OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Dr. Jeremy T. Busby
Fuel Cycle and Isotopes Division
P.O. Box 2008, MS6138
Oak Ridge, TN 37831-6138
Telephone: (865) 241-4622
Fax: (865) 241-3650
E-mail: busbyjt@ornl.gov

March 21, 2014

Dr. K. McCarthy
Director, TIO for LWR Sustainability
Idaho National Laboratory
2525 Fremont Avenue
Idaho Falls, ID 83415

Subject: Completion of LWRS Level 3 Milestone (M3LW-14OR0406023) "Status update of advanced alloys for Advanced Radiation Resistant Materials program", due 3/21/2014.

Dear Madam:

This letter is to inform you of completion of Milestone M3LW-14OR0406023 – "**Status update of advanced alloys for Advanced Radiation Resistant Materials (ARRM) program**" for the Advanced Replacement Alloys work-package within the LWRS Materials Aging and Degradation Pathway. As noted in previous reports and presentations on this topic, advanced replacement alloys with superior radiation resistance would greatly reduce the occurrence of component replacement and improve safety margins.

According to the roadmap report of the ARRM program, *"Critical issues report and roadmap for the advanced radiation-resistant materials program" EPRI, Palo Alto, CA and the U. S. Department of Energy, Washington, DC: 2012. 1026482*, a series of commercial and advanced alloys have been identified and are being procured to implement the comprehensive testing plan outlined in the report. EPRI-GE is leading the procurement of commercial alloys, including C22, 690, 625, 625-plus, X-750, 725, 718, 800, 309/310, Zr-2.5Nb, and Ti alloy (Grade 26 with 0.1Ru). Six of the eleven commercial alloys have been procured. Procurement of the rest commercial alloys is in progress.

ORNL is leading the procurement of the advanced alloys, including customized Grade 92 (9Cr ferritic-martensitic (FM) steel), customized alloy 439 (high-Cr ferritic stainless steel), 14YWT oxide-dispersion-strengthened (ODS) alloy, and two unidentified alloys from the alloy groups of 12Cr FM steel and high Cr-high Al ODS alloy, respectively. The customized Grade 92 and alloy 439 have being procured from the R&D Department of Carpenter Technology Corporation. The 14YWT ODS alloy is being fabrication at ORNL. The three advanced alloys will be available in March-May of 2014. Additionally, reference alloys of 304L, 316L, and T92 (NF616) are being procured. The procurement status of the alloys is reported in the appended report.

If you have any comments or questions, please contact me. Thank you.

Sincerely,

Dr. Jeremy T. Busby

Senior Research Scientist
Oak Ridge National Laboratory

CC: D. Williams, ORNL
T. Rosseel, ORNL
D.T. Hoelzer, ORNL
L. Tan, ORNL

(M3LW-14OR0406023) Status update of advanced alloys for Advanced Radiation Resistant Materials (ARRM) program

L. Tan, D.T. Hoelzer, and J.T. Busby
Oak Ridge National Laboratory

1. Introduction

The EPRI report of "Critical Issues Report and Roadmap for the Advanced Radiation-Resistant Materials Program" [1] reviewed the current commercial and advanced alloys that are applicable to be used as core structural materials of Light Water Reactors (LWRs). A number of alloys were down-selected as candidate materials to be tested in the ARRM program, managed by Drs. R. Pathania of EPRI and J.T. Busby of ORNL. Procurement of high quality alloys of the candidate materials is essential to successfully implement the program. The identified alloys that are to be procured are classified into two categories as commercial alloys and advanced alloys, listed in Table 1. Commercial reference alloys are also listed in Table 1.

Table 1. Identified commercial, advanced, and reference alloys to be procured for testing in the ARRM program.

	Commercial Alloys
Ni-base	C22, 690, 625, 625-plus (age hardened), X-750, 725, 718
Austenitic	800, 309/310
Others	Zr-2.5Nb, Ti alloys (Grade 26 with 0.1 Ru)
	Advanced Alloys
9Cr FM[1]	Grade 92
12Cr FM	To be determined, *e.g., HT-9, HCM12A*
High-Cr (>14Cr) Ferritic	439
9-14Cr ODS[2]	14YWT
High Cr-High Al ODS	To be determined, *e.g., PM2000, MA956, 16-ODS*
	Reference Alloys
Austenitic	304L, 316L
9Cr FM	T92 (NF616)

[1] FM: ferritic-martensitic
[2] ODS: oxide-dispersion-strengthened

EPRI and GE are leading the procurement of the commercial alloys. ORNL is leading the procurement of the advanced alloys. To ensure procurement quality, the material procurement team has conducted frequent e-mail communications and held routine monthly teleconference to discuss the progress of procurement. The procured alloys will be examined in terms of chemistry homogeneity, microstructural uniformity, and basic mechanical properties to justify their quality. All the procured commercial and advanced alloys will be stored and organized at EPRI and ORNL, respectively.

