**STUDIES OF LOW TEMPERATURE,
LOW FLUX RADIATION
EMBRITTLEMENT OF NUCLEAR
REACTOR STRUCTURAL
MATERIALS**

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EXECUTIVE SUMMARY

A large matrix of simple alloys and complex commercial type steels was irradiated over a range of fluxes at 60°C up to a fast fluence of about 3×10^{22} n/m². Combined with data in the literature, these results show a negligible effect of flux on irradiation hardening in the range of 2×10^{13} to 5×10^{18} n/m²-s. This observation lends indirect support to the proposal that the accelerated embrittlement in the High Flux Isotope Reactor surveillance steels was due to an anomalously high level of damage from gamma rays. A weak dependence of hardening on a number of elements, including copper, nickel, phosphorous, molybdenum and manganese, can be described by a simple empirical chemistry factor. Particular combinations of elements resulted in hardening differences of up to about 60% in the complex commercial type steels and up to about 100% in simple model alloys. Direct effects of microstructure appear to be minimal. Hardening varies with the square root of fluence above a threshold around 4×10^{20} n/m². The results suggest that low temperature hardening is dominated by local intracascade processes leading to the formation of small defect-solute clusters/complexes. The observed hardening corresponds to nominal maximum end-of-life transition temperature shifts in support structure steels of about 120°C.

INTRODUCTION

The individual and combined effects of irradiation and metallurgical variables on the embrittlement of pressure vessel steels at around 300°C has been reasonably well characterized [1,2]. In contrast, both experimental characterization and theoretical understanding of hardening and embrittlement relevant to the low operating temperature range of reactor support structures -- about 50 to 150°C -- is much more limited. Considerable concern about the potential for significant embrittlement of support structures emerged from the High Flux Isotope Reactor (HFIR) surveillance program [3,4], where the rates of hardening and transition temperature shifts were found to be about a factor of ten greater than for high flux test reactor irradiations. The accelerated embrittlement in HFIR has been variously ascribed to the effect of: a) low flux [4]; b) a high thermal-to-fast flux ratio (note, the preliminary belief that this ratio was very large turned out to be incorrect) [5]; and c) most recently, gamma-ray induced damage [6,7]. Theoretical considerations suggest that, at these temperatures, transient effects may be dominant and that the primary damage processes may be fundamentally different from those at higher temperatures [7]. Further, only a very limited data base exists on the effect of key metallurgical variables such as copper, nickel, phosphorous and microstructure. Recent low fluence ($< 10^{22}$ n/m²) studies have suggested that while there may be considerable metallurgically mediated variations in hardening, differences in commercial type steels are not primarily due to copper; the low copper sensitivity was attributed to a cut-off in precipitation below about 160°C [8]. Unlike, commercial type steels, however, significant effects of copper have been reported for simple model steels [7]. This report describes results of a systematic study of the effects of metallurgical variables, flux and fluence on irradiation hardening at 60°C.

EXPERIMENT

Alloys and Specimens

A large set of alloys was investigated in this study; the alloys are classified in four general categories:

- 1) The compositions and heat treatment for a set of twenty simple split melt model iron and steel alloys (VX-series) with systematic variations in Cu, C, Mn, Ti and N are shown in Table 1. The microstructures of these alloys are generally characterized by a wide distribution of ferrite grain sizes (in some cases duplex and/or with processing texture). Rapid quenching was carried out to maintain copper in solution. The low temperature

temperatures were intended to precipitate carbon in the form of dispersed but reasonably stable Fe_3C or M_3C intergranular carbides. Yield stresses averaged about 190 ± 40 MPa. The VX-series steels fall into four subgroups.

- a) VF -- Iron with average ferrite grain sizes from 17 to 138 μm (average ≈ 73 μm) containing 0.0, 0.5 and 0.9Cu at both high (100 ± 20 ppm) and low (15 ± 10 ppm) N levels and variants with 0.25Ti at high N at both 0.0 and 0.9Cu.
- b) VM -- Fe-1Mn alloys with average ferrite grain sizes from 17 to 138 μm (average ≈ 54 μm) containing 0.0 and 0.9Cu, with high (105 ± 5 ppm) and low (25 ± 15 ppm) N and a 0.9Cu high N variant with 0.25Ti.
- c) VC -- Fe-0.15C steels with average ferrite grain sizes of 13 to 244 μm (average ≈ 112 μm) containing 0.0, 0.5 and 0.9Cu at low N (10 ppm) and a 0.9Cu melt with high N (110 ppm).
- d) VA -- Fe-0.15C-1Mn steels with average ferrite grain sizes of 50 to 85 μm (average ≈ 68 μm) containing 0.0 and 0.9Cu at low N (35 ± 5 ppm).

