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Nickel-Based Gadolinium Alloy for Neutron Adsorption Application in Ram Packages

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Abstract

The National Spent Nuclear Fuel Program, located at the Idaho National Engineering & Environmental Laboratory (INEEL), coordinates and integrates national efforts in management and disposal of U.S. Department of Energy (DOE)-owned spent nuclear fuel. These management functions include development of standardized systems for packaging, storage, treatment, transport, and long-term disposal in the proposed Yucca Mountain repository. Nuclear criticality control measures are needed in these systems to avoid restrictive fissile loading limits because of the enrichment and total quantity of fissile material in some types of the DOE spent nuclear fuel. This need is being addressed by development of corrosion-resistant, neutron-absorbing structural alloys for nuclear criticality control. These materials offer distinct advantages over existing neutron absorbing materials available to the commercial nuclear industry.

This paper will outline the results of a metallurgical development program that is investigating the alloying of gadolinium into a nickel-chromium-molybdenum alloy matrix. Gadolinium has been chosen as the neutron absorption alloying element due to its high thermal neutron absorption cross section and low solubility in the expected U.S. repository environment. The nickel-chromium-molybdenum alloy family was chosen for its known corrosion performance, mechanical properties, and weldability. The workflow of this program includes chemical composition definition, primary and secondary melting studies, ingot conversion processes, properties testing, and national consensus codes and standards work. The microstructural investigation of these alloys shows that the gadolinium addition is not soluble in the primary austenite metallurgical phase and is present in the alloy as gadolinium-rich second phase. This is similar to what is observed in a stainless steel alloyed with boron. The mechanical strength values are similar to those expected for commercial Ni-Cr-Mo alloys. The alloys have been corrosion tested in simulated Yucca Mountain aqueous chemistries with acceptable results. The initial results of weldability tests have also been acceptable. Neutronic testing in a moderated critical array has generated favorable results.

An American Society for Testing and Materials material specification has been issued for the alloy and a Code Case has been submitted to the American Society of Mechanical Engineers for code qualification. The ultimate goal is acceptance of the alloy for use at the Yucca Mountain repository.

1. Introduction

Safe, long-term storage and disposal of the DOE-owned spent nuclear fuel (SNF) requires a corrosion resistant, long-lasting material that will absorb emitted neutrons for nuclear criticality control. DOE's National Spent Nuclear Fuel Program (NSNFP) is developing a corrosion-resistant, nickel-chromium-molybdenum alloy containing gadolinium for criticality control in the DOE standardized SNF storage canister. These canisters will be disposed of in the waste package at the Yucca Mountain Repository. Gadolinium is a potent neutron-absorbing element that has a very high thermal neutron absorption cross section. To meet the functional requirements for a structural material that will be used as an insert in the standardized canister, gadolinium must be alloyed into a corrosion-resistant structural metal that will meet ASME code requirements. The criticality safety requirements push the alloy development toward a gadolinium level of about 2%.

The alloy development initially examined 316L stainless steel as the base metal. It was found that there would be severe hot fabricability and localized corrosion problems with this approach [1, 2]. It was also found that the gadolinium has no solubility in the matrix of a stainless steel or a nickel-based alloy and is present as a gadolinium-rich second

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phase called a gadolinide. This has implications for the corrosion resistance and mechanical properties of the resulting alloys.

