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Development of a Weldable Neutron Absorbing Structural Material

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Abstract – *The National Spent Nuclear Fuel Program, located at the Idaho National Laboratory, 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 paper will outline the results to date 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 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 melting and secondary refining studies, ingot conversion process evaluations, mechanical/physical properties and corrosion testing, welding studies, and national consensus codes, and standards work.

I. INTRODUCTION

Safe, long-term storage and disposal of the U.S. Department of Energy (DOE)-owned spent nuclear fuel requires a corrosion-resistant, long-lasting material that will absorb emitted neutrons for nuclear criticality control. This need is being addressed by development of a weldable, neutron absorbing structural material for nuclear criticality control by DOE's National Spent Nuclear Fuel Program (NSNFP) at the INL. This new corrosion-resistant, nickel-chromium-molybdenum alloy containing gadolinium will be used to fabricate fuel baskets for criticality control in the DOE standardized spent nuclear fuel storage canister. These canisters will be stored in the waste package at the Yucca Mountain Repository.

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The material is described by UNS N06464 in ASTM standard B 932-04.[Ref.1] This material has also been approved for ASME Section III, Division 3 applications as Code Case N-728. [Ref.2] This paper will present the material properties bases used to obtain this code case and describe steps being taken to generate information to support a welded code case submittal.

This new material offers distinct advantages over existing neutron absorbing materials available to the commercial nuclear industry for use in spent nuclear fuel pools, transportation systems, and storage casks

II. OVERVIEW

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 or fuel basket in the standardized canister, gadolinium must be alloyed into a corrosion-resistant structural metal that will meet American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, Section III, Division 3 requirements. The criticality safety analysis results require a nominal 2% gadolinium level in the alloy.

The initial alloy development used 316L stainless steel as the base metal. It was found that there were be severe hot fabricability and localized corrosion problems with this approach.[Ref. 3,4,5] 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 dispersed gadolinium-rich second phase called a gadolinide based on the $GdNi_5$ compound.

Preliminary evaluations [Ref. 6,7] showed that Gd-containing alloys based on the Ni-Cr-Mo system solidified with a eutectic terminal solidification reaction, and that the solidification temperature range was acceptably narrow for hot working and welding. The preliminary studies also showed that, as expected from the chemical reactivity of gadolinium, numerous gadolinium compounds (e.g. oxides, sulfides, and phosphides) could also form in the Gd-containing alloys.

From earlier work with borated stainless steels [Ref.8],it was found that the alloy ductility decreases with increased volume fraction of the boron-rich second phase. Ni-Cr-Mo alloys containing a dispersed gadolinide exhibit similar behavior. To balance the goals of the highest possible gadolinium level, adequate corrosion performance, and meeting ASME code requirements, we are investigating control of the size, shape and distribution of the gadolinium-rich second phase. The techniques being used are initial melt chemistry control, molten metal secondary refining techniques and thermal mechanical processing treatments.

III. DEVELOPMENT OF THE NI-CR-MO-GD ALLOY

Based on corrosion requirements and favorable preliminary findings, the decision was made to pursue Ni-Cr-Mo-Gd alloys. Comparison (REF) of the hot ductility, hot working response, and mechanical properties of three commercial alloys (UNS N06455, N06022 and N06059) alloyed with approximately 2 wt% Gd implied that the most favorable behavior was obtained when Gd was alloyed into the most elementally simple of these alloys - N06455.

During primary melting and casting, the alloy solidifies first by the formation of dendritic primary austenite, and solidification terminates by the formation of a eutectic-like constituent containing austenite and $GdNi_5$ gadolinide. [Ref. 9]. Gadolinium has essentially no solubility in the Ni-Cr-Mo austenitic matrix. Ingot breakdown and hot rolling results in changes in the gadolinide distribution. Figure 1 shows the typical microstructure of straight-rolled alloy plate in the three principal orientations, and Figure 2 shows a higher magnification image of the structure. The rolled alloy consists of an austenitic Ni-Cr-Mo matrix with a $GdNi_5$ phase dispersed throughout the microstructure. The $GdNi_5$ phase is somewhat elongated in the rolling direction and flattened out in the rolling plane. An additional second phase (dark spots in the Figure 2 is gadolinium oxide (Gd_2O_3). The austenite grain size is controlled by the gadolinide distribution and is relatively fine (≈ 30-40 μm). The alloy is similar to other neutron absorbing structural alloys (e.g. borated stainless steel) in that it contains a hard and brittle phase ($GdNi_5$) within a tough and ductile austenitic matrix. The gadolinides have important implications for the corrosion resistance and mechanical properties of the alloy. The gadolinium is distributed relatively homogeneously throughout the plate and provides the neutron absorption properties.