TABLE 1 -- VX-Series Alloy Compositions

Alloy		Composition (weight per cent)*				
Group/Code		Cu	Mn	C	Ti	N(appm)
VF	VA	--	--	--	--	5
VM	VB	--	1.0	--	--	40
VA	VC	--	1.0	0.15	--	30
VM	VD	0.9	1.0	--	--	10
VA	VE	0.9	1.0	0.15	--	20
VF	VG	0.5	--	--	--	20
VF	VH	0.9	--	--	--	20
VC	VI	0.5	--	0.15	--	10
VC	VJ	0.9	--	0.15	--	10
VF	VK	--	--	--	--	100
VF	VL	--	--	--	0.25	100
VF	VM	0.5	--	--	--	120
VF	VN	0.9	--	--	--	110
VC	VO	0.9	--	0.15	--	110
VF	VP	0.9	--	--	0.25	110
VM	VR	--	1.0	--	--	100
VM	VS	0.9	1.0	--	--	110
VM	VT	0.9	1.0	--	0.25	90

* solution treat 775°C , 17h; quench in salt bath at 450°C , 3 minutes; air cool

- 2) The compositions and heat treatments of 41 complex A533B-type split melt steels (CM-series) are shown in Table 2. A total of 31 variants around a base composition were used to evaluate the effects of both: a) *combinations* of Cu (0.0 to 0.8)³, Ni (0.0 to 1.6), Mn (0 to 1.6) and P (0.005 to 0.040) contents; and b) *single* variable modifications of Mo, N, C, B, Al and As/Sn/Sb contents. All 31 alloys contained 0.005Al and 0.25Si and received the base heat treatment (c1 - Table 2), yielding prior austenite grain sizes of about $50 \pm 10 \mu\text{m}$ and microstructures ranging from tempered bainite (most CM alloys) to mixed tempered ferrite-bainite. The yield stresses for alloys with 0.5Mo averaged about 475 MPa (only 2 of the 31 base heat treated steels had yield stresses below 440 and only 2 above 520 MPa). The alloy without this secondary hardening element had a much lower unirradiated yield stress of 315 MPa. Eleven alloys received alternate heat treatments involving: a) variations in the salt bath temperature (400 or 500 versus 450°C); b) a higher (1100°C versus 900°C) austenitizing temperature; c) additional stress relief anneals at 600°C (at times of 8, 40 and 80 h); and d) a simulated temper embrittling aging treatment (480°C/100h). The higher austenitizing temperature resulted in substantially larger prior austenitic grain sizes (75-100 μm) and lower yield stresses (by about 80 MPa). Other alternate heat treatments had little systematic effects on the unirradiated yield stress or microstructures observed optically.
- 3) The compositions and heat treatment for a set of eight complex commercial type bainitic model steels (L-series) with systematic variations in copper and nickel are shown in Table 3. These steels have been irradiated in previous programs at a variety of conditions, primarily around 300°C. They have microstructures and unirradiated properties very similar to those in the CM-series.
- 4) The compositions and heat treatments for a set of four commercial CC-series steels are shown in Table 4. The CC-series consists of two Mn-C mild steels from the HFIR surveillance program and the Shippingport shield tank; and an A588 and a medium carbon A36 structural steel. The CC-alloys permit the irradiations in this program to be tied to other data, including low flux surveillance/service conditions (e.g., the HFIR and Shippingport steels).

Sheet tensile specimens with a gage section 9 mm x 2 mm x 0.5 mm were prepared by precision die punching heat treated coupons lapped to 0.5 ± 0.005 mm thick. The quality of

³ Unless otherwise indicated compositions are in weight percent.

TABLE 2 -- CM-Series Alloy Compositions and Heat Treatments

Code	COMPOSITION (weight per cent)										HT†
	Cu	Ni	Mn	Cr	Mo	P	N	Sn/As/Sn	B	C	
CM1	0.0	0.0	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM2	0.0	0.0	1.4	0.0	0.5	0.040	<50	<0.005	<1	0.15	c1
CM3	0.0	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM4	0.0	0.8	1.4	0.0	0.5	0.025	<50	<0.005	<1	0.15	c1
CM5, 5a	0.0	0.8	1.4	0.0	0.5	0.040	<50	<0.005	<1	0.15	c1, 5
CM6	0.0	1.6	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM7	0.0	1.6	1.4	0.0	0.5	0.040	<50	<0.005	<1	0.15	c1
CM8, 8a	0.0	0.8	0.0	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 3
CM9	0.0	0.8	0.7	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM10	0.05	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM11	0.3	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM12, 12a	0.8	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 6
CM13	0.1	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM14	0.1	0.8	1.4	0.0	0.5	0.040	<50	<0.005	<1	0.15	c1
CM15, 15a	0.2	0.0	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 4
CM16, 16a	0.2	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 4
CM17, 17a	0.2	1.6	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 4
CM18, 18a	0.4	0.0	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 7
CM19, 19a, 19b	0.4	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 2, 4
CM19c, 19d, 19e	0.4	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c6, 7, 8
CM20, 20a, 20b	0.4	1.6	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1, 2, 7
CM21	0.4	0.8	0.0	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM22	0.4	0.8	0.7	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1
CM23, 23a	0.0	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.05	c1, 3
CM24	0.0	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.30	c1
CM25	0.0	0.8	1.4	0.0	0.5	0.005	200	<0.005	<1	0.15	c1
CM26, 26a	0.0	0.8	1.4	0.0	0.5	0.005	<50	0.020	<1	0.15	c1, 5
CM27	0.0	0.8	1.4	0.0	0.5	0.005	<50	<0.005	10	0.15	c1
CM28	0.4	0.8	1.4	0.0	0.5	0.005	<50	<0.005	10	0.15	c1
CM29	0.2	0.0	1.4	0.0	0.0	0.005	<50	<0.005	<1	0.15	c1
CM30	0.2	0.8	1.4	0.4	0.5	0.005	<50	<0.005	<1	0.15	c1
CM31	0.0	0.8	1.4	0.0	0.5	0.005	<50	<0.005	<1	0.15	c1