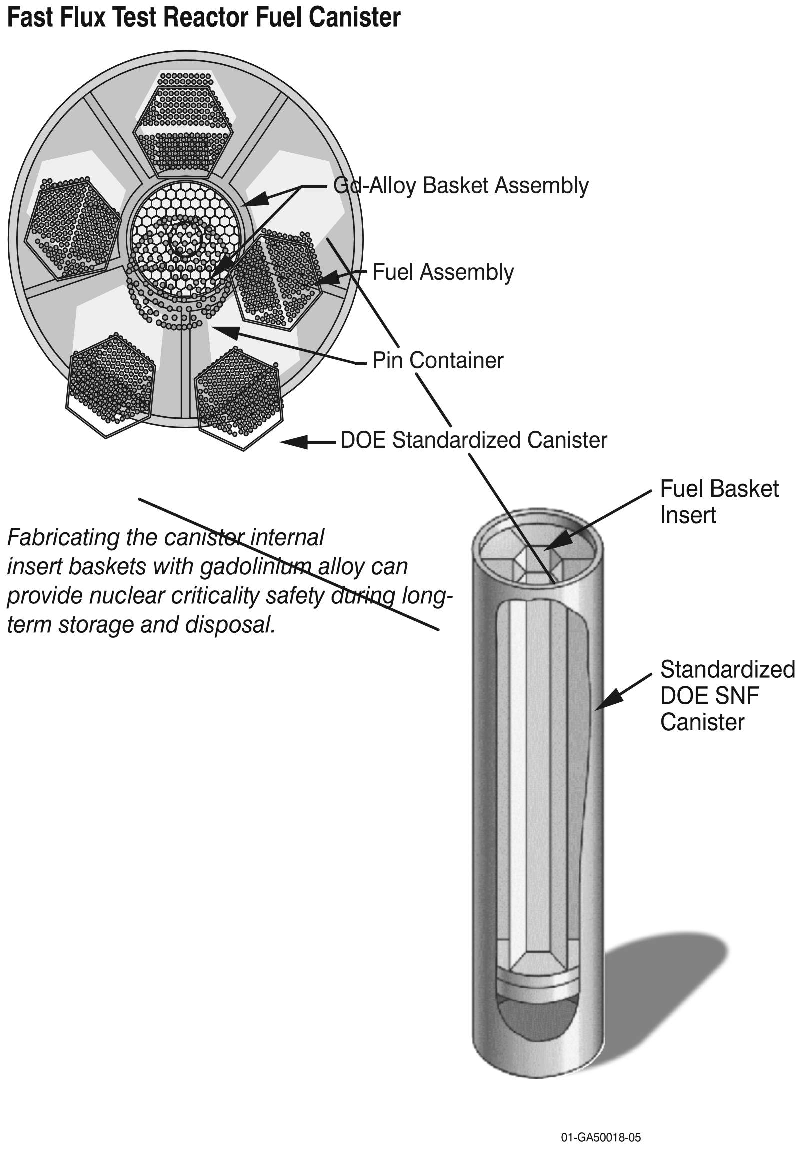
From earlier work with borated stainless steels [3], it was found that the ductility of the alloy would decrease with increased volume fraction of the boron rich second phase. To balance the goals of the highest possible gadolinium level, adequate corrosion performance, and meeting the ASME code requirements, control of the size, shape, and distribution of the gadolinide is necessary. The techniques being used are initial melt chemistry control, molten metal secondary refining techniques (vacuum arc remelting [VAR]) and thermo mechanical processing treatments.

Approximately 2,500 metric tones of SNF managed by DOE is planned for geologic disposal at Yucca Mountain. This SNF is much different from the commercial SNF produced by the power generation industry. DOE SNF has a variety of enrichments ranging from natural to fully enriched. The higher enrichments present a significant challenge for disposal packaging to avoid a conservative fissile loading limit.

Nuclear Regulatory Commission (NRC) regulations for the licensing of a geologic repository at Yucca Mountain require that criticality events be risk-informed. For both preclosure and postclosure, criticality must be evaluated in consideration of its probability and consequences as part of the overall performance assessment.

DOE SNF is expected to be codisposed in waste packages with vitrified high-level waste (HLW). This minimizes the amount of fissile material in a single waste package and takes advantage of a formally open space in the center of the HLW waste packages. DOE SNF will be packaged such that single canisters are critically safe for all storage and transportation events. However, when DOE SNF is evaluated in degraded conditions as is expected over geologic timescales, an insoluble and long-life poison will be required to avoid an extremely conservative fissile loading limit. Other poisons available (e.g., B) are highly soluble in the expected Yucca Mountain underground environment and were postulated to be easily separated from the fissile material. An extensive review of options identified gadolinium compounds as a potential solution. As the gadolinium compound in the alloy degrades, the gadolinium will chemically combine with phosphate compounds in the waste package producing an essentially insoluble neutron poison that will be stable over geologic timescales.

