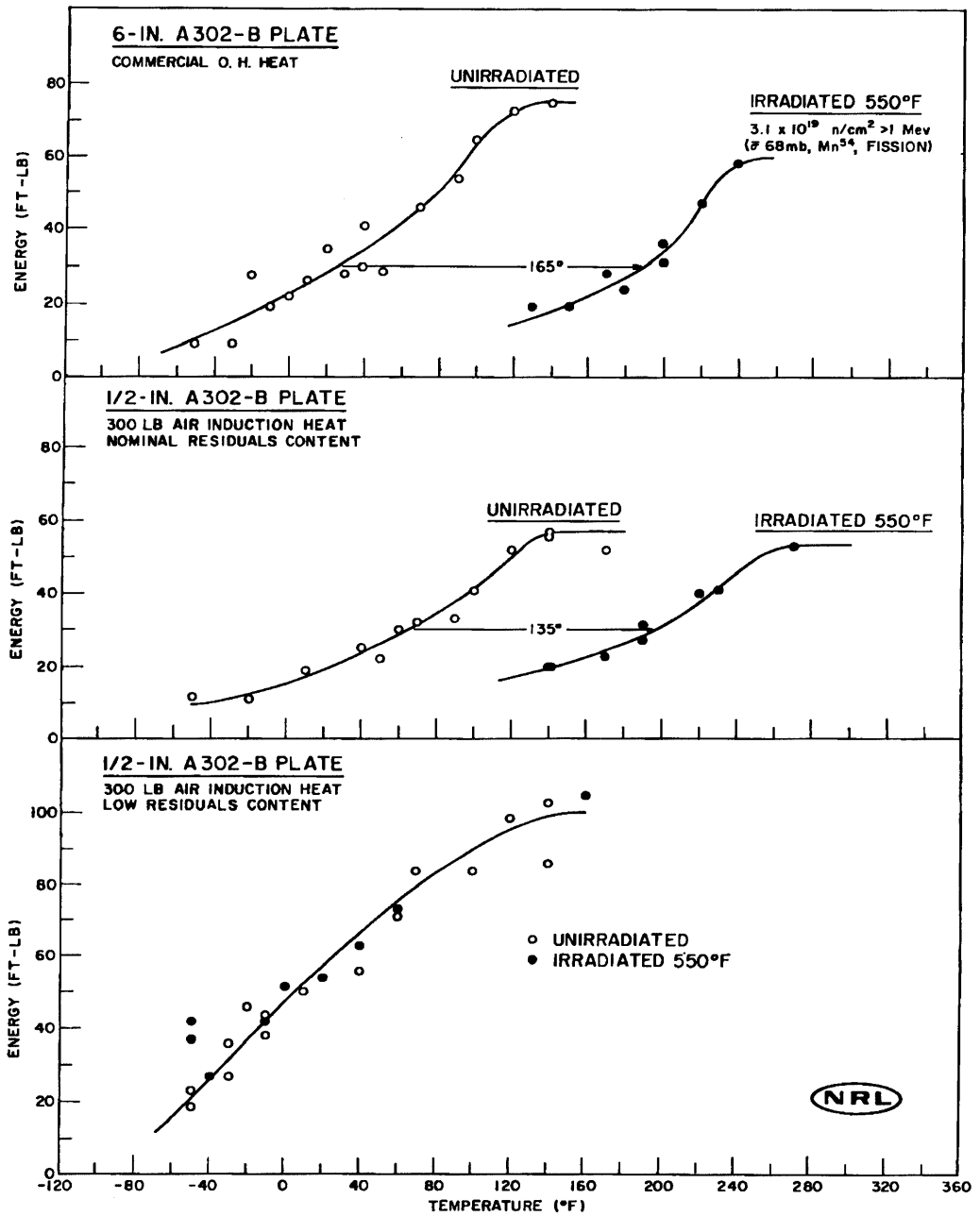


Fig. 1 - Comparison of radiation embrittlement sensitivities of one large commercial heat and two air induction heats of A302-B steel with nominal and low residual element contents based on Charpy-V notch ductility following 550° F irradiation

respective copper contents were suspected as the causative factor. Finally, nitrogen content was included in this investigation because of potential differences arising from melting furnace type (electric arc versus open hearth), melt processing (vacuum degassing), and deoxidation practices. It is noted that the possible contribution of nitrogen had been approached in the past by other investigators (7, 8) but with mixed findings.

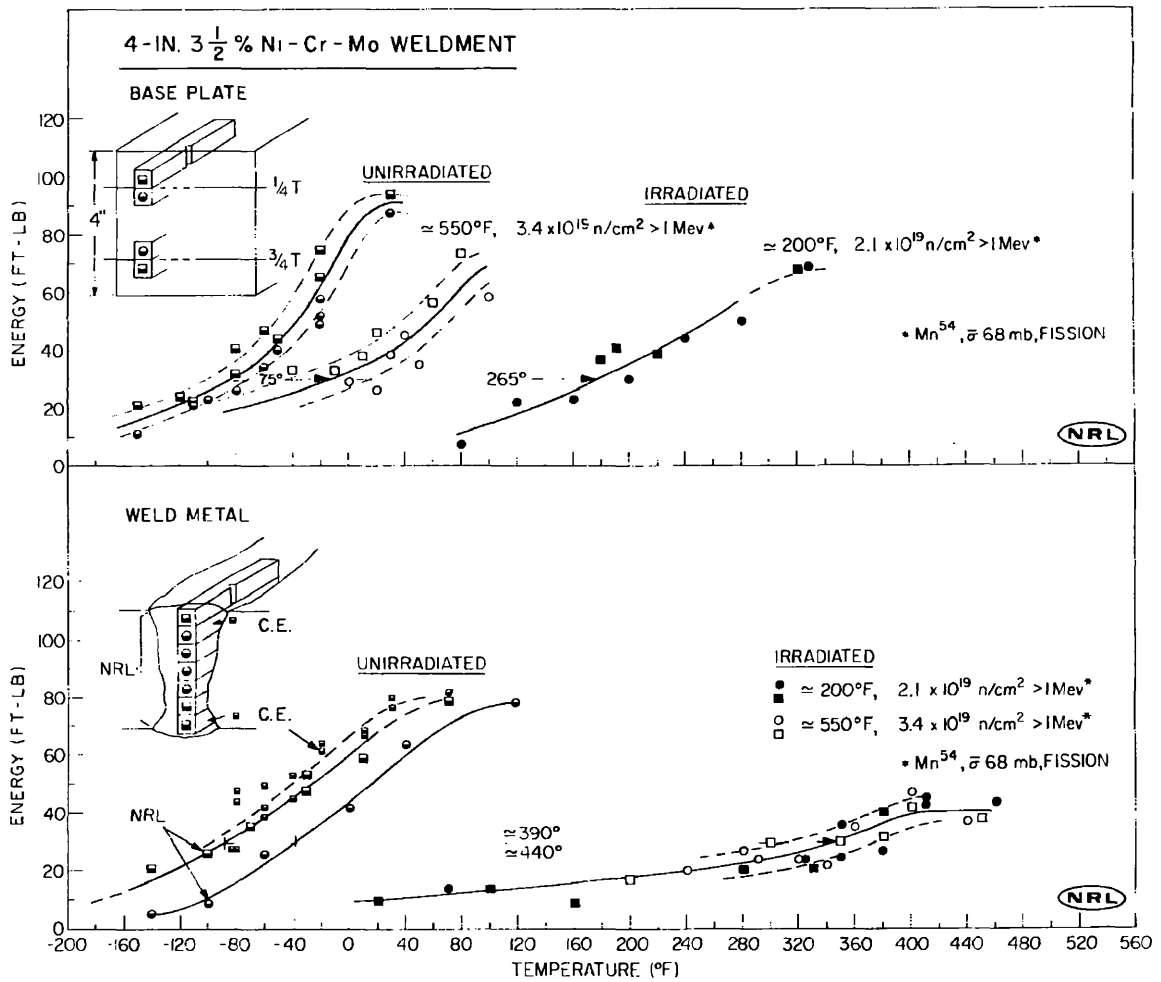


Fig. 2 – Notch ductility performance of 4-in., 3-1/2 Ni-Cr-Mo weldment after irradiation at 200° F and at 550° F

Unlike the first effort of the NRL-USS program (5), which involved low temperature (<250° F) exposures, the present investigation concentrated on 550° F irradiation conditions in the interest of developing information directly relatable to typical pressurized and boiling water reactor pressure vessel service temperatures. Specimen irradiations were performed in the Oak Ridge Low Intensity Test Reactor (LITR) using experimental assemblies and control instrumentation systems previously described (9, 10). The Charpy-V notch ductility test method was again selected as being a sensitive indicator of changes in irradiation response.

Melting and Processing of Experimental Heats

It was considered that the respective contributions of individual residual elements to radiation sensitivity could best be studied by preparing essentially pure melts of the desired base composition and selectively adding the elements under investigation to the melt, with a partial cast of the melt being made before and after each element addition. To meet total specimen requirements, a 300-lb air induction melted heat (split three ways) was used for each series of the investigation. Low residual control stock was

provided for each melt by the first 100-lb cast poured off before any test element additions were made. The second 100-lb cast contained the first test element which had been added to the remainder of the heat. Since furnace rather than ingot additions were made, the third cast contained a combination of the first and second test elements.

Five separate heats were made. Three were melted to the nominal A302-B steel composition; two were melted to Ni-Cr-Mo specifications. Chemical analyses of all individual casts produced for the study are summarized in Tables 1 and 2. The 100-lb ingots were subsequently rolled to 1/2-in. plate using 6:1 reduction and a 1:1 cross rolling ratio. The individual plates were heat treated under conditions designed to match the mechanical properties and microstructure of representative commercially produced plate. Heat treatment conditions are summarized in Tables 1 and 2. Standard Charpy-V specimens for irradiation and out-of-reactor thermal aging studies were oriented parallel to the primary plate rolling direction in all cases.

Experimental Results

Three individual reactor exposures were required to develop the intended experimental comparisons of relative radiation resistance. Experimental results for the various heats are summarized in Figs. 3 through 8. The listed neutron fluences ($n/cm^2 > 1$ Mev) were determined from iron wire neutron detectors included in each assembly and assume a fission spectrum distribution of neutrons in the exposure facilities. The fission-averaged cross section for the Fe^{54} (n, p)Mn^{54} reaction was taken as 68 mb.

Nil Sensitivity to 550° F Embrittlement With Repeat Heats - Since the first cast of each experimental A302-B steel did not contain residual element additions, a means for verifying nil sensitivity development through residual element control was provided. It can be seen in Figs. 3 through 5 that each one of the low residual element casts did prove effectively insensitive to radiation embrittlement at 550° F. The results for these three casts demonstrate further that nil sensitivity can be achieved consistently with the A302-B base composition in laboratory size heats and, possibly, in production heats with proper control.

Effects of Copper, Vanadium, and Nitrogen on Aluminum Deoxidized A302-B Base Composition - Two 300-lb heats (Y9238 and Y9239) were melted for this compositional series. Heat Y9238 was melted under an argon blanket, to maintain a relatively low nitrogen content (0.008%) comparable to open hearth practice. The second heat (Y9239) was air-induction melted, resulting in a higher nitrogen level (0.015%) more typical of electric furnace products. The test elements (Cu and V) were added to both heats in the same sequence. Chemical compositions of the six 100-lb casts are given in Table 1.