† HT	Purpose	Heat Treatment
c1	Base treatment	Austenitize 900°C/0.5h; salt bath quench 450°C/10min; air cool; temper 660°C/4h; air cool
c2	Vary structure/properties	Same as c1, except salt bath quench 500°C/10min
c3	" " "	Same as c1, except salt bath quench 400°C/10min
c4	Vary grain size/carbides	Same as c1, except austenitize 1100°C/1.0h
c5	Temper embrittlement	c1 plus 480°C/100h
c6	Stress relief	c1 plus 600°C/8h, air cool
c7	Stress relief	c1 plus 600°C/40h, air cool
c8	Stress relief	c1 plus 600°C/80h, air cool

TABLE 3 -- L-Series Alloy Compositions and Heat Treatments

Code	Composition (weight percent) ^{††}				
	C	Cu	Ni	Mn	Si
LA	0.14	0.40	0.00	1.37	0.22
LB	0.14	0.40	0.18	1.35	0.22
LD	0.19	0.38	1.25	1.38	0.23
LG	0.16	0.00	0.74	1.37	0.22
LH	0.16	0.11	0.74	1.39	0.24
LI	0.16	0.20	0.74	1.37	0.24
LJ	0.16	0.42	0.81	1.34	0.13
LK	0.13	0.80	0.81	1.13	0.13

^{††} Alloys contained P < 0.005, S ≤ 0.015, Cr ≤ 0.085, Mo ≈ 0.55; they were austenitized 900°C/1h; air cooled; tempered 664°C/4h; air cooled; stress relieved 600°C/40h; furnace cooled to 300°C; air cooled.

the die was monitored by punching and tensile testing a variety of calibration metals after about every 500 specimens had been punched. Some small angle neutron scattering (SANS) specimens were also prepared for selected materials. Specimens were loaded into aluminum capsules for irradiation. The capsules were evacuated, back-filled with helium and welded shut.

Irradiations

The results reported here are for four completed capsules out of a total of 12 capsules in the program. These capsules were irradiated in three out-of-core positions at the University of Michigan Ford Reactor (UMFR). The overall program irradiation matrix is shown in Table 5 and also includes the four UMFR capsules that are still in-reactor or yet to be tested, three capsules irradiated in high flux locations in HFIR and the High Flux Beam Reactor (HFBR) and one capsule with a high thermal-to-fast flux ratio irradiated in the HFBR. Only selected UMFR irradiations, designated by the F in Table 5, contained a full set of alloys; the other smaller capsules, designated as R, generally only contained a reduced subset of the CM-series.

TABLE 4 -- CC-Series Alloy Compositions and Heat Treatments

Alloy Code	Description	Composition, % by weight										PIA [§]
		C	Cu	Ni	Mn	Si	P	S	Cr	Mo	V	
OH	A588B	0.126	0.22	0.21	1.33	0.31	0.014	0.007	0.45	0.045	0.056	---
OC	HFIR A212B Archive	0.26	0.15	<0.20	0.85	0.29	0.006	0.04	0.075	0.02	0.005	cc1
ODa,b	HFIR A212B Surveillance	0.26	0.15	<0.20	0.85	0.29	0.006	0.04	0.075	0.02	0.005	cc2-4
OG	HFIR A350 Archive	0.18	0.11	3.3	0.55	0.29	0.01	0.02	0.09	0.03	0.001	cc1
OEa,b	HFIR A350 Surveillance	0.18	0.11	3.3	0.55	0.29	0.01	0.02	0.09	0.03	0.001	cc2-4
OA	Shippingport outer NST	0.23	0.05	0.04	0.76	0.27	0.02	0.03	0.04	<0.01	---	cc1
Ola,b	Shippingport inner NST	0.23	0.05	0.04	0.76	0.27	0.02	0.03	0.04	<0.01	---	cc2-4
OB	ORNL A36	0.21	0.05	0.07	1.10	0.03	0.009	0.026	0.04	0.03	0.001	cc1

[§] Post-Irradiation Anneals Before Reirradiation:

cc1 -- with and without post-irradiation anneal at 450°C, 50h

cc2 -- post-irradiation annealed 450°C, 50h

cc3 -- post-irradiation annealed 343°C, 290h

cc4 -- post-irradiation annealed 600°C, 5h

TABLE 5 -- The Irradiation Matrix

Flux (n/m ² /s)	Fluence (n/m ²)				Reactor
	2x10 ²¹	5x10 ²¹	3x10 ²²	7x10 ²²	
1.4 x 10 ¹⁴	F1§	F4	---	---	UMFR
1.8 x 10 ¹⁵	R2§	R5§	F7	---	UMFR
7.3 x 10 ¹⁵	---	R6	F8§	R9	UMFR
4.5 x 10 ¹⁷	---	---	R10	---	HFBR
5.0 x 10 ¹⁸	---	---	R12	R13	HFIR
3.8 x 10 ¹⁵	---	R11§§	---	---	HFBR

