A Novel Approach to Materials Development for Advanced Reactor Systems
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Annual Report for Year 1

Program goals for Year One

Year one of this project had three major goals. First, to specify, order and install a new high current ion source for more rapid and stable proton irradiation. Second, to assess the use of chromium pre-enrichment and the combination of cold-work and irradiation hardening in an effort to assess the role of radiation damage in IASCC without the effects of RIS. Third, to initiate irradiation of reactor pressure vessel steel and Zircaloy.

Program Achievements for Year One

Progress was made on all 4 tasks in year one.

Task 1. High current Ion source

The ion source was installed, tested and accepted in June of 2000. This source provides 3 to 5 times the ion current as the existing source and is considerably simpler to operate and easier to maintain. We will be utilizing the new source in years 2 and 3 of this project and we will be testing the limits of the source in terms of the maximum current available for experimentation. Factors which may limit the total amount of current on target include 1) the heat removal capability of the irradiation stage (this has been improved as well), and 2) the prompt radiation dose in the lab, which will increase in proportion to the ion current. Any problem with radiation level is anticipated to be a temporary problem until additional shielding can be installed.

Task 2. Isolation of the radiation damage microstructure in stainless steel

This task focused on two strategies for assessing the role of the radiation damaged microstructure in IASCC of stainless steel. In the first, we will make use of the tendency for chromium to pre-segregate to grain boundaries during the processing stage in order to maintain the grain boundary Cr level during subsequent irradiation. While the concentration of other elements at the grain boundary may change (enrich or deplete), the Cr concentration will be designed to remain at or above the nominal level, thus removing chromium depletion from consideration as a factor in the IASCC behavior. To date, we have completed a series of heat treatments designed to induce grain boundary Cr segregation. The heat treatments vary the cooling rate in order to bracket the condition for maximum non-equilibrium segregation. Subsequent experiments will focus on characterizing the Cr segregation profiles and assessing the behavior of the profile under

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irradiation. The final step will be to assess the role of the irradiation damaged microstructure in IASCC given a grain boundary Cr level that is near the bulk level.

The second strategy involves the production of a series of samples of fixed hardness but with varying amounts of hardening from radiation damage. This will be accomplished by interchanging cold-work and irradiation to achieve the same nominal hardness. The objective of this series of experiments is to determine if hardening alone is responsible for IASCC or if IASCC is specific to the microstructure. Thus far, we have produced samples with cold-work levels of 0%, 10%, 20%, 35% and 50%. The hardness of the 50% CW sample is designated as the nominal hardness level and the difference between that hardness and the hardness of each of the other cold-worked samples will be made up by irradiation to pre-determined doses. Subsequent experiments will focus on irradiation to the target doses, followed by hardness measurement, microstructure characterization and IASCC testing.

Task 3: Proton Irradiation of Zircaloy

Three types of Zircaloy samples were prepared for shipment by Dr. James Dougherty at Western Zirconium, Zircaloy 2, Zircaloy 4 and ZIRLO (containing Fe, Sn and Nb). They are due at the University of Michigan at the end of September 2000. Table 1 contains their respective compositions. Their nominal thickness is 0.025". If the samples are not sufficiently rigid to allow adequate heat sinking on the irradiation stage, design modification will be carried out to allow mounting shorter samples. Table 2 contains information on typical mechanical properties at room and elevated temperature, as well as texture and second-phase particle sizes for the Zircaloy batches to be used. The parameter $f(x)$ is a measure of the volume fraction of the alloy with basal planes aligned in the direction x , where l , t and n represent longitudinal, transverse and normal.

Preliminary TEM characterization of Zr samples has been conducted in order to establish the sample preparation and analysis methods.

Task 4. Proton irradiation of model alloys of RPV steels

The objective of this task is to assess the capability of proton irradiation to emulate neutron irradiation of pressure vessel steels. The irradiated microstructure and hardening are the two principal material property changes that will be used to assess the effectiveness of proton irradiation. The major effect of irradiation of pressure vessel steels is radiation hardening due to the formation of very small defect clusters or precipitates. The hardening behavior can be readily assessed using microhardness indentation techniques. The assessment of the microstructure is much more challenging due to small size of the clusters which are generally not observable by direct imaging techniques such as TEM. Hence, techniques such as small angle x-ray scattering must be used to determine the properties of the clusters responsible for the hardening.

The effectiveness of proton irradiation in emulating neutron irradiation effects can only be determined if neutron irradiation data exist on the *exact* same alloys. In this way,

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variability in material response due to differences in composition and microstructure are eliminated. We chose to do our experiments on a series of alloys made by Robert Odette of the University of California at Santa Barbara. These alloys have been well characterized both before and after neutron irradiation, thus providing an ideal database. Further, the alloys are relatively simple binary, ternary and quaternary systems that represent a systematical variation of the key alloying additions that are believed to affect hardening behavior. Our experiments focused on 3 alloys, initially, a pure Fe alloy (VA), a Fe-0.9Cu (VH) alloy and a Fe-0.9Cu-1.0Mn (VD) alloy.