Notch ductility characteristics of these casts before and after 550° F irradiation are summarized in Table 3 and shown graphically in Figs. 3 and 4. The neutron fluence was $\approx 2.3 \times 10^{19}$ $n/cm^2 > 1$ Mev. It is apparent from these data that copper has a major influence on the radiation embrittlement sensitivity of A302-B steel. The addition of 0.2% Cu (a value typical of many pressure vessel steels*) to the low residual A302-B base composition resulted in radiation-induced transition temperature shifts of $\approx$55° F and $\approx$80° F for the low and high nitrogen melts respectively. The effect of vanadium is somewhat masked by the relatively large data scatter, but it can be concluded that the

*Addition of 0.2% Cu was based on the copper content of the 6-in. A302-B reference steel plate used in radiation effects programs as a prime correlation monitor material.

Table 1
Chemical Analysis and Heat Treatment of Controlled Chemistry Laboratory Heats of A302-B Steel and of the Commercial Reference Heat

Material Identification	Heat Treatment	Chemical Analysis (wt-%)*												
		C	Mn	P	S	Si	Mo	Cu	V	Al		N		O
										Sol.	Insol.	Ester-halogen	Total	
Heat Y9238 - Cast 1A	A†	0.23	1.40	0.003	0.004	0.28	0.52	<0.005	<0.005	0.029	0.006	--	0.005	0.0057
		0.24	1.34	0.003	0.004	0.27	0.54	0.002	0.010	0.027	0.005	0.005	0.009	--
Heat Y9238 - Cast 1B (Cu added)	A	0.23	1.38	0.003	0.004	0.28	0.52	0.21	<0.005	0.026	0.004	--	0.006	0.0032
		0.24	1.34	0.004	0.004	0.24	0.54	0.20	0.010	0.021	0.006	0.005	0.008	--
Heat Y9238 - Cast 1C (Cu and V added)	B‡	0.25	1.32	0.003	0.004	0.26	0.51	0.20	0.084	0.016	0.004	--	0.006	0.0045
		0.25	1.26	0.004	0.004	0.22	0.54	0.20	0.080	0.016	0.006	0.005	0.011	--
Heat Y9239 - Cast 1A (High N)	A	0.26	1.32	0.003	0.003	0.21	0.50	<0.005	<0.005	0.029	0.005	--	0.013	0.0059
		0.26	1.24	0.004	0.005	0.21	0.54	0.002	0.010	0.027	0.005	0.012	0.017	--
Heat Y9239 - Cast 1B (High N, Cu Added)	A	0.26	1.28	0.003	0.003	0.22	0.50	0.20	<0.005	0.025	0.005	--	0.014	0.0048
		0.25	1.25	0.004	0.005	0.20	0.53	0.20	0.010	0.021	0.005	0.011	0.017	--
Heat Y9239 - Cast 1C (High N, Cu and V added)	B	0.26	1.26	0.003	0.004	0.19	0.50	0.20	0.076	0.016	0.006	--	0.014	0.0053
		0.25	1.25	0.004	0.005	0.19	0.53	0.20	0.080	0.016	0.005	0.008	0.014	--
Heat Y9240 - Cast 1A	A	0.27	1.39	0.004	0.004	0.27	0.50	<0.005	<0.005	0.029	0.007	--	0.009	0.0051
		0.26	1.30	0.006	0.005	0.23	0.54	0.002	0.010	0.027	0.005	--	--	--
Heat Y9240 - Cast 1B (S added)	A	0.26	1.39	0.004	0.021	0.27	0.50	<0.005	<0.005	0.030	0.004	--	0.010	0.0038
		0.24	1.33	0.006	0.021	0.23	0.54	0.002	0.010	0.027	0.006	--	--	--
Heat Y9240 - Cast 1C (S and P added)	A	0.24	1.38	0.031	0.021	0.26	0.50	<0.005	<0.005	0.022	0.004	--	0.010	0.0042
		0.23	1.30	0.021	0.022	0.21	0.53	0.008	0.010	0.026	0.005	--	--	--
A302-B Reference Heat (6 in. Plate)	C§	0.24	1.34	0.011	0.023	0.23	0.51	0.20	<0.001	0.038	0.002	--	0.008	--
		0.23	1.35	0.015	0.022	0.22	0.52	0.22	<0.010	0.02	--	--	0.008	--

*First number - courtesy of supplier; Second number - NRL determination
†Heat Treatment A: Austenitized at 1650°F for 1 hour, air cooled; tempered at 1200°F for 1 hour, water quenched.
‡Heat Treatment B: Austenitized at 1650°F for 1 hour, air cooled; tempered at 1275°F for 6 hours, water quenched.
§Heat Treatment C: Austenitized at 1650°F for 2 hours, water quenched; tempered at 1200°F for 6 hours, furnace cooled to below 600°F.

Table 2
Chemical Analysis and Heat Treatment of Controlled Chemistry Laboratory Heats of 3-1/2 and 7-1/2Ni-Cr-Mo Steel

Material Identification	Heat Treatment	Chemical Analysis (wt-%)*													
											Al		N		
		C	Mn	P	S	Si	Ni	Cr	Mo	Cu	Sol.	Insol.	Ester-halogen	Total	O
Heat Y9272 - Cast 2A	A†	0.19	0.43	0.002	0.007	0.18	3.64	1.83	0.49	--	.001	--	--	0.005	0.012
		0.17	0.38	0.003	0.004	0.15	3.50	1.81	0.53	0.010	<0.001	<0.001	<0.001	0.004	--
Heat Y9272 - Cast 2B (Al added)	A	0.19	0.43	0.002	0.007	0.17	3.64	1.84	0.49	--	0.022	--	--	0.005	0.004
		0.17	0.38	0.003	0.004	0.16	3.55	1.81	0.55	0.010	0.020	0.008	0.003	0.006	--
Heat Y9272 - Cast 2C (Al and N added)	A	0.19	0.42	0.002	0.007	0.15	3.68	1.75	0.49	--	0.029	--	--	0.008	0.009
		0.18	0.36	0.003	0.003	0.18	3.50	1.72	0.55	0.008	0.021	0.015	0.006	0.008	--
Heat Y9273 - Cast 2A	B‡	0.13	0.28	≤0.002	≤0.002	0.22	7.32	0.82	0.98	--	0.001	--	--	0.004	0.015
		0.12	0.26	0.003	0.003	0.20	7.55	0.81	1.09	0.008	<0.001	<0.001	<0.001	0.004	--
Heat Y9273 - Cast 2B (Al added)	B	0.13	0.28	≤0.002	≤0.002	0.19	7.40	0.83	0.98	--	0.017	--	--	0.005	0.005
		0.13	0.27	0.003	0.003	0.19	7.55	0.87	1.09	0.004	0.018	0.009	0.004	0.005	--
Heat Y9273 - Cast 2C (Al and N added)	B	0.13	0.28	≤0.002	≤0.002	0.17	7.39	0.82	0.98	--	0.021	--	--	0.007	0.007
		0.13	0.27	0.003	0.003	0.19	7.55	0.96	1.07	0.004	0.018	0.011	0.006	0.007	--

*First number - courtesy of supplier; Second number - NRL determination
†Heat Treatment A: Austenitized at 1650°F for 2 hours, air cooled; tempered at 1200°F for 2 hours, water quenched.
‡Heat Treatment B: Austenitized at 1550°F for 2 hours, air cooled; tempered at 1150°F for 2 hours, water quenched.

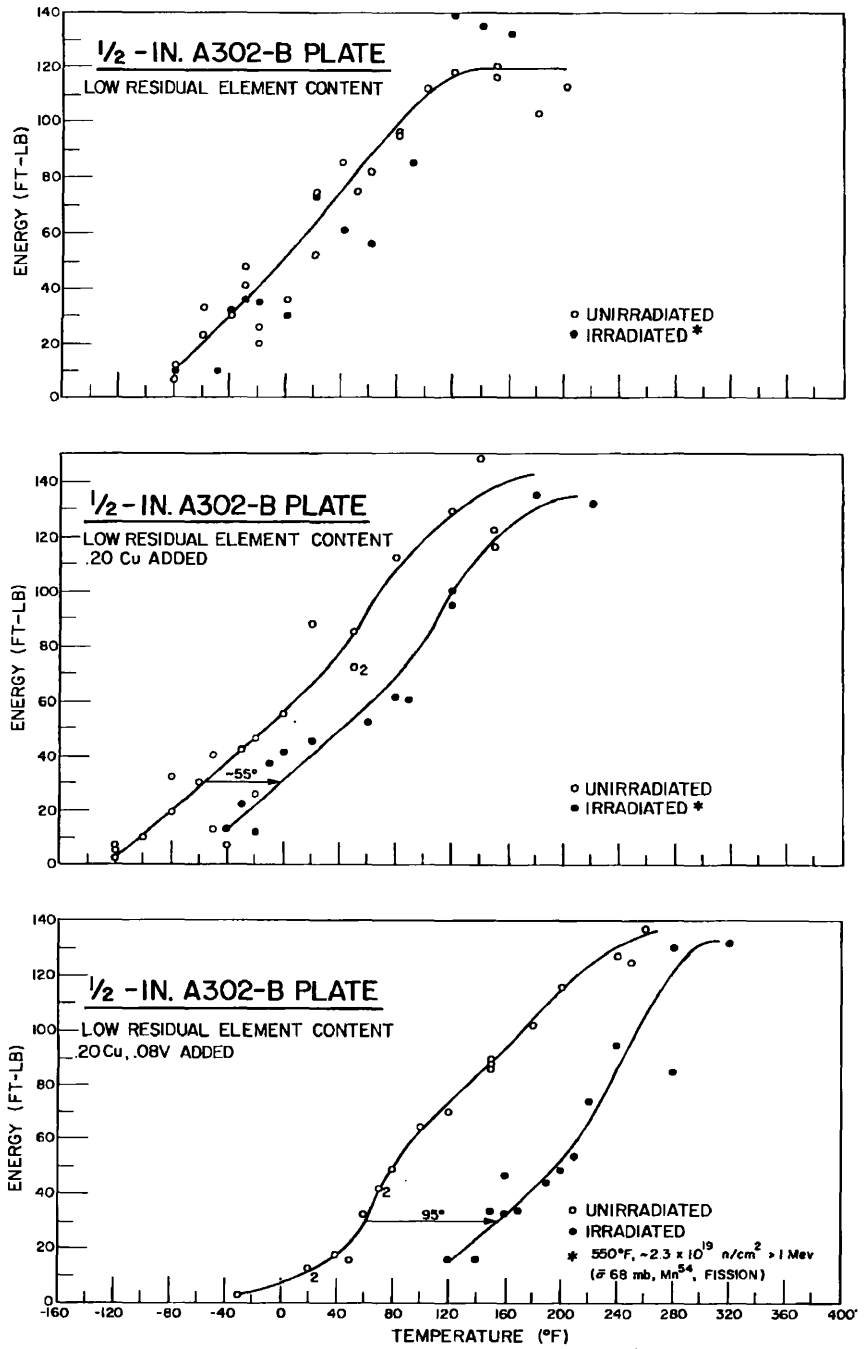


Fig. 3 - Notch ductility behavior of A302-B test plates (copper-vanadium series, low nitrogen) before and after irradiation at 550° F