The commercial alloys C22, 625, 625-plus, 718, 725, and Zr-2.5Nb have been or being procured from Carpenter Technology Corporation and ATI Teledyne Wah-Chang. The vendors, e.g., ATI Alvac, Vallinox, Sanvik, and Scot Forge, who can supply the other commercial alloys, are being contacted. The following section presents the procurement status of the advanced alloys.

2. Procurement of advanced alloys

The procurement of Grade 92 (9Cr FM), alloy 439 (high-Cr ferritic), 14YWT (9-14Cr ODS), and other advanced alloys are discussed here.

2.1. Grade 92 (9Cr FM)

Grade 92 was initially developed by Nippon Steel of Japan with a designation of NF616. According to the forms of the material, Grade 92 is specified in different designations of the ASTM and ASME standards. Table 2 lists the applicable ASTM and ASME standards of Grade 92. Grade 92 is also included in the ASME Boiler & Pressure Vessel Code Section I and VIII Division I.

Table 2. ASTM and ASME designations of Grade 92.

Material Form	Standards
Forged or rolled plate/pipe	ASTM A182, ASME SA182, ASME SA369
Pipe	ASTM A335, ASME SA335
Tube	ASTM A213, ASME SA213
Pressure Vessel	ASTM A1017

Pressure vessels and pipes are usually fabricated by hot forging. According to the ASTM A182, hot forged plates, designated as F92 (UNS K92460), are required to be heat treated by normalization at 1040-1080°C followed by air cooling and tempering at 730-800°C. The chemistry, tensile and hardness requirements of F92 are specified in Tables 3 and 4.

Table 3: Chemical requirement of F92 (UNS K92460) with Fe as balance (ASTM A182/A182M-12a).

wt%	C	Mn	P	S	Si	Cr	Mo	Ni	V	Nb	N	W	B
Min	0.07	0.30	-	-	-	8.5	0.30	-	0.15	0.04	0.030	1.50	0.001
Max	0.13	0.60	0.020	0.010	0.50	9.5	0.60	0.40	0.25	0.09	0.070	2.00	0.006

Note: Al < 0.02%, Ti < 0.01%, Zr < 0.01%, Cu no specification.

Table 4: Tensile (minimum) and hardness (maximum) requirements of F92 at room temperature.

Tensile strength MPa [ksi]	Yield strength Mpa [ksi]	Elongation in 50 mm [2 in.], % *	Reduction of Area %	Hardness Number HBW [HV]
> 620 [> 90]	> 440 [64]	> 20	> 45	< 269 [< 284]

*For miniature specimens according to ASTM A355/A355M-11, the minimum elongation value is determined by the specimen thickness (t) as E (%) = 1.25t (mm) + 10.00 or E (%) = 32t (in.) + 10.00.

Customized Grade 92 has being developed under the DOE-NE Advanced Reactor Concept (ARC) program for the Sodium-Cooled Fast Reactor. It has shown improved tensile and creep performance with similar performance on fatigue, creep-fatigue, and fracture toughness as compared to conventional Grade 92. The customized Grade 92 is selected in the alloy group of 9Cr FM steels for testing in the ARRM program. A recent heat production of the customized Grade 92 at the R&D Department of Carpenter Technology Corporation exhibited exceptional amounts of Al and Cu [2]. The source of the elements has been identified after discussions and re-examination of the heat.

A new heat of customized Grade 92 in a form of forged plates with a nominal weight of 400 lbs. is being procured from the R&D Department of Carpenter Technology Corporation. The heat chemistry is customized to have reduced amounts of Ni and Si. Vacuum-induction melting (VIM) is used to yield an 8"-diameter ingot that will be remelted by electro-slag remelting (ESR) to obtain a 7.5"x7.5" square billet. The billet will be converted into 2"-thick plates by hot forging after soaking the billet at 1130°C for 1 h and finally by tempering at 750°C for 2 h. The normalization temperature is increased from that specified in the ASTM A182 to allow complete dissolution of precipitates into solid solution of the alloy. Additionally, the higher normalization temperature is expected to improve the performance of base metal as well as weldments [3]. The delivery of the customized F92 heat is scheduled in May 2014. The chemistry, tensile, hardness, and microstructural uniformity of the procured heat will be assessed after the reception of the material.