The deployment of gadolinium into the DOE SNF canisters considered a range of options. These included, gadolinium basalt compounds, gadolinium spray coatings, loose fill gadolinium compounds, and gadolinium alloys. The option that best met packaging and long-term disposal needs was gadolinium deployment in a highly corrosion resistant alloy. The alloy will then be fabricated into fuel basket assemblies as shown in Figure 1. This deployment method supports interim storage and transportation if needed, allows for easy retrieval, and introduces a highly insoluble gadolinium compound into the waste package.



Fabricating the canister internal insert baskets with gadolinium alloy can provide nuclear criticality safety during long-term storage and disposal.

Fig. 1. DOE standardized canister.

2. Work Description

The tasks required for the development of these new alloys are shown in Figure 2. The complete processing cycle from initial melting charge makeup, primary melting in a vacuum induction furnace, secondary refining in a VAR process, and thermo-mechanical processing, which includes all steps necessary (hot working, heat treatment) to turn the cast ingot into a wrought plate. The testing program is presently concentrating on the measurement of the mechanical properties, corrosion resistance, neutron absorption capability, and weldability of the alloys. The mechanical properties samples and corrosion test specimens are machined from plates fabricated in the test program. This paper describes results from three heats of material shown in Table 1.

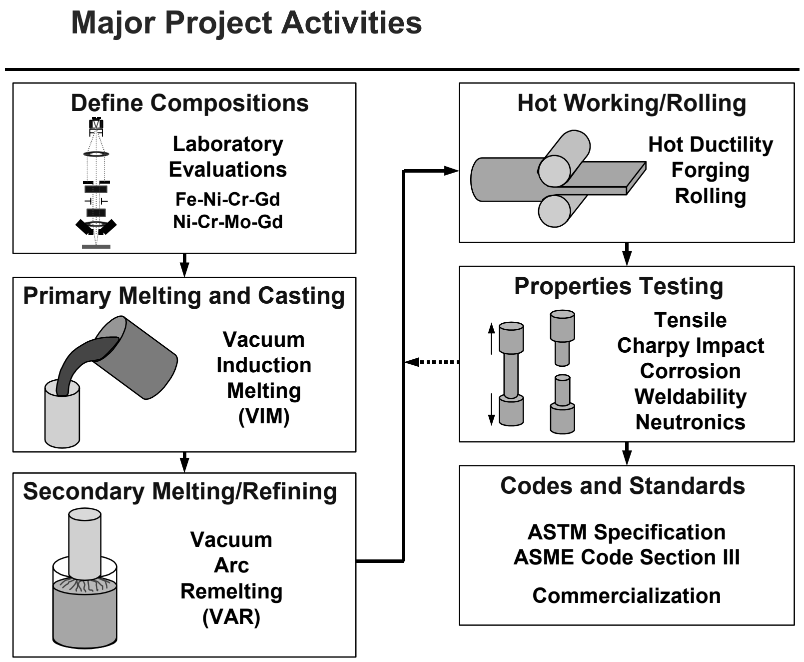


Fig. 2. Project workflow.

Element	Heat HV9810A	Heat M322	Heat M326	Heat M327
Al	0.042	0.005	Not reported	Not reported
C	0.011	<0.001	0.006	<0.001
Co	<0.1	<0.001	0.009	0/003
Cr	16.21	14.93	14.71	21.01
Fe	0.15	0.028	0.025	0.0032
Gd	1.58	2.38	2.00	1.98
Mg	Not reported	<0.001	0.002	0.002
Mn	0.10	<0.001	<0.001	<0.01
Mo	14.16	14.71	14.53	14.32
Ni	Balance	Balance	Balance	Balance
S	0.002	<0.001	<0.001	0.002
Si	0.03	<0.01	0.013	0.018

Table 1. Chemical composition of four Ni-Cr-Mo-Gd alloys.