Irradiations were conducted at 300°C and a dose rate of 7×10^{-7} dpa/s to doses in the range 0.001 to 0.01 dpa, Table 3. Following irradiation, hardness was measured using a Vickers hardness indenter. Results of all hardness measurements are shown in Table 4, and are compared to results of neutron irradiation and electron irradiation in Fig. 1. As shown in Fig. 1, the agreement with neutron irradiation data is excellent over the entire dose range of 0.001 to 0.01 dpa for both the VD and the VA alloy. The large difference in hardening between the two alloys is likely due to the formation of small precipitates in the VD alloy compared to only dislocation hardening in the VA alloy. Subsequent annealing of the 0.01 dpa VD alloy at 450°C for 24 hrs resulted in a drop in hardness by about 25 MPa or about 30% of the as-irradiated hardness increase. These values are in good agreement with annealing data on a neutron irradiated 0.35Cu-0.6Ni model alloy that experienced 40% recovery of the as-irradiated hardness increase after the same time at temperature. The magnitude of the hardness drop is further indication that the irradiated microstructure is likely due to precipitate hardening. The drop in hardness is likely due to precipitate coarsening.

Small angle x-ray scattering (SAXS) was used to begin the characterization of the microstructure. SAXS is ideal for these samples as the sample thickness requirement matches our sample thickness extremely well, about 30 microns. Samples were prepared as described in the fourth quarterly report and the experiment was conducted at the Advanced Photon Facility in collaboration with Dale Alexander of Argonne National Laboratory. Results of SAXS on the 0.001 dpa and the 0.01 dpa VD samples were analyzed using the Guinier approximation. Both low and high dose data provided good fits to a linear regression, yielding precipitate sizes of about 0.71 nm for the low dose case and 1.6 nm for the high dose case. The low dose value is smaller than that measured after electron irradiation to the same dose, but the high dose value is in good agreement with neutron data on the same alloy to the same dose. Taken together, these data indicate that the precipitate size/density combination is similar to that following neutron or electron irradiation in the same dose range. The next experiments planned will investigate the effects of dose rate and temperature on hardening in the VD alloy and also the VH alloy.

Experimental Uncertainties and Goals Not Achieved in Year One

Overall, the progress in year 1 was on track with the 3 year schedule. Task 1 was completed in year 1 as planned. However, delays in the ordering of the source due to extended negotiations with the supplier, an extension of the delivery time by the supplier

and a late delivery resulted in source installation at the end of the year. Therefore, the new source was not utilized in year 1 and this caused a delay with some of the experiments in task 2. The new source was operational as of the end of the year and will be used in years 2 and 3 as planned.

Planned irradiations in task 2 were not conducted due to difficulty in procuring the alloys and the late arrival of the ion source. However, material processing for chromium pre-enrichment and for cold work was completed and characterization and irradiation are scheduled to begin at the start of year 2.

Progress on Task 3 was on track. The goal for this task was the procurement of material, the establishment of the metallurgical condition and the pre-characterization. With the help of Ron Adamson (formerly of GE), heats of Zircaloy-2 and Zircaloy-4 with pre-characterized precipitate distributions have been procured and irradiations will begin in year 2 as planned.

Task 4 progressed extremely well and considerably more was accomplished than anticipated. The progress was aided by the selection of pre-existing model alloys (Bob Odette, UCSB) and the assistance afforded by Dale Alexander in initiating the SAXS experiments.

Table 1. Average ingot compositions for sample material, obtained from five positions along ingot length.

INGOT (alloy)	Sn (%)	Fe (ppm)	Cr (ppm)	Ni (ppm)	Nb (%)
U04805P (ZR-4)	1.35	2087	1134	--	--
U04271L (ZR-2)	1.29	1646	1043	644	--
U04755Z (ZIRLO)	1.08	939	--	--	0.96

Table 2. Properties of Zircaloy sample material. The parameter $f(x)$ is a measure of the volume fraction of the alloy with basal planes aligned in the direction x , where l , t and n represent longitudinal, transverse and normal.

ALLOY	MAJOR ELEMENTS	GRAIN SIZE (ASTM)	UTS / YS / %E (ksi)	SECOND-PHASE PARTICLE SIZE (microns)	CRYSTALLOGRAPHIC TEXTURE
ZR-4	Sn, Fe, Cr	10	L = 65 / 50 / 32% (RT) T = 64 / 52 / 34% (RT) L = 28 / 16 / 50% (315 °C) T = 27 / 17 / 48% (315 C)	.20	$f(l) = 0.10$ $f(t) = 0.15$ $f(n) = 0.75$
ZR-2	Sn, Fe, Cr, Ni	12.5	L = 77 / 62 / 32% (RT) T = 72 / 66 / 30% (RT) L = 38 / 30 / 50% (288 °C) T = 34 / 28 / 43% (288 °C)	.06	$f(l) = 0.07$ $f(t) = 0.25$ $f(n) = 0.68$
ZIRLO	Sn, Nb, Fe	10	L = 72 / 57 / 32% (RT) T = 69 / 62 / 30% (RT) L = 38 / 22 / 42% (315 °C) T = 34 / 25 / 36% (315 °C)	.06	$f(l) = 0.08$ $f(t) = 0.22$ $f(n) = 0.70$