2.2. Alloy 439 (High-Cr Ferritic)

Alloy 439 is a high-Cr ferritic stainless steel, having excellent resistance to stress corrosion cracking (SCC) and intergranular (IG) corrosion. According to the forms of the material, alloy 439 is specified in different designations of the ASTM and ASME standards. Table 5 lists the applicable ASTM and ASME standards of alloy 439. Alloy 439 is also included in the ASME Boiler & Pressure Vessel Code Section I, IV, and VIII Division I and XII.

Table 5. ASTM and ASME designations of alloy 439.

Material Form	Standards
Plate/Sheet/Strip	ASTM A240, ASME SA240
Pipe/Tubing	ASTM A268, ASME SA268, ASTM A803
Bar	ASTM A479, ASME SA479

Plate form materials are preferred for the planned testing in the ARRM program. Thus, the ASTM A240 is referred to the requirements in chemistry, tensile and hardness that are listed in Tables 6 and 7. Examples of commercially available alloy 439, i.e., AK Steel 439, ATI 439 HP™, and Outokumpu EN 1.4510, primarily in sheet and strip forms, are also included in the Tables. Additionally, the ASTM A240-13a requires Charpy impact testing for alloy 439 with 3 specimens per temperature per orientation with a lateral expansion opposite the notch not less than 0.38 mm (0.015 in.) for each specimen.

Table 6: Chemical requirement (wt.%) of alloy 439 (UNS S43035) with Fe as balance.

	C	Mn	P	S	Si	Cr	Ni	N	Ti	Al
ASTM A240-13a	<0.030	<1.00	<0.040	<0.030	<1.00	17.0-19.0	<0.50	<0.03	>=0.20+4(C+N) – 1.10 max.	<0.15
AK Steel 439	<0.025	<0.50	<0.040	<0.030	<0.75	17.0-19.0	<0.50	<0.03	>=0.20+4(C+N) – 0.50 max.	<0.15
ATI 439 HP™	0.012	0.45	0.020	<0.001	0.55	17.5	0.23	0.013	0.40	
Outokumpu EN 1.4510	0.015					17			0.4	

Table 7: Tensile, hardness, and bending test requirements of alloy 439 (UNS S43035) with Fe as balance.

	Yield MPa	Tensile MPa	Elongation in 50 mm [2 in.], %	Brinell HBW	Rockwell B	Cold Bend* degree
ASTM A240-13a	>205	>415	>22	<183	<89	180
AK Steel 439	296 – 331	455 – 483	32 – 36		74 – 78	
ATI 439 HP™	290	455	34		78	
Outokumpu EN 1.4510	>205	>415	>22			

* Cold bend test is not required for plate thicker than 25 mm [1 in.]

To prevent the formation of radiation-induced γ'-phase that enriched with Ni and Si, the amounts of Ni and Si are decreased to 0.2 wt.% for each element. A heat of customized alloy 439 with a nominal weight of 400 lbs. has been cast using VIM at the R&D Department of Carpenter Technology Corporation. Its target and VIM pour chemistry are listed in Table 8. The target composition is within the ASTM A240-13a specification with tighter restrictions. The VIM pour chemistry satisfies the target composition.

Table 8: Chemistry (wt.%) of the customized alloy 439 with Fe as balance.

	C	Mn	P	S	Si	Cr	Ni	N	Ti	Al
ASTM A240-13a	<0.030	<1.00	<0.040	<0.030	<1.00	17.0-19.0	<0.50	<0.03	>=0.20+4(C+N) – 1.10 max.	<0.15
Target	0.015	0.4	<0.01	<0.001	0.2	17.5	0.2	<0.01	0.4	<0.01
VIM pour	0.02	0.4	<0.005	0.001	0.09	17.5	0.21	0.002	0.39	0.01

The VIM ingot is being converted to 2"-thick plates by hot forging at 1093°C after soaking the ingot at 1250°C for 2 h. The hot forged plates will be air cooled and finally annealed at 850°C for 2 h followed by water quenching to room temperature. The final heat chemistry of the plates from both the top and bottom of the processed ingot will be analyzed to check chemistry homogeneity. The delivery of the customized alloy 439 heat is scheduled in March 2014. The chemistry, tensile, hardness, Charpy impact resistance, and microstructural uniformity of the procured heat will be assessed after the reception of the material.