3. Results

3.1. Microstructure

Figure 3 is a light optical micrograph of the microstructure of Heat M322, which was produced by Vacuum Induction Melting with no secondary refining. The gadolinium has no solubility in the austenite phase of the alloy and solidifies as a gadolinium-rich second phase. The composition of the second phase (light gray) of the rolled plate was measured with electron probe microanalysis and electron backscattered diffraction (EBSD), which identified the second phase as a Ni_5Gd intermetallic mixed with other dissolved elements such as chromium, molybdenum, and iron. An additional second phase (dark spots) was identified as gadolinium oxide (Gd_2O_3). To further refine the microstructure for improved mechanical properties and corrosion resistance, heats M322, M326, and M327 were VARed.

Additional work is being performed that includes detailed microstructural characterization of a number of alloy heats using a variety of electron microscopy techniques. These data will be used to understand the influence of thermo-mechanical processing on microstructure. The microstructure will then be related to the measured mechanical properties.

3.2. Mechanical Properties Testing

The strength values for the Ni-Cr-Mo-Gd alloys are similar to those expected for commercial Ni-Cr-Mo corrosion resistant alloys, and will be suitable for repository applications (Table 2). In general, the alloys exhibit slightly higher strength properties with slightly reduced ductility. The ASME Boiler and Pressure Vessel Code requirements [4] for impact toughness in nuclear applications call for a minimum of 20 J (15 ft-lb) impact energy and 0.38 mm (0.015 inch) lateral expansion. It is clear that the test results in the longitudinal orientation for all alloys easily meets this requirement. Impact toughness in the transverse orientation is marginal in this respect. For these alloys impact toughness is controlled by the particle shape and spatial distribution as well as volume fraction. Additional measurements will be made on alloys with differing gadolinium contents and the results correlated with the microstructural characterization studies.

3.3. Welding

Initial welding tests were performed with the electron beam (EB) and gas tungsten arc processes. Figure 5 shows light optical photomicrographs of the autogeneous electron beam weld made on the 9810A alloy in the as-polished and etched conditions. The weld exhibits columnar grains, which grow epitaxially from the base metal, and this grain morphology is typically observed in fusion welds. No solidification cracks or other defects were observed in this weld. Varestraint solidification cracking test were performed on Heat HV9810A in order to determine the weldability of these alloys. The results obtained were compared to nickel-based alloys IN 718 and IN 625. The test results indicate a response that this alloy composition compares favorably with these commercially available alloys.

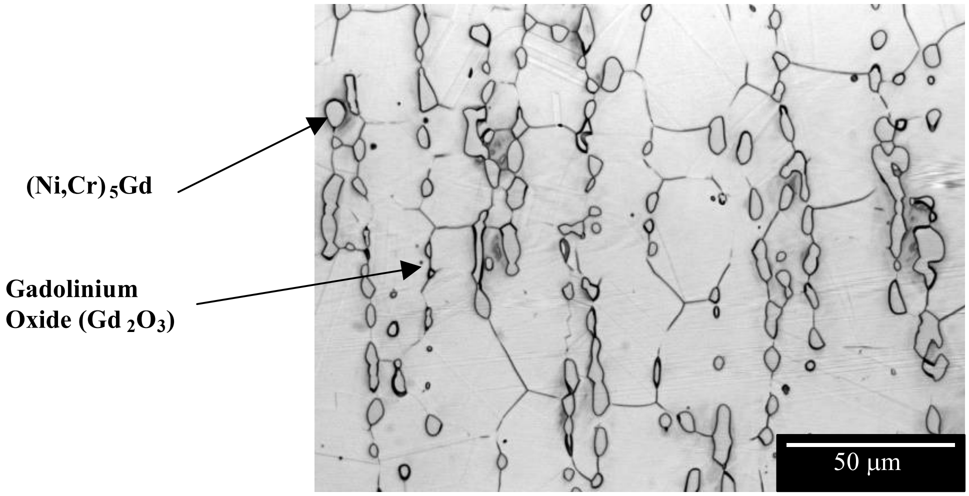


Fig. 3. Microstructure of Heat M322.