UTS – ultimate tensile strength

L – longitudinal

T – transverse

RT – room temperature

Table 3. Proton irradiation plan for alloy VA, VD and VH

Irrad. No.	Sample No.	Dose (10^{-3} dpa)	Dose rate (10^{-7} dpa/s)	Irradiation temp. ($^{\circ}$ C)	Irradiation time (min)	Fluence (ions/cm 2)	Counts: (6.28×10^{12} ions)	Flux (ions/cm 2 /s)	Current (μ A)
1*	VD1-4 VA1,2#	10	7×10^{-7}	300	240	1.02×10^{17}	26000	7.11×10^{12}	1.82
2*	VD5,6 VA3,4	3	7×10^{-7}	300	72	3.06×10^{16}	7800	7.11×10^{12}	1.82
3*	VD7,8 VA5,6	1	7×10^{-7}	300	24	1.02×10^{16}	2600	7.11×10^{12}	1.82
4	VD9, 10 VH7,8	100	7×10^{-7}	300	2400	1.02×10^{18}	260000	7.11×10^{12}	1.82
5	VD11,12 VH9,10	10	7×10^{-6}	300	24	1.02×10^{17}	26000	7.11×10^{11}	18.2
6	VD13,14 VH11,12	10	7×10^{-7}	330	240	1.02×10^{17}	26000	7.11×10^{13}	1.82
7	VD15,16 VH13,14	10	7×10^{-7}	360	240	1.02×10^{17}	26000	7.11×10^{11}	1.82

* irradiation completed
irradiation not yet completed

Table 4. Hardness and yield strength changes in alloys VA and VD following proton irradiation at 7×10^{-7} dpa/s and 300°C.

VD alloy					VA alloy			
Dose (dpa)	H_v^{irrad} (kg/mm ²)	ΔH (kg/mm ²)	$\Delta\sigma$ (MPa)	$\Delta\sigma_{\text{avg}}$ (MPa)	H_v^{irrad} (kg/mm ²)	ΔH (kg/mm ²)	$\Delta\sigma$ (MPa)	$\Delta\sigma_{\text{avg}}$ (MPa)
0.001	159.0	53.0	192		92.2	9.7	35.1	
	157.0	51.0	185	189	91.9	9.4	34.0	34.6
0.003	165.2	59.2	216		91.5	9.0	32.6	
	166.7	60.7	220	218	92.2	9.7	35.1	33.9
0.01	184.8	78.8	285					
	190.8	84.8	307	296				
0.01+ 450°C/24 hrs	176	61.0	221	221				

H_v^0 for alloy VD = 107 kg/mm², H_v^0 for alloy VA = 82.5 kg/mm²

$\Delta\sigma$ (MPa) = 3.62 x ΔH (kg/mm²)

Figure 1. Yield strength increase as a function of dose for several alloys and several irradiating particles (n=neutron, p=proton, e=electron).

The table and chart below show the progress of the experimental program. Dates in bold indicate a change from the third quarter report.

Planned and Actual Completion Date of Major Tasks for the Entire Program

Milestone/Task Description	Planned Completion Date	Status
1. Installation the high current ion source	6/30/00	Complete
2. Isolation of microstructure in stainless steel	8/31/02	In Progress
Establish heat treatments for pre-enrichment	2/28/00	Complete
Conduct heat treatment, STEM analysis, irradiation	2/28/01	Year 2
Establish and perform CW to various levels	6/30/2000	Complete
Irradiate, TEM, hardness	11/20/00	Year 2
CERT testing	8/31/02	Years 2 and 3
3. Proton irradiation and characterization of Zircaloy	8/31/02	In Progress
Alloy specification, procurement, sample preparation, precharacteriz.	11/30/00	Year 2
Irradiation, TEM, hardness measurement	8/31/00	Years 2 and 3
4. Proton irradiation and characterization of RPV steel	8/31/02	In Progress
Alloy specific., procurement, sample fabric.	2/28/00	Complete
Irradiation, hardness measurement, TEM, SASX	8/31/02	Substantial progress made

Phase 1 Tasks

Milestone/Task Description	Planned Completion Date	Status
1a, b Installation the high current ion source	6/30/00	Complete
2a Chromium pre-enrichment	2/28/01	In Progress
2b Variable CW/irradiation	2/28/01	Year 2
3a-d Zircaloy preparation through precharacterization	8/31/00	Complete
4a-d RPV steel preparation through precharacterization	8/31/00	Complete

Updated Task time schedule by project year (time increments in quarters)
(items in bold indicated completed task)

	Quarter											
Task	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
1	_____											
1a	_____											
1b			_____									
2	_____											
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Cost Performance:

The figure below shows the spending profile over the first year of this project. Spending is on track.