2.3. 14YWT (9-14Cr ODS)

ODS alloy 14YWT with potential both low and high strength applications is selected for testing in the ARRM program. The alloy, also named as nanostructured ferritic alloy (NFA), was developed under the DOE Fuel Cycle Research & Development (FCRD) program. The advanced ODS FCRD-NFA1 heat was produced using a new approach for preparing Ar gas atomized powders that consisted of directly adding yttrium (Y) to the melt prior to gas atomization and controlling the O level in the powders. Research and development on ball milling experiments at ORNL using the Simoloyer CM08 have been improved to reduce the contamination levels of primarily C and N in the powders during ball milling. These conditions were provided to Zoz, GmbH, Germany, for ball milling the powders produced with the new approach. The following describes the steps in the production of the FCRD-NFA1 plates for the ARRM program.

Production and ball milling of pre-alloyed powder

The FCRD-NFA1 ferritic alloy was produced using pre-alloyed powder that was prepared by Ar gas atomization by ATI Powder Metals (~55 kg mass) with a composition of Fe - 13.8Cr - 3.0W - 0.37Ti -

0.21Y - 0.012O (wt.%). The powder was sieved into three lots of -35/+100 mesh (150-500 □m), -100/+325 mesh (45-150 □m) and -325 mesh (<45 □m). Chemical analysis of the atomized powder indicated that the specified compositions for the alloying elements, including the addition of Y to the melt, and interstitial O, C and N levels were achieved by ATI Powder Metals.

The three sieved lots of pre-alloyed powders were shipped to Zoz for ball milling at the pilot facility in Wenden, Germany. Powder from the V540-02 lot was used for producing the FCRD-NFA1 heat for the ARRM program. The V540-02 lot consisted of blended powders of -100/+325 mesh and -325 mesh sizes. The powder was ball milled for 40 h in Ar gas using the high kinetic energy CM100 Simoloyer. The ball milling parameters were supplied by the FCRD processing team to Zoz for the ball milling runs. The chemical analysis of the ball milled powder shown in Table 9 indicated that O, N and C levels were within the specifications of the contract with Zoz.

Table 9. Chemical analysis results of ball milled powder (V540-02).

Fe	Cr	W	Ti	Y	O	C	N
Bal.	12.77	2.95	0.38	0.22	0.125	0.014	0.007

<u>*Extrusion and fabrication of FCRD-NFA1 plates*</u>

The ARRM program supported the extrusion and fabrication of FCRD-NFA1 plates using the ball milled powder of the V540-02 lot supplied by the FCRD program. Two cans were fabricated from 304L stainless steel stock with dimensions of 3.9 in diameter and 8.5 in length. Each can was filled with ~2.25 kg of ball milled powder, degassed at 400ºC and then sealed. The cans were heated at 850ºC for 2 h and extruded through a 2.5 in x 1.2 in rectangular die to produced extruded bars of the FCRD-NFA1. One of the extruded bar is shown in Figure 1. The leading and trailing ends of each extruded bar was cut off to reveal ODS sections that were ~14.75 in long. The bar was then cut into 3 equal lengths and annealed at 1000ºC for 1 h in high vacuum. The 3 bar sections were rolled into plates normal to the extrusion direction at 1000ºC to a total reduction in thickness of 50%. Figure 2 shows the plates hot-rolled from the two extruded bars. The 304L SS can enclosing the ODS FCRD-NFA1 plates is currently being machined off, i.e. decanning. The microstructure, hardness, and tensile properties of the plates will be investigated.

Figure 1. Digital image of the extruded FCRD-NFA1 bar.

Figure 2. Digital image of the 6 fabricated FCRD-NFA1 plates with the steel can intact.

2.4. 12Cr FM steel and high Cr-high Al ODS alloy

Specific alloys in the alloy groups of 12Cr FM steel and high Cr-high Al ODS alloy have not been determined. Alloy HT-9 was initially selected in the 12Cr FM alloy group due to its availability of comprehensive data compared to other alloys in this group. However, its irradiation embrittlement occurs after neutron irradiation below 400°C may significantly limit its applications in the LWR condition. It's not easy to alleviate the low-temperature irradiation embrittlement in the HT-9 chemistry, which is generally induced by irradiation hardening, radiation-induced precipitation and helium production. Based on the commercialized PM2000 and MA956 and the recently developed 16Cr-4.5Al ODS alloy, new high Cr-high Al ODS alloys are being developed for accident tolerant fuel cladding applications under the DOE FCRD program. It is expected to receive invaluable insights from this study to guide a selection of a candidate alloy in the high Cr-high Al ODS alloy group in this or next fiscal year.