Mechanical Properties (23°C)						Charpy Impact Energy (ft-lb)		
Alloy	Orientation	YS (ksi)	UTS (ksi)	Elongation (%)	RA (%)	-40°C	23°C	300°C
HV9810A	Long	54.0	118.1	44.4	38.4	25.4	24.9	33.1
HV9810A	Trans	55.1	114.5	33.3	28.8	13.6	14.6	21.3
M 322	Long	82.5	127.5	42.6	29.2	23.0	23.0	28.0
M 322	Trans	83.3	100.0	7.4	5.5	7.5	7.8	9.0
M 326	Long	60.9	118.5	46.1	35.2	27.5	27.3	—
M 326	Trans	60.0	104.7	22.3	18.6	14.0	14.1	—
M 327	Long	60.7	115.7	51.1	38.5	29.5	33.1	—
M 327	Trans	61.4	108.1	24.1	21.0	14.3	16.3	—

Table 2. Summary of Mechanical and Charpy Impact properties.

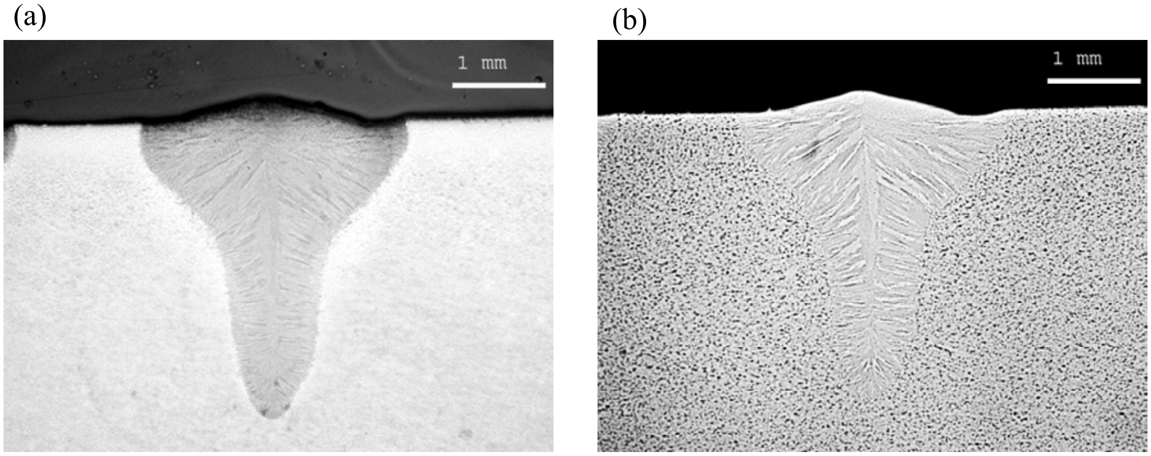


Fig. 4. Light optical photomicrographs of an autogeneous electron beam weld made on the 9810A alloy in the as-polished (a) and etched (b) conditions.

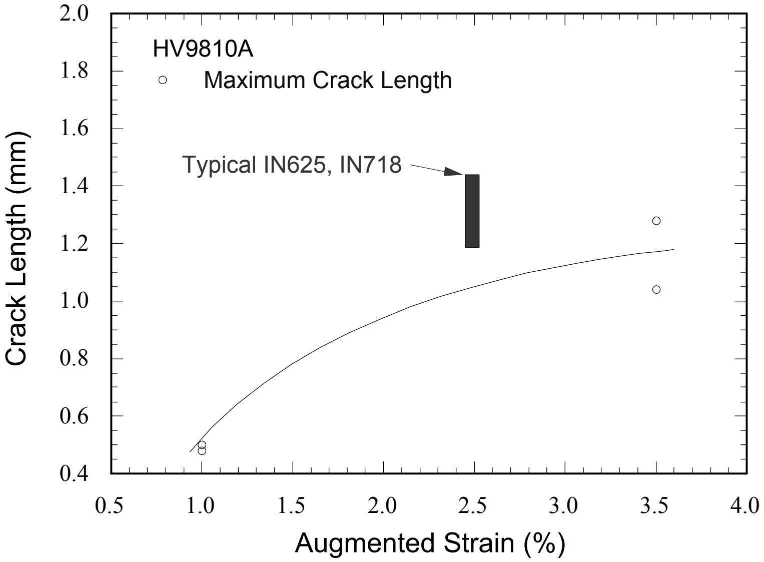


Fig. 5. Varestraint weldability test result comparison between Ni-based alloys.