(a) Heat Y9238, cast 1A

(b) Heat Y9238, cast 1B

(c) Heat Y9238, cast 1C

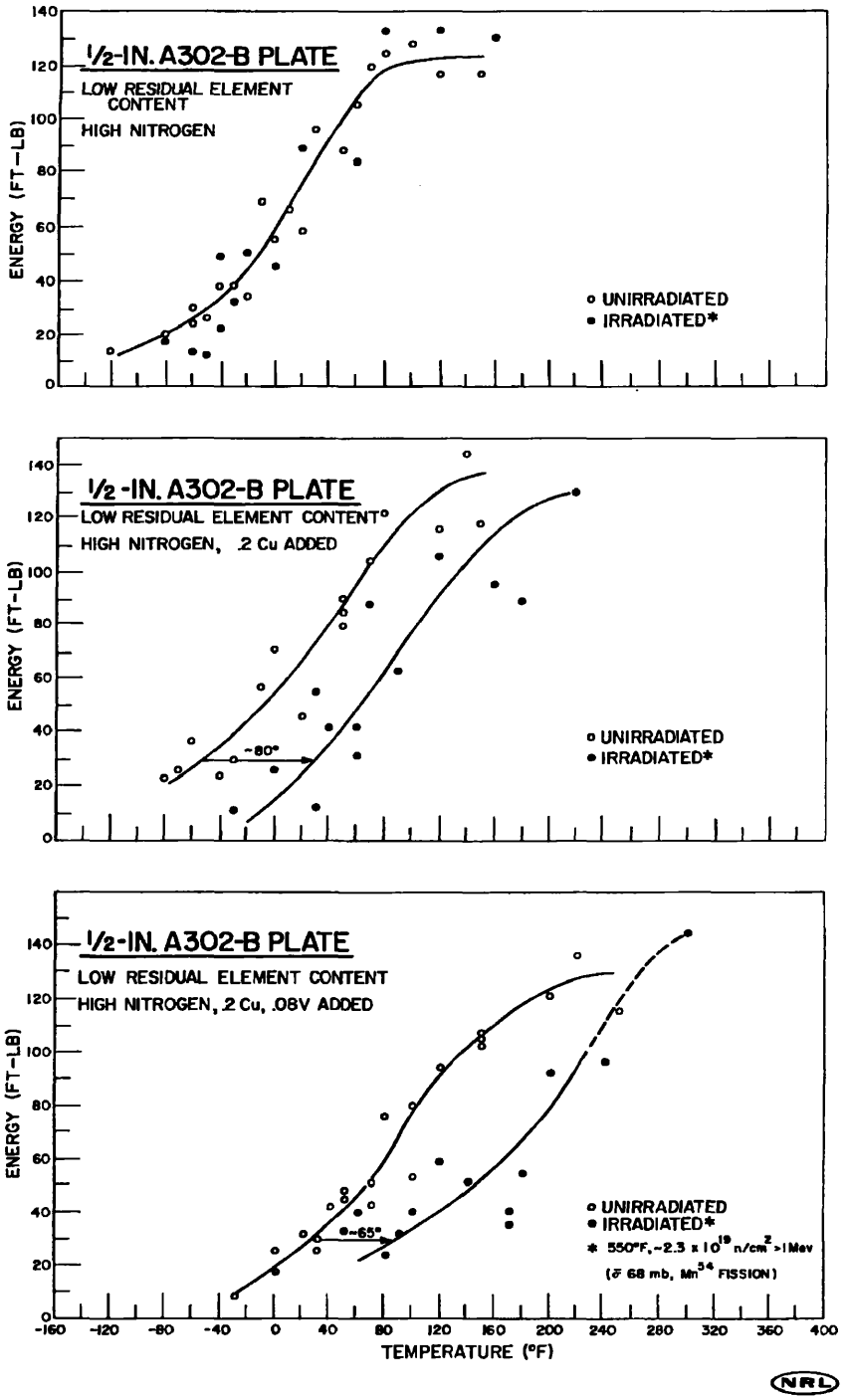


Fig. 4 - Notch ductility behavior of A302-B test plates (copper-vanadium series, high nitrogen) before and after irradiation at 550° F
(a) Heat Y9239, cast 1A
(b) Heat Y9239, cast 1B
(c) Heat Y9239, cast 1C

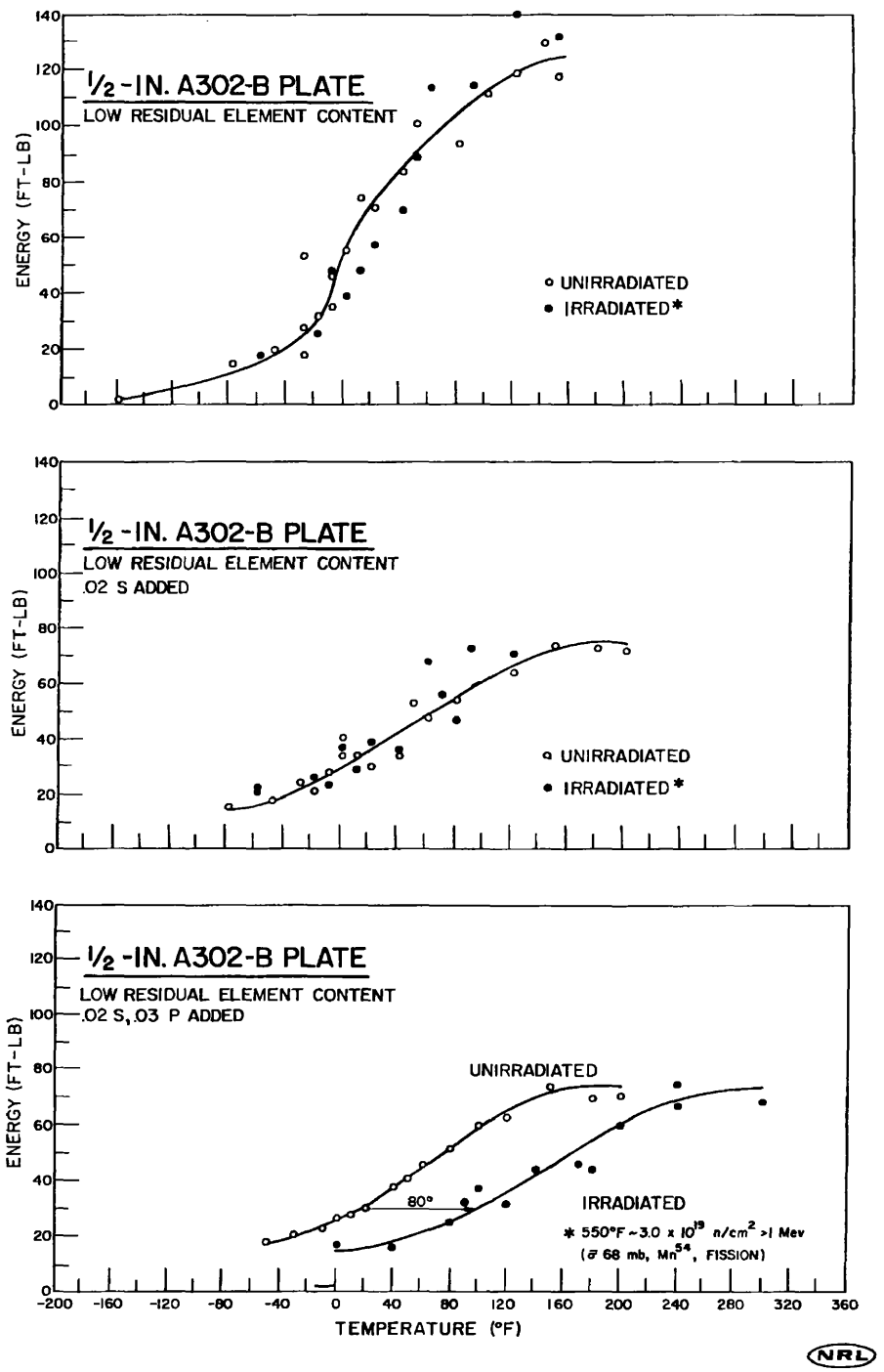


Fig. 5 - Notch ductility behavior of A302-B test plates (sulfur-phosphorus series) before and after irradiation at 550°F
(a) Heat Y9240, cast 1A
(b) Heat Y9240, cast 1B
(c) Heat Y9240, cast 1C

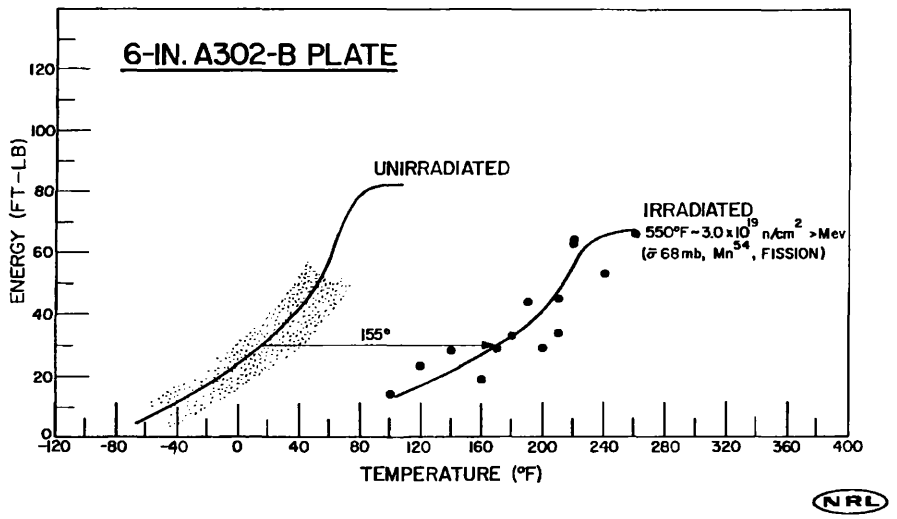


Fig. 6 - Notch ductility behavior of the A302-B reference heat before and after irradiation at 550° F

addition of ≈ 0.08% vanadium to the A302-B base composition has only a small or secondary effect on its radiation response. It should be noted that the vanadium-containing plates were tempered at a higher temperature to produce the same strength level as the non-vanadium-bearing plates. Similarly, the two nitrogen levels investigated (0.008% and 0.015%) did not produce significant differences in either unirradiated or irradiated notch ductility properties of comparable casts (Fig. 3 vs Fig. 4). This comparison suggests that nitrogen in the range investigated does not play a significant role in determining radiation embrittlement sensitivity of aluminum-deoxidized (≈ 0.03% Al), A302-B steel. Additional studies of nitrogen effects, conducted using Ni-Cr-Mo base composition, are discussed later.

Effects of Sulfur and Phosphorus on A302-B Base Composition - A single, 300-lb heat (Y9240) provided the required chemistry variations, as listed in Table 1. In considering the unirradiated notch ductility properties (Fig. 5), it can be seen that the additions of sulfur as well as of phosphorus in the quantities indicated tend to slightly increase the transition temperature of the steel. The most significant effect attributed to the sulfur addition (≈ 0.02%) was the reduction in full shear energy absorption level of the test plate (125 to 75 ft-lb). Figure 5b shows that the sulfur-containing plate, like the low residual element plate, did not experience measurable radiation embrittlement with a 550° F exposure to $\approx 3 \times 10^{19}$ n/cm^2 > 1 Mev. The data thus suggest that sulfur is not influential in determining the radiation embrittlement sensitivity level of A302-B steel at this temperature. A significant postirradiation transition temperature increase (80° F) was observed, however, when both sulfur and phosphorus were added (Fig. 5c), implying that phosphorus, or possibly phosphorus in combination with sulfur, contributes significantly to radiation embrittlement sensitivity. For comparison, Fig. 6 shows the irradiation response of a 6-in. commercial A302-B plate which was irradiated together with the specimens from heat Y9240. The 155° F shift in Charpy-V 30-ft-lb transition temperature is in good agreement with previous data on this material. Advanced studies are in progress to assess the possible cumulative effects of phosphorus, sulfur, and copper additions on irradiation response.