3. Procurement of reference alloys

Stainless steels 304L and 316L are selected as reference steels due to their large amount of available data from the LWR relevant conditions. Commercial vendors of the two types of stainless steels are being identified. In the mean time, a small piece of ITER grade 316LN-SPH, in a size of 2.7"x1.2"x9" sectioned from heat #T1103, is identified at ORNL. This material was developed specifically for the Superphenix (SPH) program and produced by Cruesot Loire. The 316LN-SPH has a significantly lower nitrogen level (0.06-0.08 wt.%), close to that found in the US 316L, than either the Japanese 316LN (0.06-0.12 wt.%) or the US 316LN (0.1-0.16 wt.%). The heat was hot rolled and solution annealed at 1050°C for 0.5 h followed by water quench. The heat treatment produced a maximum ferrite content of 0.5% and an average ASTM grain size of 3.5. The data of this heat, including composition, microstructure, mechanical properties, etc., were developed by the Institute of Advanced Materials at the

European Commission's Joint Research Centre, Ispra, Italy. Despite of the limited size of the 316LN-SPH, it would be valuable for irradiation-related studies due to the comprehensive database from this heat.

Most of the data and experience of Grade 92 have been accumulated from fossil industry since its development. Radiation-induced property changes of Grade 92 have been rarely reported. To better understand the performance of the customized Grade 92, a classic NF616 (T92) heat with an amount of ~200 lbs. has been procured from Nippon Steel of Japan. The T92 heat is in a form of 1-1/4" outer diameter with a 1/4" wall thickness.

4. Summary

The selected commercial and advanced alloys are being procured for testing under the ARRM program. EPRI-GE is leading the procurement of commercial alloys. Some of the commercial alloys (six out of eleven) have been procured. The procurement of the rest commercial alloys is in progress. ORNL is leading the procurement of advanced alloys, including customized Grade 92, customized alloy 439, 14YWT ODS alloy, and two other alloys that are to be determined in the alloy groups of 12Cr FM and high Cr-high Al ODS alloy.

The customized Grade 92 and alloy 439 are being fabricated by means of VIM/ESR and hot forging at the R&D Department of Carpenter Technology Corporation. A nominal weight of 400 lbs. is to be procured for each alloy. The procured heats will be in 2"-thick plate form. The 14YWT ODS alloy (~10 lbs.) has been extruded and cross-rolled at ORNL. Decanning will be conducted to obtain the ODS alloy by removing the surface canning material 304 SS. Table 10 summarizes the procurement status of advanced alloys for the ARRM program. The procured heats will be assessed according to respective ASTM standards and general materials quality requirement, e.g., chemistry homogeneity, microstructural uniformity, tensile, hardness, and Charpy impact resistance. Additionally, reference alloys, i.e., 304L, 316L, and T92 (NF616) are being procured.

Table 10. Procurement status of advanced alloys for the ARRM program.

Alloy Group	Identified Alloy	Producer	Expected Available Time
9Cr FM	Customized Grade 92	Carpenter R&D	May 2014
12Cr FM	TBD		
High-Cr FM (>14Cr)	Customized Alloy 439	Carpenter R&D	March 2014
9-14Cr ODS	14YWT	ORNL	April 2014
High Cr-High Al ODS	TBD		About mid 2015

The procured commercial and advanced alloys will be stored and organized at EPRI and ORNL, respectively. A material tracking system will be established and used during the progress of the ARRM program.

References

[1] Critical Issues Report and Roadmap for the Advanced Radiation-Resistant Materials Program, EPRI, Palo Alto, CA and the U.S. Department of Energy, Washington, DC: 2012. 1026482.

[2] L. Tan, Y. Yamamoto, T.-L. Sham, Materials procurement and related examinations of advanced ferritic-martensitic and austenitic alloys, ORNL/TM-2013/325, September 23, 2013.

[3] C.R. Das, S.K. Albert, A.K. Bhaduri, G. Srinivansan, B.S. Murty, Effect of prior microstructure on microstructure and mechanical properties of modified 9Cr-1Mo steel weld joints, Mater. Sci. Eng. A 477 (2008) 185-192.