3.4. Neutron Absorption Measurement

A critical experiment was carried out at the Los Alamos National Laboratory Critical Experiments Facility (LACEF). To benchmark the Ni-Cr-Mo-Gd alloy (Heat M322) developed by the NSNFP that could be used for disposal criticality control of SNF. The number of "units" necessary to reach criticality (no gap between bottom and top stack) was 11 plates of Ni-Cr-Mo-Gd alloy and 11 3/4 "units" of highly enriched uranium (HEU) foils. A "unit" consisted of one plate of polyethylene, four HEU foils, and one plate of the Ni-Cr-Mo-Gd alloy. The total critical experiment mass consisted of 3207 g of HEU and 10211 g of the Ni-Cr-Mo-Gd alloy. This translates to approximately 239 g of gadolinium based on the average weight percent of gadolinium in the Ni-Cr-Mo-Gd alloy plates of approximately 2.34 percent. The Ni-Cr-Mo-Gd alloy-HEU experiment had a measured k_{eff} of 1.002 verses a predicted value of 1.001. These initial measurements and calculations suggest that the negative worth of the gadolinium alloy plates was about 8.8$ of reactivity. In the same configuration, the calculated negative worth of an equivalent volume of borated stainless steel plate (1.7% B) is approximately 6.4$ of reactivity [5]. The results of the experiment were of high quality and were documented according to International Criticality Safety Benchmark Evaluation Project guidelines [6]. Similar experiments have been performed at LACEF with various waste matrix materials [7, 8].

3.5. Corrosion Testing

Electrochemical (Cyclic Polarization) corrosion testing methods were used to test samples of alloy HV9810A, M322, and M327 in the following environments and a simulated Yucca Mountain Project chemistry: (a) 0.1 M HCl, 30°C, (b) 0.1 M HCl, 60°C, (c) 0.028 M NaCl, 30°C, (d) 0.028 M NaCl, 60°C, and (e) Yucca Mountain J-13 solution, 30°C. The acidic chloride solutions were chosen for known propensity to initiate localized corrosion. The J-13 solution is representative of the Yucca Mountain in-drift chemistry at the end of the regulatory period (10,000 years) in a fully flooded condition.

The corrosion test results show that in the acidic, chloride containing solutions, the alloy will be subjected to initial loss of gadolinium through localized attack of the gadolinides that intersect the exposed metal surface [9]. The testing has shown that the corrosion rate will then drop off to very low levels as the newly exposed metal surface (Ni-Cr-Mo matrix) passivates after removal of the second phase. Long-term immersion corrosion tests of Heat M322 exposed to J-13 chemistry at 30ºC gave a measured corrosion rate of 49 nm/yr (10^{-9} m/yr) with no localized corrosion of the gadolinides.

Two hydrogen embrittlement mechanisms have been identified as possible concerns. It is noted that nickel alloys are much less susceptible toward hydrogen embrittlement than steels. Micro-cracking associated with internal hydrogen embrittlement or environmental hydrogen embrittlement mechanisms in both aqueous and mechanical tests has not been observed with the alloy.

Galvanic couples between the (Ni, Cr)$_5$Gd precipitates and the surrounding Ni-Cr-Mo matrix have been identified as a potential degradation mechanism. Preliminary data based on simple long-term immersion tests in a Yucca Mountain 50X solution indicate that galvanic corrosion induced by the electrochemical differences between the two material phases is not a great concern. In a period of over 14 months, there was very little weight loss and no changes in microstructure as examined with light optical microscopy. If galvanic processes were active, one would observe preferential localized corrosion of one of the two metallurgical phases.

3.6. National Consensus Technical Standards

A consensus standard for Ni-Cr-Mo-Gd alloys has been issued by the American Society for Testing and Materials (ASTM) [10]. A Code Case inquiry and data package has been submitted to the American Society of Mechanical Engineers for code approval for use of these materials for Yucca Mountain Repository applications [11].

4. Conclusions and Discussion

The alloy development program is proceeding with these materials. The focus of the research is to develop methods for large-scale hot working procedures while maximizing the alloy mechanical properties.

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