§ tested and reported in this paper;

§§ thermal/fast flux ratio ~370

The UMFR capsules were moved to remote locations during periods of reactor startups, shutdowns and variable power operation to minimize transient effects. Measurements on dummy capsules and gamma heating/heat transfer calculations indicated specimen temperatures of $60 \pm 5^\circ\text{C}$. The estimated flux and fluence ($E > 1 \text{ MeV}$) matrix is shown in Table 5. All capsules contained nickel activation wires and, generally, the large capsules contained more complete dosimeter sets including on a selected basis Al-0.1 Co, Nb, Ni, Fe, Ti, Cu, ²³⁸U and ²³⁷Np. Fluence estimates used here are based on the reactor full power hours combined with flux maps for these locations. Existing flux maps were supplemented and corrected using removable nickel dosimeter wires inserted at the beginning of the experiment. The relative fluence estimates are believed to be precise within about $\pm 20\%$ and the effects of spectral variation should be minor, with a corresponding estimate for the displacement cross section ($E > 1 \text{ MeV}$) of about $1500 \pm 150 \text{ b}$.

Post Irradiation Mechanical Testing

Static tensile tests were carried out at room temperature ($20 \pm 2^\circ\text{C}$) at a strain rate of 10^{-3} s^{-1} on an automated tensile tester. Testing involves loading twenty-nine specimens, including the calibration samples, in a precision alignment cartridge, which is positioned under pneumatically-activated, hydraulic grips by a linear stage in an Instron 1122 load

frame. The cartridge/stage also serves as the lower grip. A computer actuates the specimen positioning, gripping and loading sequence and records, plots and analyzes the load-displacement record. Displacements are monitored by an LVDT which measures the movement of the upper grip relative to the lower grip. A minimum redundancy of 2 tests was used in all cases. Although there are steel-to-steel variations, the average precision of the yield stress measurements was less than about ± 15 MPa. A limited number of post-irradiation annealing (PIA) and SANS experiments were also performed.

RESULTS

Flux and Fluence

The results of data from the four capsules tested in this program cover a range of flux from about 0.014×10^{16} to 0.73×10^{16} n/m²/s and fluences from about 0.2 to 3×10^{22} n/m². Figure 1a plots the average yield stress change versus the square root of the fluence for the base set of CM-series alloys contained in all four capsules.⁴ Note the bars on the data are not 'errors', but indicate the standard deviation of the individual $\Delta\sigma_y$ values around the average. The data closely follow a flux independent relation

$$\Delta\sigma_y \text{ (MPa)} = 92.1 \sqrt{\phi t (10^{22} \text{ n/m}^2)} - 17.7 \quad (1)$$

Figure 1b shows a similar plot for the VX, CC and L-series steels where the solid line is the fit to the CM-series data in Figure 1a. While only two data points are not sufficient to reliably establish flux-fluence dependence, the data trends are similar and consistent with hardening that is independent of flux and depends on the square root of fluence. Again, the large bars on the VX data do not indicate errors, but rather a larger variation (shown later to be due to copper differences) in the $\Delta\sigma_y$ values in the simple model steels. Given the similarity of the alloys, it is not surprising that the results for the L-series alloys are almost exactly the same as for the CM-series alloys. Figure 1c extends the flux range by comparing the CM-series data from this study with the results from the literature. The solid circles are data from Farrell et. al. for irradiations of 5 alloys (including the HFIR and Shippingport A212 B and the A36 steels irradiated in this program) in HFIR at very high fluxes of about 2 to 5×10^{18} n/m²-s [7]. The filled diamond is from samples taken from the Shippingport shield tank itself at a flux of about 2×10^{13} n/m²-s and a fluence of about 6×10^{21} n/m² [9]. Clearly all of the data follow a nearly identical trend, indicating independence of low temperature hardening

⁴ CM: 1,3,5,6,11,12,13,16,18,19,20,22

FIG. 1-- Variation of the change in yield stress with square root of fluence: a) average values of yield stress change for the CM-series alloys b) yield stress changes for the VX, CC and L-series alloys; c) comparison to results in the literature

over a flux range of more than 10^5 . Note comparisons of the individual steels are equally consistent; however, one exception (not shown) is data for the HFIR A212B steel irradiated in the Oak Ridge Research Reactor which falls considerably below data for all other irradiations [4].