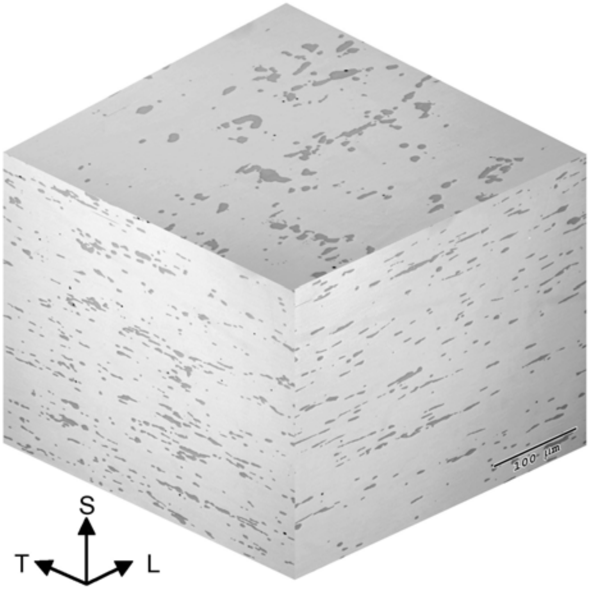

Figure 1. Microstructure of Ni-Cr-Mo-Gd alloy in the three principal plate orientations. Light areas are the Ni-Cr-Mo matirix and dark constituent is the gadolinide. T, L, and S refer to the transverse, longitudinal, and short transverse directions relative to the rolling direction.

The microstrucure of an etched sample is shown in Figure 2. The gadolinide is the blocky constituent located at the austenite grain boundaries.

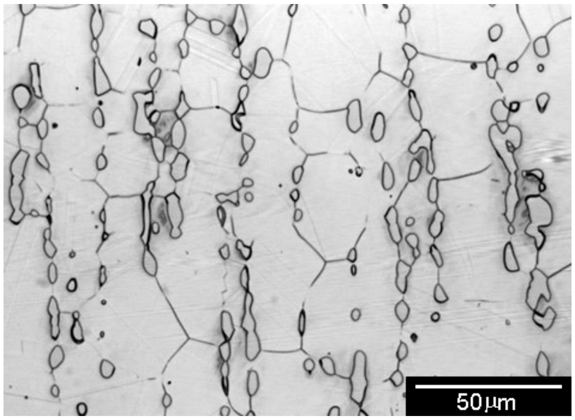

Figure 2. Microstructure of Ni-Cr-Mo-Gd alloy, etched

Table 1 compares the compositions of the base Gd-free N06455 alloy with the N06464 Gd-containing alloy. In general, allowable concentration ranges for the various elements were determined from several considerations. The most important of these is the partitioning of the Gd to the two microstructural constituents (the Ni-Cr-Mo austenite matrix and the gadolinide). From electron micropobe measurements [REF.9] it was found that some of the alloying elements (notably Cr and Mo) partition in small amounts to the gadolinide phase while the austenite matrix phase contains no detectable Gd. Electron microprobe studies of experimental Ni-Cr-Mo-Gd ingots showed that the composition of the gadolinide falls within the ranges shown in Table 2.

Table 1. ASTM Specified Compositions of UNS N06464 and UNS N06455.