Table 3
Charpy-V Notch Ductility Characteristics of Controlled Chemistry Laboratory Heats of A302-B Steel and of the Commercial Reference Heat Before and After Irradiation at 550°F

Material Identification	Neutron Fluence $n/cm^2 > 1$ Mev x 10^{19}	C_v 30-ft-lb Transition Temp. (°F)			Approximate Full Shear Energy Absorption (ft-lb)	
		Unirradiated	Irradiated	ΔT	Unirradiated	Irradiated
Heat Y9238 - Cast 1A	2.3	-40	-40	0	120	120
Heat Y9238 - Cast 1B (Cu added)	2.3	-55	0	55	140	130
Heat Y9238 - Cast 1C (Cu and V added)	2.3	60	155	95	140	135
Heat Y9239 - Cast 1A (High N)	2.3	-50	-50	0	125	125
Heat Y9239 - Cast 1B (High N, Cu added)	2.3	-50	30	80	135	130
Heat Y9239 - Cast 1C (High N, Cu and V added)	2.3	25	90	65	130	140
Heat Y9240 - Cast 1A	3.0	-20	-20	0	125	125
Heat Y9240 - Cast 1B (S added)	3.0	0	0	0	75	75
Heat Y9240 - Cast 1C (S and P added)	3.0	20	100	80	75	75
A302-B Reference Heat (6-in. Plate)	3.0	15	170	155	82	67

Effects of Aluminum and Nitrogen Additions to Ni-Cr-Mo Base Compositions - The effects of consecutive aluminum and nitrogen additions on radiation sensitivity were investigated using 3-1/2Ni-Cr-Mo and 7-1/2Ni-Cr-Mo base compositions (heats Y9272 and Y9273). The chemical compositions and heat treatments of the individual casts are summarized in Table 2. The transition temperature response of the 3-1/2Ni-Cr-Mo specimens is shown in Fig. 7 (and Table 4). It can be seen that the addition of approximately 0.03% aluminum to the low residual element base composition produced a slight increase in 550°F radiation embrittlement sensitivity (60°F vs 35°F transition temperature shift). This increased sensitivity may be attributed to the aluminum addition directly or to the lowering of the free or uncombined nitrogen contents associated with this addition. A correlation showing variation in the embrittlement sensitivity of pressure vessel steels with their free nitrogen contents (determined by the extent of aluminum deoxidation) has been reported by Powers (7). The addition of excess nitrogen (Fig. 7c) had no marked effect on the transition temperature behavior, as would be expected from the previously reported copper-vanadium series (high and low nitrogen) using A302-B base composition. The behavior of 7-1/2Ni-Cr-Mo base composition subjected to the same compositional variations (Fig. 8) closely paralleled that of the 3-1/2Ni-Cr-Mo series.

Table 4

Charpy-V Notch Ductility Characteristics of Controlled Chemistry Laboratory Heats of 3-1/2 and 7-1/2Ni-Cr-Mo Steel Before and After Irradiation at 550°F to 2.2×10^{19} n/cm^2 >1 Mev

Material Identification	C_v 30-ft-lb Transition Temp. (°F)			Approximate Full Shear Energy Absorption (ft-lb)	
	Unirradiated	Irradiated	ΔT	Unirradiated	Irradiated
Heat Y9272 - Cast 2A	-235	-200	35	100	85
Heat Y9272 - Cast 2B (Al added)	-240	-180	60	120	115
Heat Y9272 - Cast 2C (Al and N added)	-220	-160	60	105	105
Heat Y9273 - Cast 2A	-345*	-315*	≈30	80	70
Heat Y9273 - Cast 2B (Al added)	-370*	-310*	≈60	105	95
Heat Y9273 - Cast 2C (Al and N added)	-370*	-325*	≈45	95	85

*Extrapolated values.

Metallographic and Thermal Aging Studies - Routine metallographic examinations were conducted on all laboratory casts. Typical microstructures are shown in Figs. 9 and 10. Figure 9 illustrates the similarity of structures of the three casts of heat Y9239 (high nitrogen, copper-vanadium series). The structures shown are identified as tempered bainite and free ferrite. The higher tempering temperature of the vanadium bearing cast 1c is evidenced by structure spheroidization. Microstructures of the low nitrogen heat (Y9238) were found very similar. Photomicrographs of the sulfur-phosphorus series (Y9240) are presented in Fig. 10. The microstructures do not differ significantly from those shown in the previous figure (Cu-V series), with the exception that manganese sulfide inclusions are seen in casts 1B and 1C. On the other hand, the Ni-Cr-Mo plate microstructures (heats Y9272 and Y9273) consisted largely of tempered martensite, typical of this class of material.

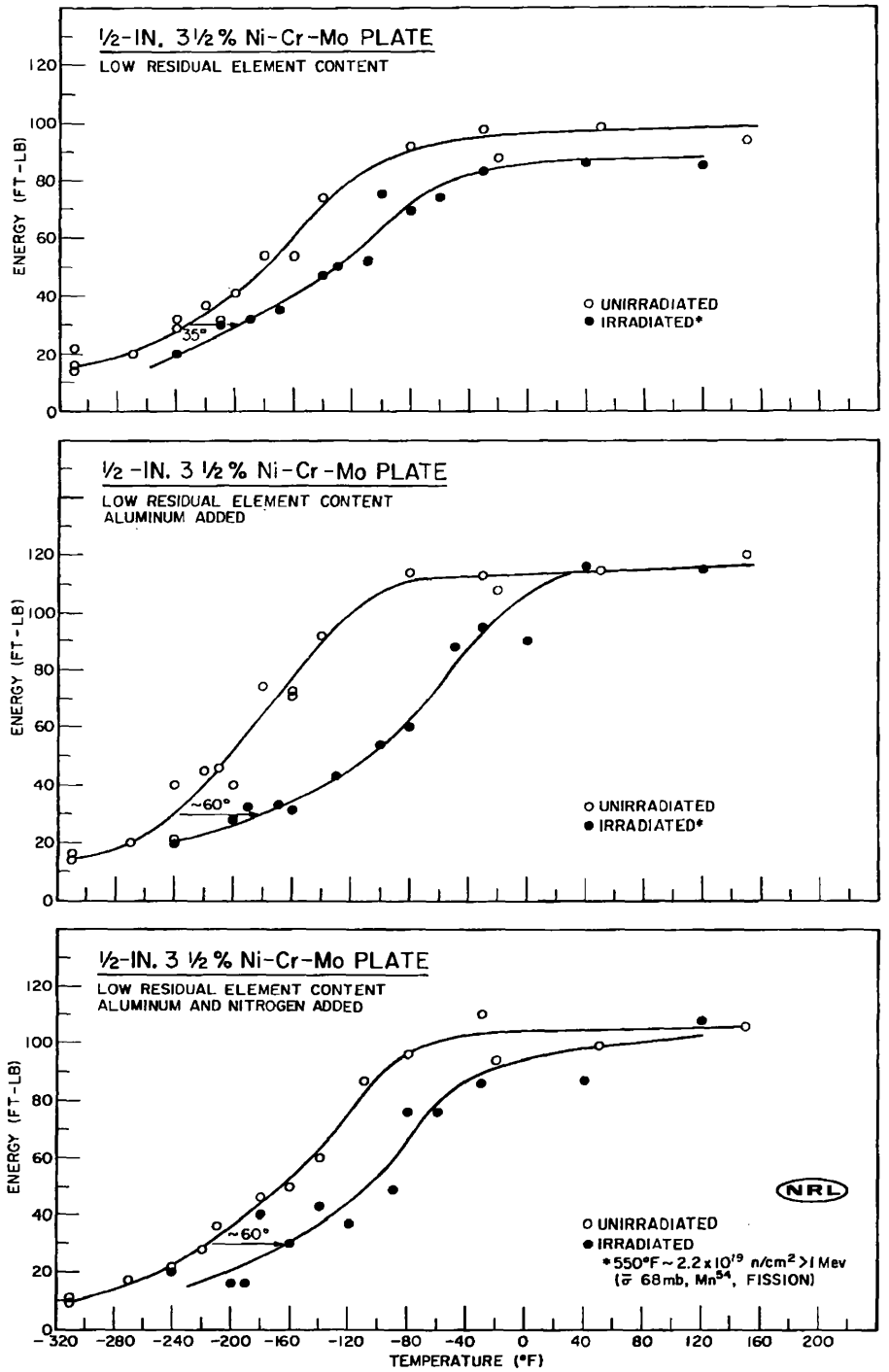


Fig. 7 - Notch ductility behavior of 3-1/2Ni-Cr-Mo test plates before and after irradiation at 550° F