Compositional Variables - Complex Steels

The effects of compositional variables for the high fluence/high flux F8 capsule irradiated to 3×10^{22} n/m² are shown in Figure 2. Table 6 summarizes these results in terms of: a) the element studied; b) the figure showing the data; c) the range of copper and or nickel in the alloys studied; d) the observed effect -- negligible (N), weak (W), moderate (M) or strong (S); and d) qualifying comments, if any. In general the influence of individual elements is negligible to moderate. The strongest effects appear to be a decrease in $\Delta\sigma_y$ by an average of about 35 MPa between both 0.040 and 0.005P (Fig. 2e) and between 0.0 and 0.5 Mo (Fig. 2f). The phosphorous effect is strongest in the high nickel alloy, with a 60 MPa difference between the high and low levels; this may indicate nickel-phosphorous interaction. The $\Delta\sigma_y$ in low nickel steel without molybdenum is consistent with that observed in similar alloys in the CC-series (Fig. 2f). The effects of several other variables appear to be weak (Mn, Figure 2g) or negligible (C - Figure 2h, Sn/Sb/As, N and B for the 0.4Cu alloy - not shown). While copper effects at high nickel and nickel effects at high copper are negligible to

TABLE 6 -- Summary of Effect of Composition in Complex Alloys

Element	Figure 2	Cu/Ni Range	Effect*	Comment
Cu	a,b	0.8	N	
Cu	b	0.0 & 1.6Ni	M	1.6Ni/0.0Cu lower
Ni	c	0.4Cu	W	
Ni	d	0.0&0.2Cu	M	
P	e	0.0Cu/0.0, 0.8 & 1.6Ni; 0.1Cu/0.8Ni	S	Ni interaction?
Mo	g	0.2Cu/0.0Ni	S	
Mn	f	0.0&0.4Cu/	W	
C	h	0.0Cu/0.8Ni	N	
B	not shown	0.4Cu/0.8Ni	N	+B @0.0Cu/0.8Ni lower
**	not shown	0.0Cu/0.8Ni	N	

* N-negligible; W-weak; M-moderate; S-strong

** Cr, Sn, Sb, As, N

FIG. 2-- Variation of yield stress change in the complex steels at 3×10^{18} n/cm² with a) Cu at 0.8 Ni; b) Cu at various Ni contents; c) Ni at 0.4 Cu; d) Ni at two Cu levels; e) P; f) Mn at two Cu levels; g) Mo; h) C at low Cu (Continued next page)

FIG. 2 -- Continued

weak (Figures 2a and c), there is some evidence of moderate copper effects at low nickel and nickel effects at low copper (Figure 2b and d).

While the individual effects of the various elements are generally modest, in combination, composition variations result in a substantial spread in the $\Delta\sigma_y$ values ranging from about 110 to 180 MPa. Figure 3a shows that while there is some scatter in the data, $\Delta\sigma_y$ for the base (Mn, Mo, B, N, C, ...) steels increases roughly linearly with the square root of the effective copper plus nickel content and is greater for high (circles) versus low (diamonds) phosphorous steels. The square root function was chosen to reflect the possible interactive effects of copper and nickel described above. The effective dissolved copper (Cu') for the 0.4 and 0.8Cu commercial alloys has been taken as 0.3 to account for pre-precipitation during tempering [2]. The effects of phosphorous, as well as manganese and nickel, were treated as linear terms in a least squares fit of the yield stress change at a fluence of $3 \times 10^{22} \text{ n/m}^2$ [$\Delta\sigma_y(3)$] to a chemistry term shown in Figure 3b and given by

$$\Delta\sigma_y(3) \approx 137 + 26\sqrt{Cu' + Ni} + 790P + 15Mn - 70Mo \text{ (MPa)} \quad (2)$$

The two data points labeled in Figure 3b fall somewhat below the trend band. However, in these cases the errors (shown) are relatively large and, hence, these data may not be inconsistent with the general trend. Even if these data are included, however, the standard error in the predicted $\Delta\sigma_y$ is only about 8 MPa. The results at $3 \times 10^{22} \text{ n/m}^2$ can be extrapolated to other fluences by combining the square root dependence of $\Delta\sigma_y$ on fluence above a threshold (Equations 1) and with the chemistry dependence at $3 \times 10^{22} \text{ n/m}^2$ (Equation 2) to obtain

$$\Delta\sigma_y \text{ (MPa)} \approx CF \left(\sqrt{\phi t (10^{22} \text{ n/m}^2)} - 0.2 \right) \quad (3a)$$

where

$$CF = 89.4 + 16.9 \sqrt{Cu + Ni} + 516P + 9.7 Mn - 45.7 Mo \quad (3b)$$

It is important to emphasize that this simple formulation is neither a unique best fit nor a physically-based model. Hence, Equation 3 cannot be reliably extrapolated or even interpolated. However, the empirical correlation does reflect the cumulative and combined effects of the most important compositional effects and clearly illustrates that composition can influence low temperature hardening.

FIG. 3-- Variation of yield stress change with: a) square root of Cu plus Ni b) a chemistry factor defined by Equation 2.

Figure 4 plots the differences in the values of $\Delta\sigma_y$ for the materials with the base and the alternative heat treatments for the CM-series. There is a slight tendency towards less hardening in the higher normalizing temperature (differences averaging 20 MPa) and following the temper embrittlement aging (differences averaging 11 MPa). No consistent pattern is observed for various salt quench temperatures (differences averaging 0 MPa). However, in general the effects of heat treatment on hardening are relatively small and within or close to the estimated error limits.