Element	N06464 ASTM B932-04	N06455 ASTM B575-04
Molybdenum	13.1 - 16.0	14.0 - 17.0
Chromium	14.5 - 17.1	14.0 - 18.0
Iron	1.0 max	3.0 max
Tungsten	Not Listed	…
Cobalt, max	2.0	2.0
Carbon, max	0.010	0.015
Silicon, max	0.08	0.08
Manganese, max	0.5	1.0
Vanadium, max	Not Listed	…
Phosphorus, max	0.005	0.04
Sulfur, max	0.005	0.03
Titanium	Not Listed	0.7 max
Nickel	Remainder	Remainder
Aluminum	Not Listed	…
Copper	Not Listed	…
Tantalum	Not Listed	…
Oxygen, max	0.005	No Listed
Nitrogen, max	0.010	Not Listed
Gadolinium	1.9 - 2.1	Not Listed

Table 2. Composition of Gadolinide in Ni-Cr-Mo-Gd Alloys.

Element	Concentration (wt %)
Molybdenum	0.53 – 0.84
Chromium	2.00 – 2.82
Iron	0 – 0.52
Tungsten	0
Silicon	0.04 – 0.11
Manganese	0
Nickel	61.41 – 63.13
Aluminum	0 – 0.5
Gadolinium	34.93 – 35.96

Specification of the overall alloy composition must consider the elemental partitioning to the matrix and gadolinide phases. From mass conservation considerations we can write for any element, *i*, in the alloy:

$$\text{wi,alloy} = (\text{wi,aust})(\text{xaust}) + (\text{wi,gad})(\text{xgad}) \qquad [1]$$

where $w_{i,\mathrm{alloy}}$ is the weight fraction of *i* in the alloy, $w_{i,\mathrm{aust}}$ is the weight fraction if *i* in the austenite matrix, $w_{i,\mathrm{gad}}$ is the weight fraction of *i* in the gadolinide, x_{aust} is the mass fraction of austenite, and x_{gad} is the mass fraction of gadolinide. For gadolinium, Eq. [1] is:

$$w_{Gd,\mathrm{alloy}} = (w_{Gd,\mathrm{aust}})(x_{\mathrm{aust}}) + (w_{Gd,\mathrm{gad}})(x_{\mathrm{gad}}) \qquad [2]$$

Since $w_{Gd,\mathrm{aust}}$ is zero, Eq. [2] reduces to

$$x_{\mathrm{gad}} = (w_{Gd,\mathrm{alloy}})/(w_{Gd,\mathrm{gad}}) \qquad [3]$$

which shows that the mass fraction of the gadolinide phase is a simple function of the amount of gadolinium in the alloy. In addition, by using the relationship

$$x_{\mathrm{aust}} + x_{\mathrm{gad}} = 1 \qquad [4]$$

and substituting Eq. [3] into Eq. [1] we have:

$$w_{i,\mathrm{alloy}} = (w_{i,\mathrm{aust}})[1- (w_{Gd,\mathrm{alloy}}/w_{Gd,\mathrm{gad}})] + (w_{i,\mathrm{gad}})(w_{Gd,\mathrm{alloy}}/w_{Gd,\mathrm{gad}}) \qquad [5]$$

Through the use of Eq. [5], we can estimate the overall alloy composition for any given gadolinium content and any *desired* matrix composition.

The composition ranges for Cr and Mo in ASTM B932 were thereby determined by first identifying the *desired* ranges for these elements in the austenite matrix followed by the use of Eq. [5]. Initially, in selecting the desired Cr and Mo matrix ranges it was determined that, for simplicity, these ranges should approximately mimic those of the commercial UNS N06455 alloy. However, corrosion studies being conducted in parallel [Refs 12-14] indicated that corrosion performance would be enhanced by biasing the matrix Cr concentration toward the upper end of the range for UNS N06455. Thus, the desired matrix range for Cr was constrained to the range of 15.5 to 18.0 wt%, and the desired Mo matrix range was 14.0 to 17.0 wt% (which is identical with UNS N06455). It should also be noted that the calculation was conducted at the gadolinium concentration extremes of 1.9 and 2.1 wt%, which were set by criticality considerations and mechanical property observations. Within rounding considerations, the Mo concentration range in ASTM B932 provides a matrix austenite composition which approximates Mo concentration in the commercial UNS N06455 alloy. Similarly, the Cr concentration range provides a matrix austenite composition which approximates the upper part of the Cr concentration in the commercial UNS N06455 alloy.