(a) Heat Y9272, cast 2A

(b) Heat Y9272, cast 2B

(c) Heat Y9272, cast 2C

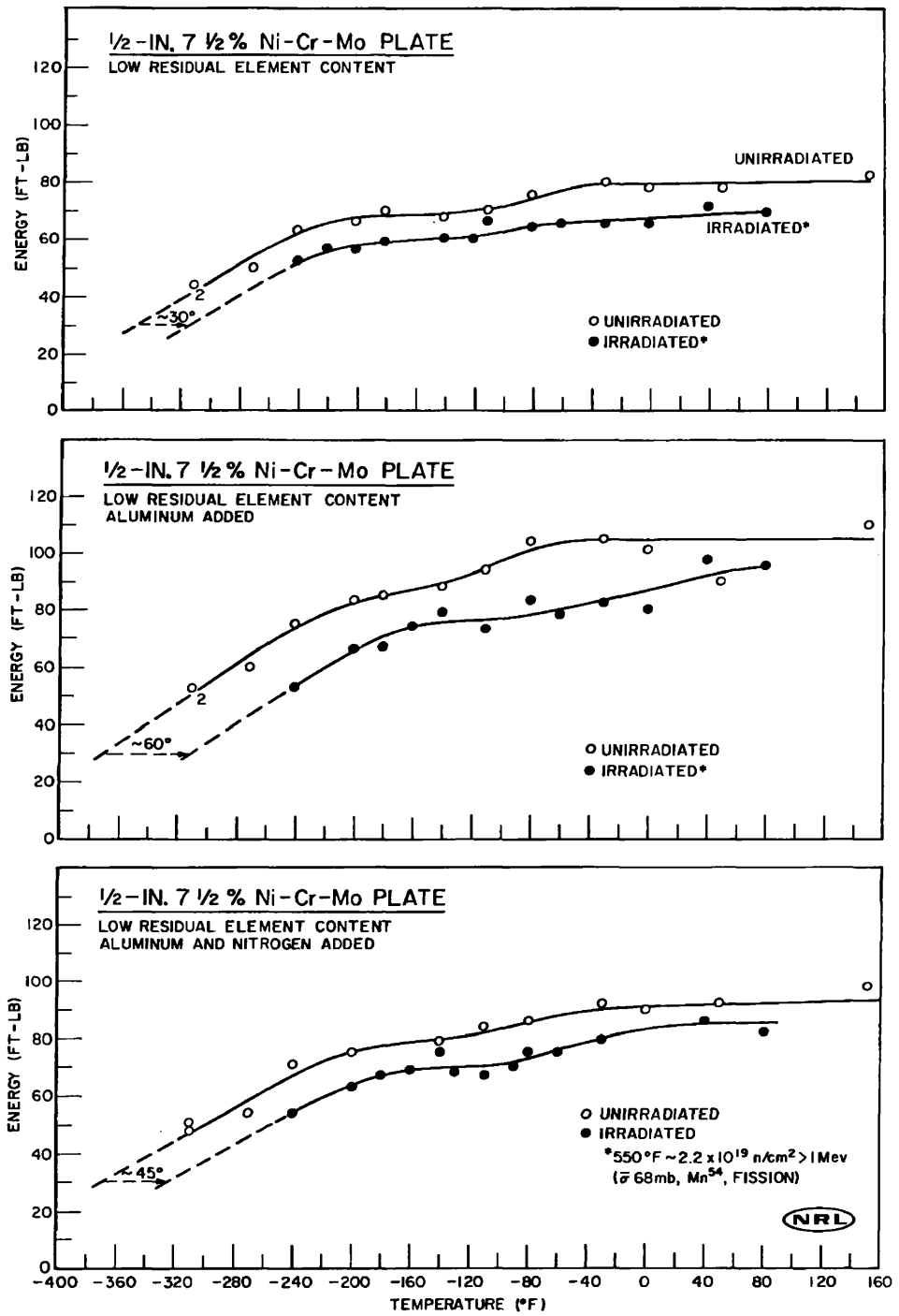
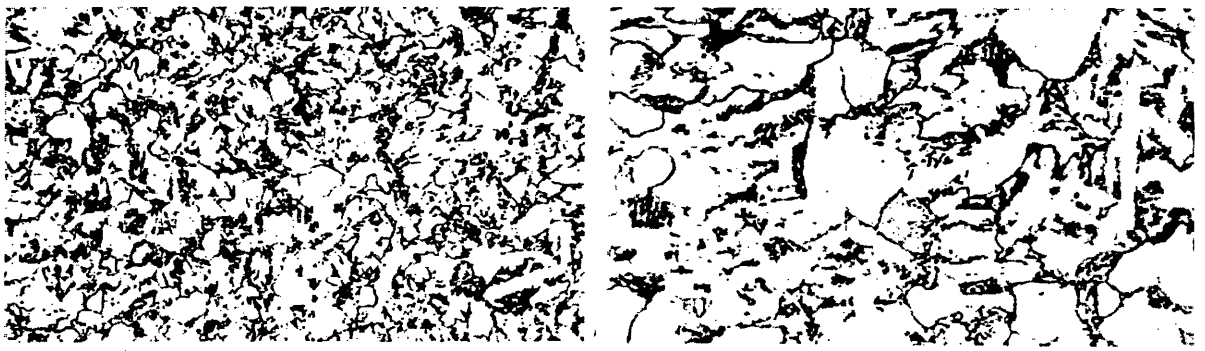


Fig. 8 - Notch ductility behavior of 7-1/2Ni-Cr-Mo test plates before and after irradiation at 550° F

(a) Heat Y9273, cast 2A

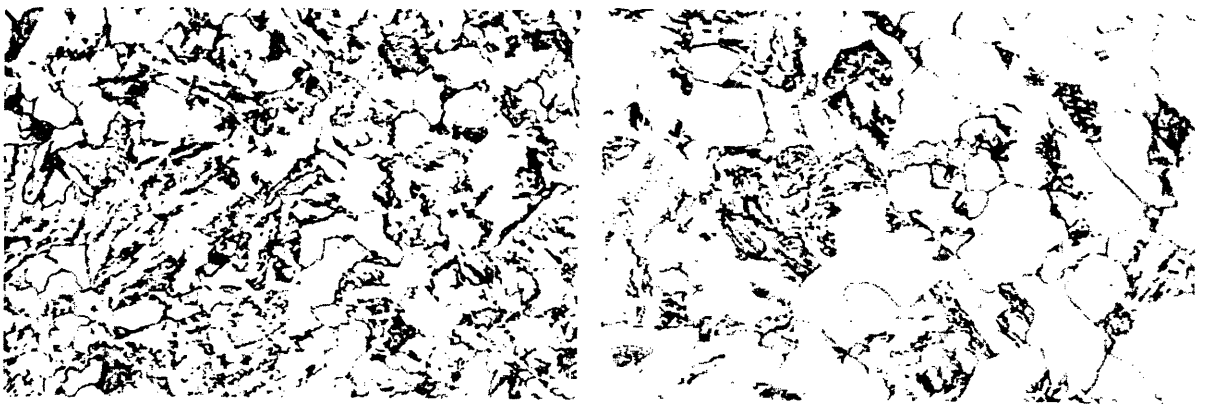
(b) Heat Y9273, cast 2B

(c) Heat Y9273, cast 2C



500X 1000X

a. Heat Y9239-1A Low residual element content, 014% N



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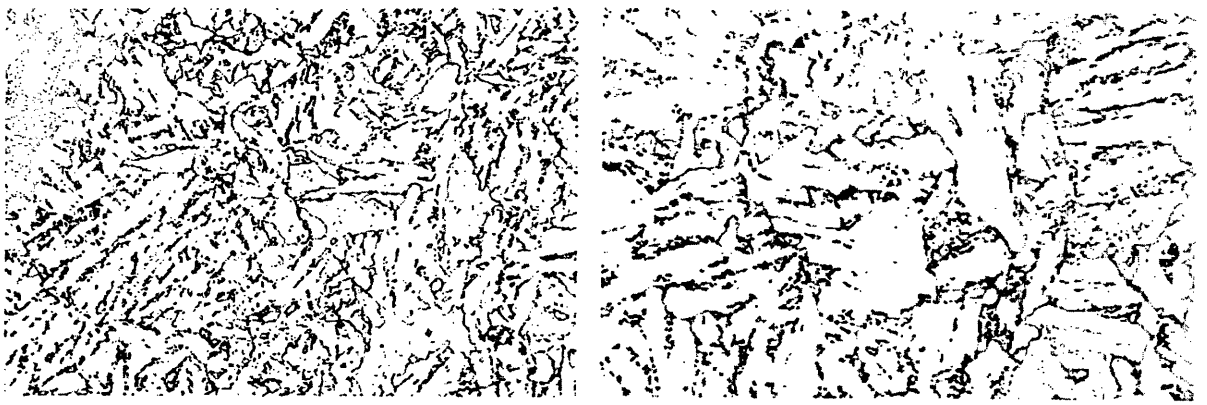
b. Heat Y9239-1B, Same as "a" except .20% Cu added



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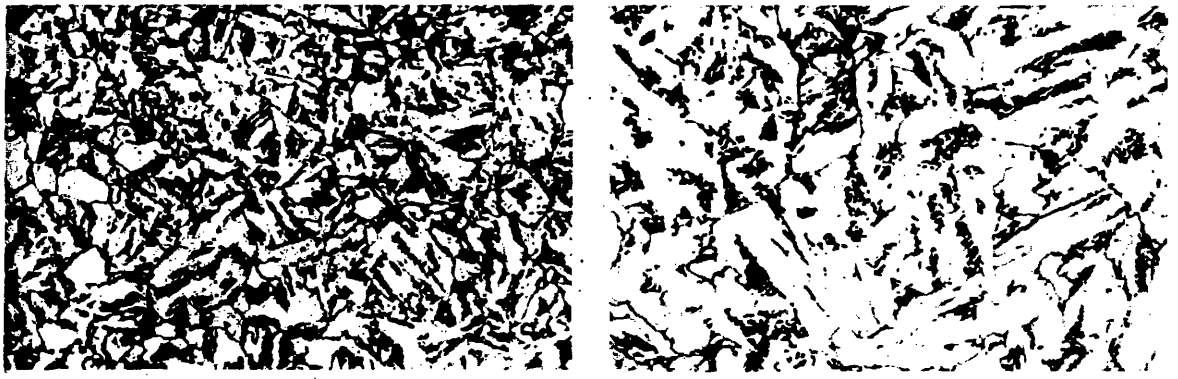
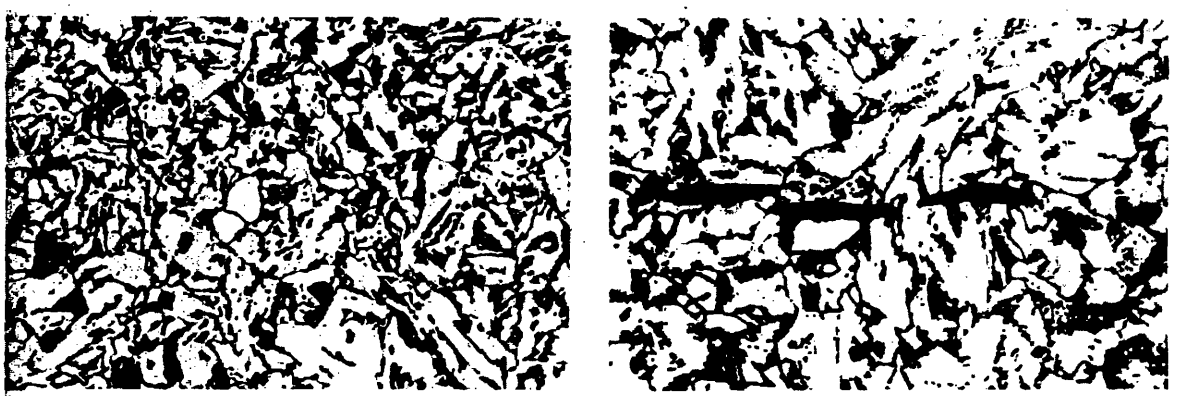
c. Heat Y9239-1C, Same as "a" except .20% Cu and .08% V added

Fig. 9 - Microstructure of laboratory heat Y9239 (copper-vanadium series, high nitrogen). All photomicrographs show structures consisting of proeutectoid ferrite and tempered upper bainite. In cast 1C, the carbides are largely spheroidized due to a higher tempering temperature.



