A Novel Approach to Materials Development for Advanced Reactor Systems

NERI Project # 99-0101

DE-FG03-99SF21927/A000

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Quarterly Progress Report

Year 1; Quarter 3

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Overall 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 low temperature irradiation and chromium pre-enrichment in an effort to isolate a radiation damage microstructure in stainless steel without the effects of RIS. Third, to initiate irradiation of reactor pressure vessel steel and Zircaloy.

Program goals for Third Quarter, Year One

In year 1 quarter 3, the project goal was to complete irradiation of model alloys of RPV steels for a range of doses and begin sample characterization. We also planned to prepare samples for microstructure isolation in stainless steels, and to identify sources of Zircaloy for irradiation and characterization.

Program achievements for third Quarter, Year One

Task 1: RPV Steel Irradiation

The initial plan calls for 7 irradiations (4 samples per irradiation) at different values of the key irradiation parameters of dose, dose rate and temperature, table 1. To date, we have completed three irradiations to a dose of 0.001, 0.003 and 0.01 dpa, at a dose rate of 7×10^{-7} dpa/s and at a temperature of 300°C. Irradiations at the two lowest doses were conducted on alloys VA (Fe only) and VD (Fe-0.9Cr-1.0Mn), and the highest dose was conducted on alloy VD only.

Hardness Measurement

Hardening of the irradiated samples is an indication of the precipitation of copper rich phases during irradiation. We used a Vickers hardness indenter with a 25 g load and a 20 sec loading time. At least 20 indents were made for each material condition. Hardness

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is reported in units of kg/mm^2 and the hardness increase is also converted to yield strength increase using the relation [1]:

$$\Delta\sigma_y [\text{MPa}] = 3.62 \Delta H [\text{kg/mm}^2].$$

Results are presented in the table 2 and compared to those from neutron irradiation in Figure 1. The unirradiated hardness values for each alloy represent an average of the values of several different samples. Results for the VD alloy are very encouraging in that both the magnitude of the hardness increase and the trend with dose is very similar to that found after neutron and electron irradiation. The amount of hardening at all dose levels is essentially indistinguishable from that due to neutrons. Of equal interest is the hardening of the VA alloy (Fe only), which is similar to that of the Fe-1.0Mn alloy irradiated with neutrons. The fact that the hardness increase is only about 1/6 that of the Fe-Cu-Mn alloy at the same dose indicates that something other than radiation damage is contributing to the hardening of the Fe-Cu-Mn alloy. Given the magnitude of the hardness increase, the likely cause is precipitation of Cu-rich clusters.

Microstructure investigation

As a first step in characterizing the microstructure, we began sample preparation and initial analysis of the unirradiated and irradiated samples with small angle x-ray scattering (SAXS) with the help of Dale Alexander at Argonne National Laboratory. Samples of alloy VD irradiated to 0.001 dpa, 0.01 dpa and unirradiated were prepared for SAXS. The samples are scheduled for analysis in June, 2000 at the Advanced Photon Source at ANL. Results of the analysis are expected to yield information on the size and density of precipitates for comparison to data on neutron- and electron-irradiated samples of the same alloy.

Task 2: Identification of Zircaloy Alloys for Irradiation and analysis

Our effort on Zircalloys concentrated on planning of future experiments and identifying sources of material. In preparation for our research, we have communicated with Dr. Ronald Adamson (consultant, formerly of General Electric Nuclear energy). He visited the University of Michigan to give a seminar about his work on Zircalloys at GE. We have incorporated his input into our research plans.

The main process that limits Zircaloy performance is corrosion. Under the current design, uniform corrosion is the main obstacle. In order to accommodate the push for higher burnup, it will be necessary to increase the average size of precipitates so that they

survive at higher burnups and prevent uniform corrosion. However, such a change will decrease the resistance to nodular corrosion, since such resistance is enhanced by precipitate dissolution. This indicates a likely need to find an optimum precipitate size and size distribution.

The main first goal will be to establish the conditions of proton irradiation, which yield microstructural changes similar to those observed in neutron-irradiated Zircalloys. Both Zircaloy 2 and Zircaloy 4 will be investigated. Specific alloys will be selected for which neutron damage has been characterized extensively. Given the proton irradiation geometry, specimens will be used that are flat as received or flattened and stress relieved. Because the effect of corrosion is within a few μm of the surface, we will be able to obtain high displacement rates by using energies of 1-2 MeV, significantly below the energy we have used for studies of intergranular cracking. This fact, in combination with the new ion source, will enable us to reach total damage in excess of 10 dpa within a reasonable length of time. The range of irradiation temperatures will be above that in the reactor in order to account for the higher displacement rates. The potential presence of hydrogen will be investigated, but it is unlikely because of the high mobility of hydrogen in Zr at the irradiation temperature.