Compositional Variables - Simple Steels

The results for the simple VX-series model alloys for the high fluence/high flux F8 capsule are shown in Figure 5. Figure 5a plots $\Delta\sigma_y$ versus copper for the nitrogen and titanium variants in the simple iron based VF-series. Note, the nominal copper content is

FIG. 4 -- Comparison of the difference between yield stress change in materials given the base heat treatment and materials given an alternative heat treatment.

FIG. 5 -- Variation of yield stress change in the VX-series alloys at 3×10^{18} n/cm² with: copper for the a) VF-series, b) VM-series and c) VF and VA series

used for the model alloys since the heat treatment is expected to retain most of this element in solution. Within scatter in the data (± 15 MPa), there is little apparent effect of nitrogen or titanium. It may be notable that the iron-titanium-high nitrogen alloy had somewhat lower hardening (83 MPa) compared to either the iron-low nitrogen (127 MPa) or the iron-high nitrogen alloy (112 MPa). However, the effect of nitrogen-titanium interactions, if any, is weaker than the systematic increases in hardening with increasing copper. Similar copper trends are observed in Figure 5b for the VM alloys containing manganese and low nitrogen; however, the 0.0Cu-1.0Mn-high N alloy has a much higher $\Delta\sigma_y$ than the corresponding VF (without manganese)-high nitrogen alloy. The apparent Mn-N interaction is not observed in the VM-alloy with 0.9Cu. Figure 5c compares the $\Delta\sigma_y$ versus copper for the VC and VA steels with the simple VF-iron alloy series. No significant differences are observed. It is noted that similar trends are observed in the low flux, low fluence specimens, including the manganese-nitrogen interaction at low copper content.

The relatively strong copper effect in the simple iron alloys and steels appears to be inconsistent with the generally weaker trend in the complex steels. However, as discussed below, this is probably due to higher matrix copper concentrations and the absence of nickel in the VX-series (see below). The effect of nitrogen variations is generally minimal in both the simple model VX-series alloys without manganese and the complex CM-series steels. However, this element has been found previously to be an important factor in hardening of low copper mild steels, consistent with our observation of a strong manganese-nitrogen interaction in the simple VM alloy without copper. Further, the smaller $\Delta\sigma_y$ observed in the 0.25Ti/0.0Cu alloy may be due to a more complete gettering of nitrogen than in the nominally low nitrogen alloys without titanium. The apparent copper-manganese-nitrogen-molybdenum-titanium interaction is not understood, but may be due to a combination of: a) gettering of nitrogen in alloys with high concentrations of copper and molybdenum; and/or b) suppression of strengthening contributions from nitrogen related features due to hardening by Mo_2C and copper rich precipitate phases; and/or c) a plateau in nitrogen effects above about 10-15 ppm.

Microstructural Variables

As noted previously, alloys studied in this program cover a very wide range of microstructures and unirradiated properties, including: a) simple VX-series iron alloys and ferritic steels ($\sigma_{yu} \approx 190$ MPa); b) mild steels without secondary hardening elements ($\sigma_{yu} \approx 310$ MPa); and c) bainitic A533B pressure vessel type steels with secondary hardening

phases (Mo_2C , $\sigma_{yu} \approx 475$ MPa). The effects of microstructure/unirradiated property variations are shown in Figure 6a which plots $\Delta\sigma_y$ versus σ_{yu} for the data at 3×10^{22} n/m². The circles are for the CM and L-series, with the open symbols the base heat treatment and the triangles the alternate CM-series heat treatments. The diamonds represent the CC-series with low molybdenum and lower σ_{yu} (note the CM-steel without molybdenum also falls into this grouping). The squares represent the simple VX-series iron alloys and steels with varying amounts of copper.

The CC and CM data suggests that the lower strength steels without molybdenum (and Mo_2C phases) experience a slightly higher $\Delta\sigma_y$. However, the comparisons of the CM and VX-series to assess microstructural and yield stress effects are confounded by dissolved copper variations. Direct application of the chemistry factor in Equation 2 does not predict the high yield stress values observed in the VX-series steels. However, this is not surprising given the significant microstructural and unirradiated property differences and the fact that the empirical treatment for the complex steels is restricted to a much lower range of copper in solution. A more direct comparison is given in Figure 6b, which plots $\Delta\sigma_y$ versus copper for the 0.0Ni CM-series alloys (circles) and other CM-series steels (triangles) along with the corresponding averages for the VX-series (squares), excluding the 0Cu-1Mn-high N alloy. Here the data have been corrected to a common manganese (1.0), molybdenum, phosphorous and nickel content (0.0) using Equation 2. Recall the maximum copper content of the CM alloys was taken as 0.3 to account for pre-precipitation. The predictions of Equation 2, shown as the dashed line in Figure 6b, under-predict $\Delta\sigma_y$ for the simple VX-series model steels at higher copper contents. However, both data sets fall along the least squares fit to the VX-series data shown as the solid line.

Equation 2 is not unique and, indeed, alternate formulations (e.g. terms that are linear in copper and nickel) may fit a wider range of data. More importantly, however, cumulative and particular combinations of compositional factors influence hardening over a wide range of microstructures and unirradiated properties. In contrast, the microstructure does not appear to play a significant role, per-se, in low temperature hardening.