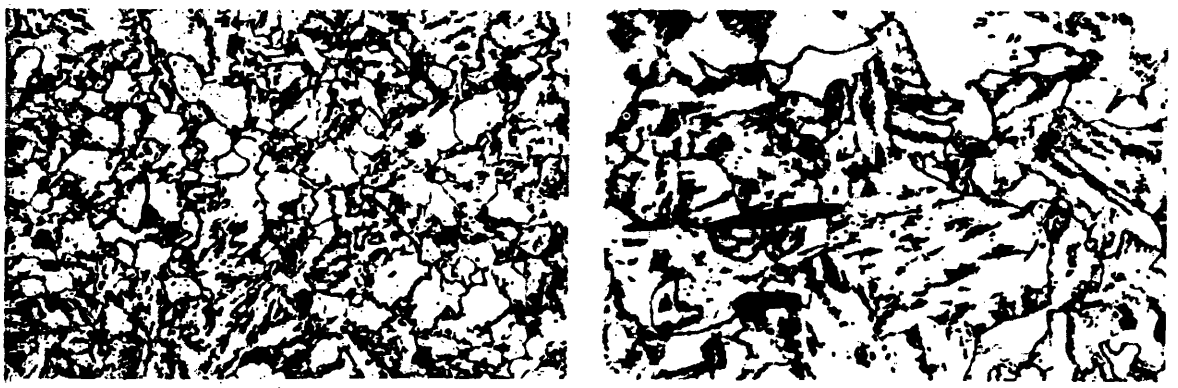
500X 1000X

a. Heat Y9240-1A - low residual element content



500X 1000X

b. Heat Y9240-1B - low residual elements, .021% S added



500X 1000X

c. Heat Y9240-1C - low residual elements, .021% S and .031% P added

Fig. 10 - Microstructure of laboratory heat Y9240 (sulfur-phosphorus series). All photomicrographs show structures consisting of proeutectoid ferrite and tempered bainite. Manganese sulfide inclusions are invisible in Casts 1B and 1C

In summary of these studies, no significant conclusions regarding the variable radiation embrittlement sensitivity of the different casts could be drawn from the metallographic comparisons. Additional work consisting of electron microscopy and electron fractography is planned.

Thermal stability tests were made on each composition variation by aging Charpy-V specimens at 550°F for time periods equivalent to the in-reactor exposure (75 days for the Cu-V and Ni-Cr-Mo series and 45 days for the S-P series). Typical thermal aging responses for the A302-B base composition and the Ni-Cr-Mo base compositions are shown in Figs. 11 and 12 respectively. All A302-B base specimens behaved in a similar manner, showing slight improvement in Charpy-V notch ductility (i.e., a lowering of the ductile-brittle transition temperature by approximately 10 to 25°F) accompanied by approximately a 2-point decrease in Rockwell-B hardness. Good thermal stability was also noted in the 3-1/2Ni-Cr-Mo and 7-1/2Ni-Cr-Mo specimens, which gave no indication of a measurable difference between the as-received condition and the thermally aged condition.

WELD METAL INVESTIGATIONS: NRL-B&W COOPERATIVE PROGRAM

A543 Class I (3-1/2Ni-Cr-Mo) steel represents a high strength composition recently approved by the ASME Code for pressure vessel construction. Initial assessments revealed this material to have superior resistance to radiation embrittlement when compared to the lower strength, A302-B composition which has seen extensive use in the construction of current-generation nuclear power plants (1). New data on the notch ductility behavior of one 8-in. A543 plate irradiated to high fluences at temperatures ranging from 550° to 740°F are shown in Fig. 13 for reference.

As was discussed (Fig. 2), the evaluation of one heavy section weldment of A543 parent plate following 550°F irradiation revealed severe embrittlement of the weld deposit relative to the base plate. It therefore appeared that nuclear applications of A543 steel would be limited by the irradiation performance of companion weld metals. These indications prompted the initiation of a cooperative program between NRL and B&W to investigate the causes of the observed high embrittlement and, further, to attempt the development of a suitable, low-radiation-sensitivity weld filler composition for joining A543 steel.

Experimental and Commercial Filler Test Weldments

Four experimental weldments (1-in. plate) were prepared by the manual metal arc process using different welding rod compositions. Guided by the most recent findings of the NRL-USS cooperative program on plate sensitivity discussed in a previous section, low copper contents were specified for these weldments. Nickel and chromium contents were adjusted within the range required to meet the necessary strength requirements.

In addition, two submerged arc weldments were made using 2-in. plate and commercially available weld filler. Both of the commercial weld wires selected were relatively high in copper (0.24% and 0.43%), thus providing a further evaluation of copper content as related to radiation embrittlement sensitivity. The chemical analyses of the individual weld deposits are given in Table 5. Specific welding parameters and heat treatments are summarized in Table 6. Charpy-V specimens were taken in all cases with their long axes perpendicular to the welding direction and with the notch centered in the weld deposit.

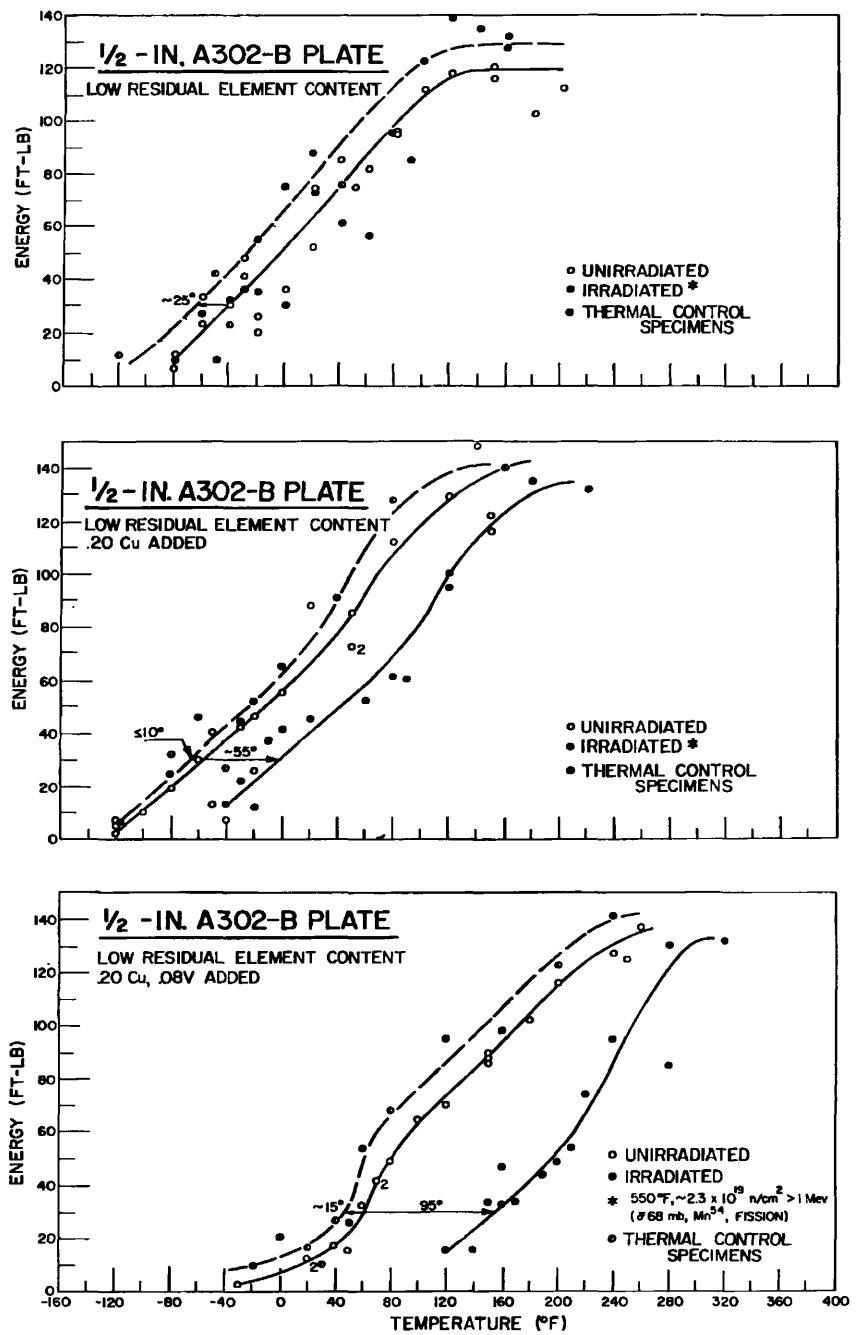


Fig. 11 - Thermal Aging (75 days at 550°F) response of the copper-vanadium series of A302-B test plates
(a) Heat Y9238, cast 1A
(b) Heat Y9238, cast 1B
(c) Heat Y9238, cast 1C

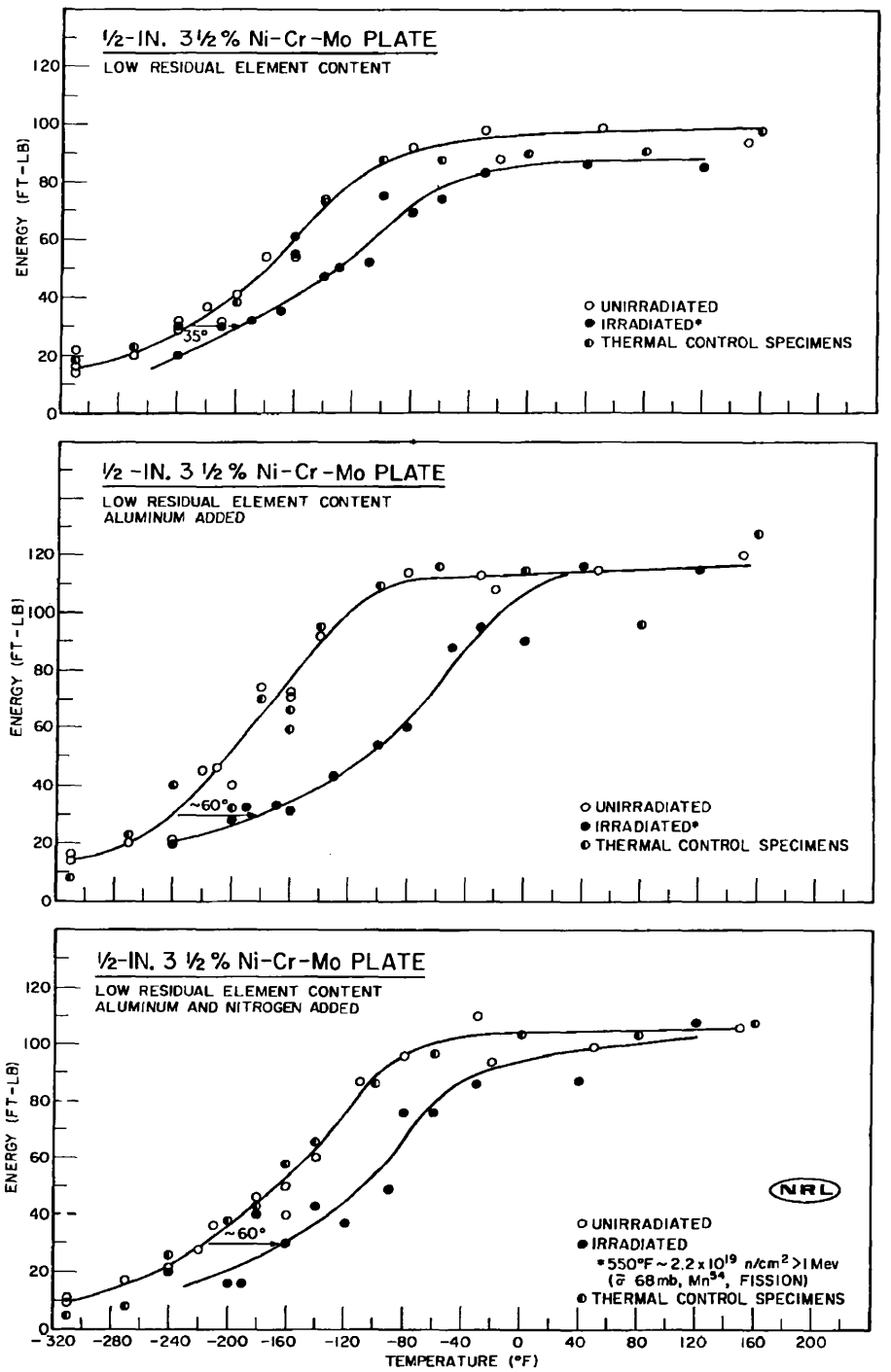


Fig. 12 - Thermal aging (75 days at 550° F) response of the 3-1/2% Ni-Cr-Mo, 1/2-in. laboratory test plates
(a) Heat Y9272, cast 2A
(b) Heat Y9272, cast 2B
(c) Heat Y9272, cast 2C