Initially, samples will be characterized for the precipitate size distribution, dissolution and amorphization. Once the appropriate irradiation conditions have been identified, the hardness and corrosion behavior will be determined. The oxide thickness will be determined by cross-sectional scanning electron microscopy. At a later point, after sufficient experience is gained with proton irradiation of well-characterized Zircalloys, new modifications designed for high burnup will be investigated.

Direct observation of precipitates in Zircaloy with transmission electron microscopy has been very difficult due to the small and/or coherent nature of the precipitates in the matrix. However, the most recent development and improvement of the field emission gun transmission electron microscopes (FEG TEM) has pushed the evolution of electron microscopy through a new milestone. The University of Michigan has recently obtained such a state-of-the-art FEG TEM through a NSF grant with UM matching funds. This modern FEG TEMs is equipped with a scanning TEM system (STEM) with a high angle annular dark-field (HAADF) detector and a Gatan energy filter (GIF) in addition to an energy dispersive x-ray spectrometer (EDS). The combination of the above extends the image resolution, energy resolution, and analytical sensitivity to remarkable heights, ideal for the analysis of local variation in structure and chemistry at nanometer to atomic scale. For example, the STEM system of the microscope is capable of focusing an electron probe at the specimen with a probe size under 1 nm (as small as 0.15 nm) but still

providing a current approximately 1 nA (15 pA at 0.15 nm). The extremely small probe size and high beam current allow the acquisition of two dimensional chemical information (elemental maps) within seconds or minutes. Further, with a beam spot less than 0.2 nm in size, the HAADF technique is capable of atomic resolution Z-contrast imaging. With the GIF system, elements can be mapped with 512 x 512 pixel resolution in 1 minute or less using advanced mapping software, and electron energy loss spectra with a range from 50 eV to 1 keV and less than 1 eV energy resolution can be collected in parallel on a CCD camera. The advanced electron optics of the imaging filter and high sensitivity of the CCD camera combine to deliver the most sensitive elemental analysis possible (<0.1 at. %) in an electron microscope. The installation of this new microscope has just been completed in June 2000 and we have started to be trained on using it. We will fully utilize this added resource at UM during the next year to study the evolution of irradiation-induced evolution of precipitates in proton-irradiated Zircaloy and the RPV steel model alloys. In addition, in situ TEM during ion irradiation using the IVEM-Tandem DOE User Facility at Argonne National Laboratory will be conducted to study the evolution (amorphization and dissolution) of precipitates in Zircaloy for establishing a structure-corrosion property relationship for proton irradiated Zircaloy.

References

1. G. R. Odette and G. E. Lucas, Irradiation embrittlement of reactor pressure vessel steels: mechanisms, models, and data correlations, in Radiation Embrittlement of Nuclear Reactor Pressure Vessel Steels: an international review, Vol. 2, p.206, American Society for Testing and Materials, Philadelphia, PA 1986.
2. D. E. Alexander, G. R. Odette, "Understanding the Role of Defect Production in Radiation Embrittlement of Reactor Pressure Vessels," Proc. 9th International Conference on Environmental Degradation of materials in Nuclear Power Systems Water Reactors, Newport Beach, CA, August 1-5, 1999, in press.

Table 1. 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. ($^{\circ}\text{C}$)	Irradiation time (min)	Fluence (ions/cm 2)	Pulse Counts: N_p (6.28×10^{12} ions)	Flux (ions/cm 2 /s)	Current (μA)
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 VA7,8	100	7×10^{-7}	300	2400	1.02×10^{18}	260000	7.11×10^{12}	1.82
5	VD11,12 VA9,10	10	7×10^{-6}	300	24	1.02×10^{17}	26000	7.11×10^{11}	18.2
6	VD13,14 VA11,12	10	7×10^{-7}	330	240	1.02×10^{17}	26000	7.11×10^{13}	1.82
7	VD15,16 VA13,14	10	7×10^{-7}	360	240	1.02×10^{17}	26000	7.11×10^{11}	1.82

* irradiation is completed

not yet done

Table 2. 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	296	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	189				

H_v° for alloy VD = 107 kg/mm², H_v° for alloy VA = 82.5 kg/mm²
 $\Delta \sigma$ (MPa) = 3.62 x ΔH (kg/mm²)

Planned and Actual Completion Date of Major Tasks

Task	Planned Completion Date	Actual Completion Date
1. Installation of the high current ion source	6/30/2000	
2. Isolation of microstructure in stainless steel	8/31/01	
3. Proton irradiation and characterization of Zircaloy	8/31/02	
4. Proton irradiation and characterization of RPV steel	8/31/02	

Task time schedule by project year (time increments in quarters)

Estimated expenditures for the period: March 1, 2000 through May 31, 2000

Salaries:	\$13,084
Fringe Benefits	2,166
Supplies	35367
Travel	1,229
Indirect Cost	11,290
Tuition	<u>92.69</u>
TOTAL	\$33,227

At the three-quarters point of the project, expenditures constitute 81% of the total budgeted for the fiscal year.