COMPARISON WITH OTHER DATA

While it is certainly not possible to review the entire literature, it is useful to briefly note similarities and differences between this work and the results of other studies. With regard to the effect of flux at low irradiation temperatures, long ago Barton et. al. reported a negligible effect of flux on mild steels irradiated down to 100°C in the range of about 3×10^{15}

FIG. 6 -- Variation of yield stress change with a) unirradiated yield stress and b) copper, correcting for differences in compositional variables using Equation 2.

to 3×10^{17} n/m²-s for fluences up to about 5×10^{21} n/m² [10]. A similar result was found by Hinkle et. al for low temperature irradiations of high purity (ferrovac) iron at higher fluence [11]. Based on these and other data, Buswell et. al. have proposed a temperature dependent-flux independent matrix hardening model, which is presumably applicable down to the low temperatures in this study [12]. Yield stress data reported on the Shippingport steels by Chopra et al. [9] versus Hawthorne and Rosinski [13] could be interpreted to indicate a moderate flux effect (e.g. 51 MPa versus 28 MPa elevations for low and high flux irradiations, respectively). However, the more extended range of data for this steel in this work did not reveal a significant flux effect (note, based on transition temperature shifts, these workers also concluded that there was no flux effect).

With regard to composition effects, a large body of 60°C hardening data reported by Nikolayev et. al on both simple model alloys and complex Cr-V-Mo Russian VVER steels is qualitatively consistent with the effects of copper, nickel and manganese we have observed [14]. However, these irradiations were at a much higher fluence ($>10^{19}$ n/cm²) and, in general, Nikolayev et. al. found the relative effects of individual elements to be larger than observed in this study. Further, these workers did not observe a hardening effect of phosphorous or molybdenum found in this work. Barton et. al observed a metallurgical sensitivity in mild steels which they attributed to the free nitrogen content [10]. With the exception of the 0.0Cu-1Mn-high N model alloy, nitrogen effects were not seen in this study. More recent studies by Farrell and coworkers have observed effects of copper and nickel in simple model steels which increased with increasing fluence [7]. However, contrary to our results, these workers suggested that composition did not influence the corresponding low temperature hardening in complex alloys. A similar conclusion concerning both simple and complex steels was reached by Boydon et. al. for 70°C irradiations to high fluence (note, however, they also find a phosphorous effect in low copper model steels) [15]. Hawthorne also reports a lack of compositional sensitivity for low fluence, low temperature irradiations of complex steels [16]; he had also previously reported a lack of sensitivity for low temperature irradiations to phosphorous but not copper [17, 18]. The data of both Farrell and Hawthorne on complex steels may be confounded by uncontrolled variables and a detailed analysis of the type presented here has not yet been carried out on the data reported by Boydon et. al.

In summary, within experimental error and considering possible confounding factors, the present results are generally consistent with most data in the literature. However, in contrast to some conclusions of other workers, the systematic, single variable experimental matrix employed here reveals subtle but significant effects of composition. This

compositional sensitivity is different than that observed at higher temperatures and suggests dominance of a different type of hardening feature, viz., a matrix type defect due to a cut-off of precipitation resulting from long range copper diffusion below about 150°C (this matrix type defect is also observed at the higher temperatures in conjunction with copper precipitates in steels with significant trace quantities of this element).

DISCUSSION -- SOME POSSIBLE HARDENING MECHANISMS

The observations in the previous section can be summarized as follows. Irradiation hardening at 60°C varies with the square root of fluence above an extrapolated threshold around 4×10^{20} n/m² up to the maximum fluence in this study of about 3×10^{22} n/m². The hardening is remarkably independent of flux over a range from about 2×10^{13} n/m²-s to 5×10^{18} n/m²-s. However, hardening is dependent on compositional factors including phosphorous, molybdenum, manganese, copper, nickel and nitrogen (the latter only in simple model alloys containing manganese). While not unique, the compositional effects in the data base can be represented by a simple empirical chemistry factor that reflects hardening behavior over a wide range of alloy types and conditions. This suggests the operation of a common mechanism.

The dominant mechanism must be consistent with: a) the observed dependence on flux, fluence, composition and irradiation temperature [8]; b) the magnitude of hardening; c) limited microstructural data; and d) the annealing response. It is clear that the hardening is due to very small features since they have not been imaged by TEM in this fluence range and result in very weak SANS signals (see below). The insensitivity to coarser scale microstructures is consistent with highly localized damage production. The square root fluence dependence is also consistent with the number of dispersed barrier dislocation obstacles increasing in proportion to fluence. Together these observations suggest that the hardening features are formed in displacement cascades. Assuming a rate of one for every two cascades, a fluence of 3×10^{22} n/m² would produce about 4×10^{23} /m³ obstacles (N) with an estimated diameter (d) of about 1.5 nm. The obstacle hardening efficiency (β) can be approximated as $\beta \approx \Delta\sigma_y / 3Gb\sqrt{Nd}$. For a typical $\Delta\sigma_y = 150$ MPa, $\beta \approx 0.1$. This value is consistent with previous estimates for very small defect clusters or cluster complexes [19]. Significant hardening recovery following a short 4 h post irradiation anneal is observed at 300°C and approaches 100% at 400°C⁵. Small vacancy clusters would anneal in this temperature range also resulting in the dispersion of complexed solutes.