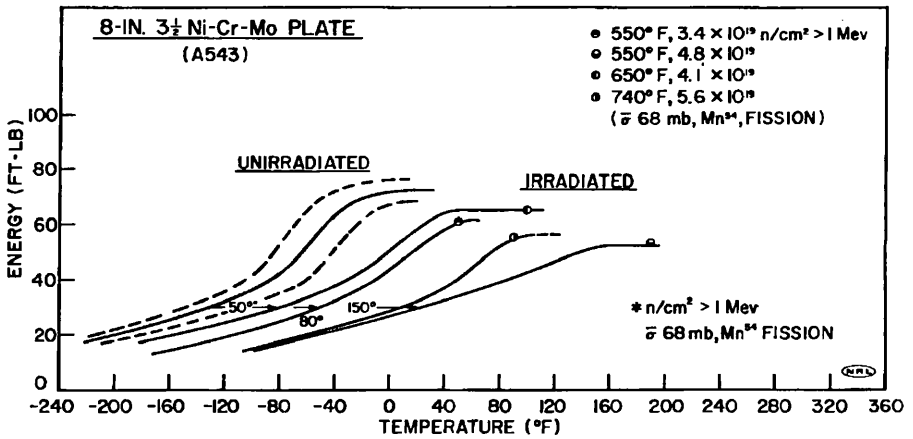


Fig. 13 - High temperature irradiation response of 3-1/2% Ni-Cr-Mo steel

Experimental Results

Paralleling investigations of plate behavior, a 550° F irradiation temperature was selected for this series as well. Specimens of all six weldments were irradiated in a single experimental assembly together with control specimens taken from the 8-in. A543 plate referred to in Fig. 13. The exposure, performed in the LITR, obtained a fluence of approximately 3.5×10^{19} n/cm^2 > 1 Mev. Specimen encapsulation and dosimetry techniques employed were identical to those used in the plate investigation program.

It can be seen from Fig. 14 that the radiation embrittlement sensitivities of the experimental weldments, with the exception of composition 1938, are approximately equal or superior to that of the 8-in. A543 plate (Fig. 15), which exhibited a 105° F Charpy-V 30-ft-lb transition temperature increase. Comparing the relative transition temperature shifts of the experimental weld compositions (Table 7) to their respective chemical analyses (Table 5), a relationship between copper content of the individual weld metals and their irradiation responses is apparent. The weld composition (1936) which proved to be least sensitive to radiation embrittlement had the lowest copper content of the series (0.02%). The data are also seen to suggest that the nickel contents of the weldments, in the concentrations indicated, may have had some influence on their irradiation behavior. Specifically, the two weld compositions (1938 and 1948) which contained approximately 1.7% to 2% nickel showed a higher embrittlement sensitivity than the other two weldments which contained approximately 0.7% nickel.

The influence of copper content on the radiation sensitivity of Ni-Cr-Mo weld metal is even more apparent in Fig. 15, which shows the radiation responses of the two submerged arc commercial weldments with higher copper contents (0.24% and 0.42%). The respective Charpy-V 30-ft-lb transition temperature shifts for these compositions were ≈415° F and 530° F. These data are in good agreement with the earlier results on the heavy section A543 weldment used for ASME Code Case studies (Fig. 2), and they substantiate the findings of the plate sensitivity program presented in this report. Thermal stability tests were made on all weld compositions to verify the experimental results. From unirradiated Charpy-V specimens of the respective materials exposed to 550° F for 1200 hours (equivalent to in-reactor exposure), no differences in notch ductility could be detected between the unirradiated and the thermally aged conditions of any one weld metal.

Table 5
Chemical Analysis of Experimental and Commerical Weld Deposits and of the A543 Reference Plate

Material Identification	Analysis, wt-%*												
	C	Mn	P	S	Si	Cr	Ni	Mo	Cu	V	As	Sn	Sb
Experimental Composition 1934	0.04 0.04	0.96 0.87	0.010 0.008	0.016 0.010	0.45 0.40	2.04 2.08	0.79 0.77	1.01 1.01	0.14 0.06†	0.02 0.02	- 0.005	- < 0.007	- < 0.01
Experimental Composition 1936	0.06 0.06	0.94 0.86	0.012 0.007	0.016 0.010	0.26 0.30	2.12 2.08	0.71 0.78	1.02 1.01	0.02 0.02†	0.02 0.02	- 0.007	- < 0.007	- < 0.01
Experimental Composition 1938	0.03 0.03	0.74 0.72	0.011 0.009	0.017 0.010	0.32 0.34	2.39 2.39	1.95 1.62	0.99 0.92	0.14 0.07†	0.02 0.03			
Experimental Composition 1948	0.05 0.05	0.98 0.82	0.012 0.007	0.017 0.006	0.22 0.20	2.31 2.32	1.66 1.56	0.94 0.92	0.02 0.05†	0.02 0.03			
Commercial Filler (.24% Cu)	0.06 0.07	1.24 1.07	0.011 0.011	0.009 0.006	0.37 0.37	0.17 0.25	1.25 1.58	0.33 0.37	0.24 0.24	- -			
Commercial Filler (.48% Cu)	0.09 0.09	1.38 1.15	0.013 0.011	0.011 0.006	0.27 0.22	0.32 0.39	2.13 2.46	0.48 0.52	0.43 0.42	- -	- 0.010	- < 0.007	- < 0.01
8-in. A543 Plate	0.17 0.17	0.38 0.34	0.013 0.013	0.023 0.015	0.29 0.25	1.88 1.93	3.65 3.45	0.51 0.51	- 0.06	- 0.02			

*First number - courtesy of supplier; Second number - NRL determination
†Average of 3 check analyses.

NOTE: The 8-in. A543 base plate was heat treated as follows:
1650° F/2 hours - water quench
1500° F/2 hours - water quench
1185° F/2 hours - water quench
Welding and heat treatment conditions for all weldments are given in Table 6.

Table 6
Welding Parameters and Heat Treatment of the Experimental and Commercial Weldments

Experimental Weld Compositions 1934, 1936, 1938 and 1948	
Welding Process:	Manual Metal Arc
Electrode:	5/32 dia., Type 15 coating
Current:	165 Amperes
Voltage:	25 Volts
Travel:	6 in./min.
Pre-heat Temp:	300°F
Interpass Temp:	375°F max.
Post Weld Heat Treatment:	1125-1150°F/30 hours, Furnace cool to 600°F
Commercial Weld Wire	
Welding Process:	Submerged Arc
Electrode Dia.:	1/8 in.
Flux:	Type: 1092, Size: 20 × 200
Type of Power:	AC
Current:	450 Amperes
Voltage:	32 Volts
Travel:	14 in./min.
Pre-heat Temp:	250°F
Interpass Temp:	350°F max.
Post Weld Heat Treatment:	1050-1075°F/65 hours, Furnace cool to 600°F. 1075-1100°f/15 hours, Furnace cool to 700°F.

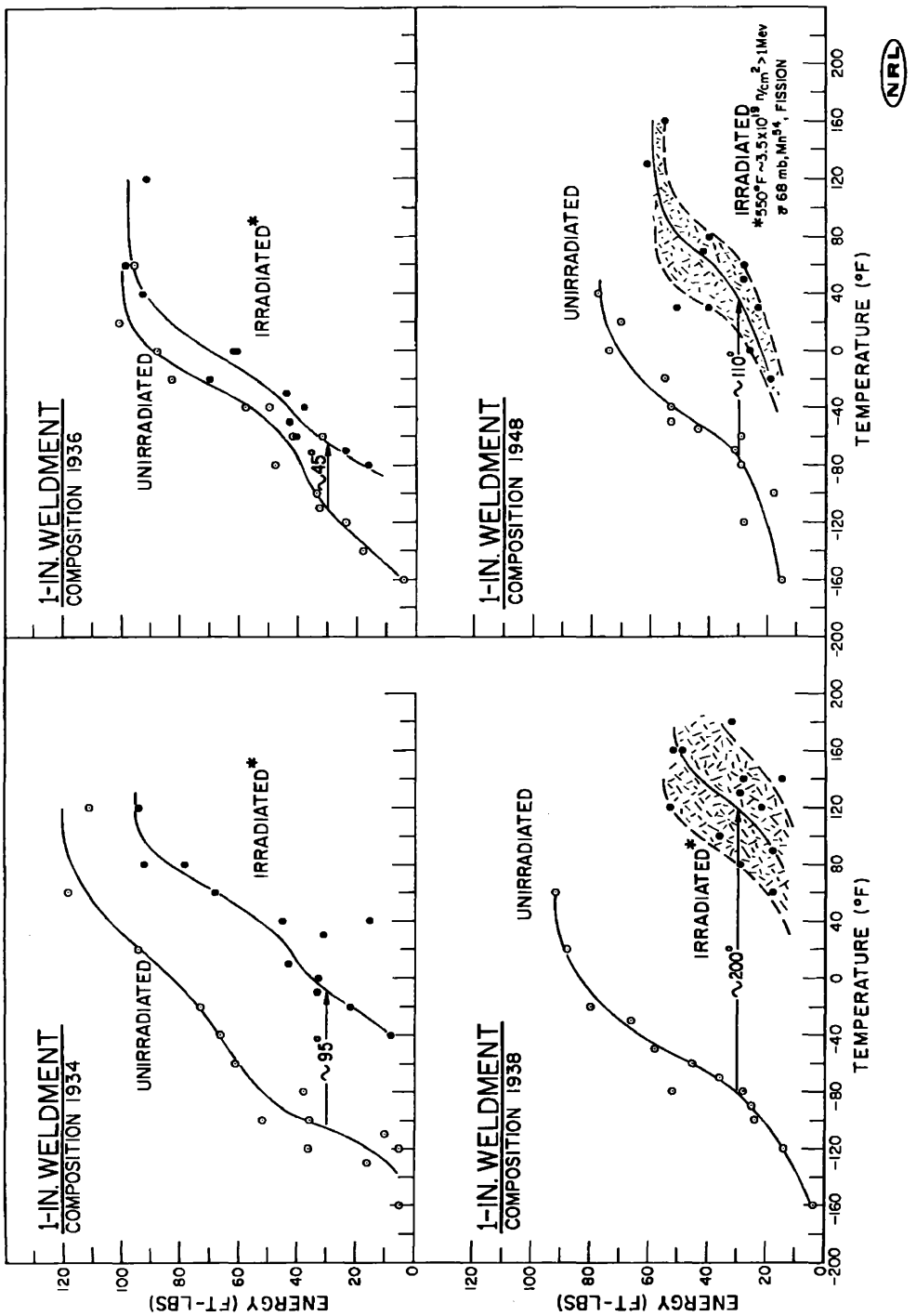


Fig. 14 - Notch ductility behavior of manual metal arc deposited experimental weld metal compositions for joining A543 steel before and after irradiation at 550°F

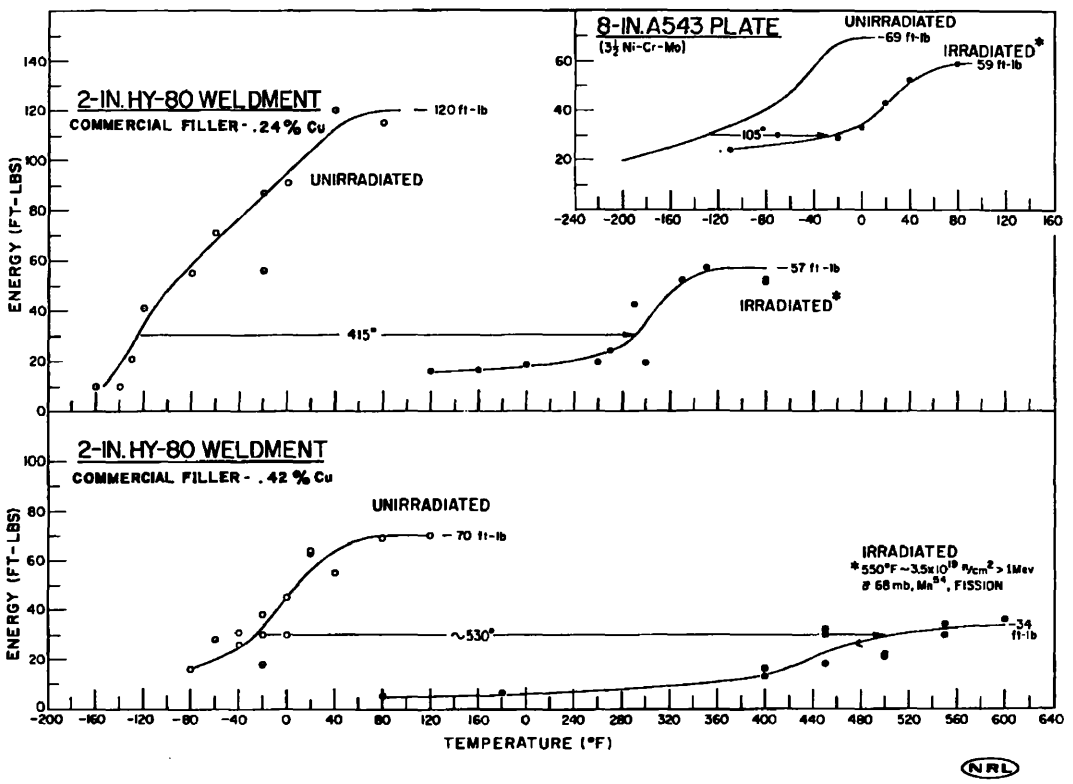


Fig. 15 - Notch ductility behavior of 2-in. HY-80 weldments (submerged arc commercial filler) and 8-in. A543 plate before and after irradiation at 550°F

SUMMARY AND CONCLUSIONS

Both NRL cooperative research programs have yielded significant new information concerning radiation embrittlement sensitivity development in carbon and low alloy steels. The NRL-U. S. Steel Corporation program on plate performance has demonstrated that low sensitivity to 550° F radiation embrittlement can be consistently achieved in laboratory size heats of A302-B and Ni-Cr-Mo pressure vessel steels. In addition, several chemical elements have been isolated as significant contributiors to radiation embrittlement, while other suspect elements have been shown to have a negligible effect. Based on the results of this program, a commercial-size heat (30 tons) of A533-B steel has been procured, under AEC sponsorship, to determine if low 550° F embrittlement sensitivity achieved repeatedly with small laboratory heats can also be approached with large commercial heats through proper specification and control. The commercial heat used a selected scrap (low copper, low phosphorus) charge but was conventionally air-arc melted followed by vacuum stream degassing. Initial irradiation response data for the 6-in. test plate should be available by late 1968.

Studies of plate behavior on the laboratory scale are being continued to supplement and refine the experimental data described herein. The aims of the current NRL-U. S. Steel cooperative program include:

Table 7
Charpy-V Notch Ductility Characteristics of Experimental and Commercial Weld Deposits and of the A543 Reference Plate Before and After Irradiation at 550°F to ≈ 3.5×10^{19} n/cm^2 > 1 Mev

Material Identification	Weldment or Plate Thickness (in.)	C_v 30-ft-lb Transition Temp. (°F)			Approximate Full Shear Energy Absorption Level (ft-lb)	
		Unirradiated	Irradiated	ΔT	Unirradiated	Irradiated
Experimental Composition 1934	1	-105	-10	95	120	95
Experimental Composition 1936	1	-110	-65	45	100	100
Experimental Composition 1938	1	- 80	120	200	90	50
Experimental Composition 1948	1	- 75	35	110	80	60
Commercial Filler (0.24% Cu)	2	-125	290	415	120	57
Commercial Filler (0.42% Cu)	2	- 25	505	530	70	34
A543 Reference Plate	8	-130	-25	105	70	60

- Quantitative assessment (critical concentration studies) of copper and phosphorus in A302-B steel,

- Combined or additive effects of copper and phosphorus as well as phosphorus and sulfur in A302-B steel,

- The effect of microstructure on embrittlement sensitivity,

- The effect of other potential embrittling elements - arsenic, tin, antimony,

- The effect of copper and vanadium on Ni-Cr-Mo base metal composition, and

- Better understanding of the mechanisms of radiation embrittlement through special techniques, such as electron microscopy, electron fractography, and microprobe analysis.

The NRL-Babcock and Wilcox Company cooperative program on weld metal sensitivity has markedly improved the potential of A543 steel as a higher strength candidate material for nuclear reactor pressure vessel service. Having demonstrated that suitable low radiation sensitivity weld compositions can be developed for joining this steel, this program is also continuing. Submerged arc weldments utilizing the two lowest sensitivity experimental weld wire compositions are being produced to verify if the superior performance of the experimental test welds can be duplicated in heavy section weldments representative of commercial practice.

The significant conclusions of the two programs can be enumerated as follows:

1. Type A302-B steel can be made insensitive to 550°F irradiation embrittlement (as measured by the Charpy-V transition temperature increase) by keeping the total residual element content at a very low level.

2. Copper has been isolated as a significant contributor to the radiation embrittlement sensitivity of A302-B steel. Experimental data also indicate that copper is largely responsible for accelerated radiation embrittlement observed in several Ni-Cr-Mo (A543) steel weldments.

3. Experimental data indicate that it is feasible to develop a suitable low radiation embrittlement sensitivity weld filler for joining A543 steel, the primary requirement being a low copper content (<0.1%).

4. The addition of up to 0.02% sulfur to low residual A302-B steel decreases the unirradiated full shear energy absorption shelf but does not contribute to observed radiation embrittlement at 550°F.

5. The addition of 0.03% phosphorus and 0.02% sulfur to low residual A302-B steel causes a significant increase in 550°F radiation embrittlement sensitivity, suggesting that either phosphorus or phosphorus in combination with sulfur is a significant factor in irradiation behavior.

6. Variations in the total nitrogen content between 0.008 and 0.015% of an aluminum deoxidized A302-B composition have no measurable effect on radiation embrittlement response.

7. Vanadium additions (to 0.08%) do not significantly affect the 550°F radiation embrittlement sensitivity of low residual A302-B steel.

8. The addition of 0.03% aluminum to low residual Ni-Cr-Mo steel results in slight increase of 550° F radiation embrittlement sensitivity. This effect might also be attributed to the reduction of the free nitrogen content of the material.

ACKNOWLEDGMENTS

The NRL Metallurgy Division research on factors responsible for variable radiation embrittlement sensitivity of steel plate and weld metals is supported jointly by the Office of Naval Research and the U. S. Atomic Energy Commission, Division of Reactor Development and Technology.

The authors gratefully acknowledge the continuing efforts of the U. S. Steel Corporation, Applied Research Laboratory, in providing the special laboratory heats for the cooperative program. The authors particularly thank Mr. J. V. Alger of the Applied Research Laboratory for his helpful suggestions and many contributions to the overall plan of the investigations and for his direction of the melting and heat treatment of the special steels used in this program. The success of the NRL-USS effort is measurably attributed to his personal interest and active participation. The continuing interest and cooperation of Mr. M. W. Lightner, Vice President, U. S. Steel, Research and Technology Division, in supplying the requisite materials for the irradiation effects studies are also appreciated.

The authors express their gratitude to the Babcock and Wilcox Company for its contribution of special experimental test weldments. The personal efforts of Messrs. S. P. Grant and G. N. Emmanuel, of the B&W Power Generation Division, in the fabrication of the initial weldment series for the joint program are particularly acknowledged.

The authors are indebted to each member of the Reactor Materials Branch for their individual interest, efforts, and contributions to the rapid development of the irradiation effects data and also thank the Analytical Chemistry Branch, NRL Metallurgy Division, for providing the many detailed chemistry analyses required in this study.

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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Research Laboratory Washington, D.C. 20390	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE
THE EFFECT OF RESIDUAL ELEMENTS ON 550° F IRRADIATION RESPONSE OF SELECTED PRESSURE VESSEL STEELS AND WELDMENTS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
This is a final report on one phase of a continuing problem.

5. AUTHOR(S) *(First name, middle initial, last name)*
Uldis Potapovs and J. Russell Hawthorne

6. REPORT DATE November 22, 1968	7a. TOTAL NO. OF PAGES 32	7b. NO. OF REFS 10
8a. CONTRACT OR GRANT NO. NRL Problem M01-14 b. PROJECT NO. RR007-01-46-5409 c. USA-ERG-3-67 d. AEC-AT(49-5)-2110	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6803 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT
This document has been approved for public sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES Also sponsored by the Atomic Energy Commission	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research); and Army Nuclear Power Program

13. ABSTRACT
The effect of variable residual element contents on 550° F radiation embrittlement sensitivity of pressure vessel steels has been examined in a continuing cooperative program between the Naval Research Laboratory (NRL) and the U. S. Steel Corporation (USS), Applied Research Laboratory. Results indicate that phosphorus and copper can contribute significantly to the 550° F radiation embrittlement sensitivity of Type A302-B steel. The results also show that vanadium may have a slight adverse effect and that sulfur is neutral, although it serves to decrease the full shear energy absorption level of the steel. Nitrogen variations from ≈0.008% to 0.015% in aluminum deoxidized steel have no significant effect, while the addition of aluminum to Ni-Cr-Mo steel with a given nitrogen content may slightly promote irradiation embrittlement. The program results demonstrate that apparent insensitivity to 550° F irradiation embrittlement can be consistently achieved with laboratory heats of a nominal A302-B steel composition by maintaining the total residual element contents at a low level.

Radiation embrittlement sensitivity of weldments has been investigated in a cooperative program, between NRL and the Babcock and Wilcox Company, aimed at the development of low sensitivity weld fillers for joining Ni-Cr-Mo steel. Data from this new program again point to copper as a dominating factor in determining radiation embrittlement sensitivity, further verifying the results obtained in the NRL-USS A302-B steel investigation. Two experimental weld wire compositions with low copper contents (< 0.1%) are shown to possess resistance to 550° F irradiation embrittlement equal or superior to that of A543 base plate.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Radiation embrittlement sensitivity						
Nuclear reactors						
Reator structural materials						
Pressure vessels						
Weldments						
Radiation effects						
Residual elements						
Neutron irradiation						
A 302-B steel						
A 543 Steel						

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