⁵ This discussion cites limited data generated in our program.

Preliminary SANS measurements reveal very weak scattering in the complex L-series steels⁵. The failure to observe copper rich precipitates (CRP) is consistent with the previously proposed cut-off in precipitation by long range copper diffusion at low temperatures [8]. Notably, the SANS signal decreases with increasing copper and nickel content: the magnetic scattering is independent of nickel but decreases with increasing copper; nuclear scattering decreases with increasing nickel but is independent of copper. Annealing at 400°C for 4h coarsens the scattering centers. In contrast to the commercial type steels, scattering in simple iron-copper alloys increases with increasing copper. The scattering magnitudes and ratios of nuclear-to-magnetic scattering are consistent with vacancies complexed with dilute atmospheres of copper.

Taken together, these observations are broadly consistent with low temperature hardening features formed in isolated displacement cascades composed of relatively dilute atmospheres of solutes (manganese-nickel-copper...) surrounding a very small vacancy cluster (a looser sponge-like arrangement may also be possible but is thermodynamically less likely). The co-clustering of vacancies and copper at the core of cascades has been previously modeled [20]. Significant copper segregation occurs due to a small binding energy with both vacancies and free surfaces. The segregated copper lowers the free surface energy, thermally stabilizing the small clusters. Even in relative small concentrations, the complexed solutes may also increase the hardening efficiency of the cascade features. Dilute solute clusters following elevated temperature irradiations have been observed in FIM/AP studies [21]. Co-clustering may also be the mechanism for CRP nucleation at low copper concentrations [20, 21].

In spite of this general consistency, other possible mechanisms should be considered. For example, small interstitial clusters produced directly in displacement cascades would act as dislocation obstacles. Interstitial clusters may also be complexed with solutes. While interstitial clusters have high binding energies and would not be expected to recover quickly by normal self-diffusion controlled processes at 400°C, immobile interstitial clusters could co-anneal with vacancy clusters. More significantly, however, it is now known that small interstitial clusters are highly mobile in perfect iron lattices; thus recovery might be due to thermally activated release of interstitial clusters from trapping sites [22].

Compositional effects may also be mediated by other mechanisms. For example the effect of molybdenum is probably related to the presence (or absence) of Mo₂C secondary hardening phases. Post-irradiation annealing studies and computer simulations have suggested that superposition of a significant hardening contribution from such strong dislocation obstacles may decrease the effective hardening efficiency of weaker radiation induced barriers [23].

HARDENING FROM GAMMA-RAYS AND ELECTRONS -- A CONUNDRUM

The most significant residual question relates to the accelerated embrittlement in HFIR which now seems unlikely to be due to flux effects. Recent suggestions that displacement damage from very high fluxes of high energy gamma rays appears to be the most plausible explanation [6,7]. However, gamma-rays, along with electrons and thermal neutrons produce low energy primary recoil atoms, yielding isolated defects rather than cascades. Similar hardening in electron versus neutron irradiations at the same dpa have also been reported for both commercial steels and simple Fe-Cu alloys [23]. Some recent preliminary data in this program (capsule R11) shows extra hardening apparently due to thermal neutrons in mixed spectrum irradiations, consistent with enhanced residual defect production relative to fast neutrons by a factor of about two. Hence, while a near-dpa equivalence provides some level of rationalization of the HFIR data, the gamma ray, electron and thermal neutron results seem to be inconsistent with the proposed cascade mechanism. An alternative explanation is that the irradiations yielding low energy primary recoil atoms harden by an entirely different mechanism. Hardening depends on a combination of factors including: a) the type and fate of the defects (i.e. migrating free defects, immobile clusters, diffusional clustering, recombination or loss to sinks); b) the defect production efficiency; and c) respective hardening efficiencies of the induced features. This conundrum can only be resolved by additional research on the mechanisms and microstructures of hardening.

CLOSING REMARKS -- IMPLICATIONS TO SUPPORT STRUCTURE EMBRITTLEMENT

A major motivation for this study was the concern about the potential for accelerated embrittlement of support structures irradiated at low temperatures and fluxes to exposures in the range of 4 to 6 mdpa (equivalent to about 2.5 to 4×10^{22} n/m^2 $E > 1$ MeV). The remarkable insensitivity of hardening to flux that was observed in this work should largely resolve this issue, although the data at very low fluxes are limited. However, while accelerated embrittlement is unlikely, substantial shifts may still occur under support structure irradiation conditions. At the highest fluence, molybdenum free steels with high phosphorous would be predicted to have a $\Delta\sigma_y$ of about 200 MPa or more depending on the nickel content. Based on a typical shift/hardening coefficient of $0.6^\circ\text{C}/\text{MPa}$ [2, 4, 22], the

corresponding transition temperature elevations would be 120°C. The significance of such shifts to the integrity of support structures should be evaluated.

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