With respect to minor alloying elements such as Fe, Mn, Si, and Co were based on comparison with specification limits for commercial Gd-free Ni-Cr-Mo alloys with allowance for potential partitioning of these elements to the gadolinde phase. The approach was to set the desired matrix composition by considering corrosion performance. For these minor alloying elements the corrosion considerations generally resulted in desired matrix compositions which are toward the lower end of the UNS N06455 ranges. From these desired ranges, Eq. [5] was applied to determine the overall alloy composition.

Impurity (e.g. P, S, O) concentrations were specified at minimal levels in order to minimize the formation of Gd-containing compounds with these elements.

The current preferred production route for the alloy involves primary melting by using the vacuum induction melting (VIM) process followed by secondary melt refining using the vacuum arc remelting (VAR) process. These vacuum processes are preferred because of their ability to minimize the potential for reaction of the Gd with atmospheric or other impurities. The goal of these is to produce a cast ingot with as uniform a distribution of the gadolinide eutectic constituent as possible.

Following ingot casting, the alloy is hot worked into plate form by using conventional rolling procedures, and results in the microstructure shown in Figure 1. The hot working modifies the morphology of the gadolinide, and due to the importance of the gadolinide in determining mechanical properties (especially ductility), various hot working procedures have been investigated. In addition to determination of the optimal temperature for hot working, both straight- and cross-rolling procedures have been investigated. The microstructure of straight rolled plate is shown in Figure 1 - cross rolled microstructures are similar to this, except that the gadolinides are generally less elongated in the longitudinal orientation. This results in a reduction in the properties anisotropy. The room temperature properties for both straight- and cross-rolled plate are summarized in Table 2. This data is from the four heats used in the ASME Code Case N-728 qualification. [Ref.2]Further optimization of hot working procedures is under evaluation.

The strength values for the Ni-Cr-Mo-Gd alloy are similar to those expected for commercial Ni-Cr-Mo corrosion resistant alloys, and are considered suitable for repository applications. In general, the alloys exhibit slightly higher strength with slightly reduced ductility compared with Gd-free Ni-Cr-Mo alloys. The mechanical properties data for the transverse samples for the cross rolled product is shown in Figures 3 through 8. ASME requirements (informal) for impact toughness in nuclear applications call for a minimum of 0.38 mm (0.015 inch) lateral expansion. It is clear that the test results in the transverse orientation for all alloys easily meet this requirement. Lateral expansion in the transverse orientation is just above the required minimum.

A variety of other properties have been determined for the alloy. These include the yield and tensile strength temperature trend curves have been determined and were used to support ASME Code Case N-728. The tensile trend curves for the G-containing alloy exhibit a temperature dependence that is similar to the Gd-free N06455 alloy. In addition to these, low cycle fatigue, fracture toughness, thermophysical properties, and elastic constants have been determined [Ref. 10,11].

Table 3. Summary of Average Room Temperature Mechanical Properties of ASTM B-932-04 Heats

Rolling schedule	Orientation	YS MPa (ksi)	UTS MPa (ksi)	Elongation (%)	RA (%)	Impact Energy J (ft-lb)	Lateral Expansion mm (inch)
SR Four Heat Average	Transverse	399.2 (57.9)	700.5 (101.6)	23.4	22.1	18.7 (13.8)	0.51 (0.020)
SR Four Heat Average	Longitudinal	403.4 (58.5)	784.6 (113.8)	42.9	31.7	37.2 (27.4)	0.76 (0.030)
CR Four Heat Average	Transverse	406.1 (58.9)	728.1 (105.6)	28.3	20.6	20.9 (15.4)	0.53 (0.021)
CR Four Heat Average	Longitudinal	398.5 (57.8)	774.3 (112.3)	39.9	30.2	32.3 (23.8)	0.69 (0.027)

Notes:
SR and CR denote straight- and cross-rolled heats, respectively.
Minimum of three tests per heat per condition.
Orientation of Cross-Rolled heats is relative to primary rolling direction.

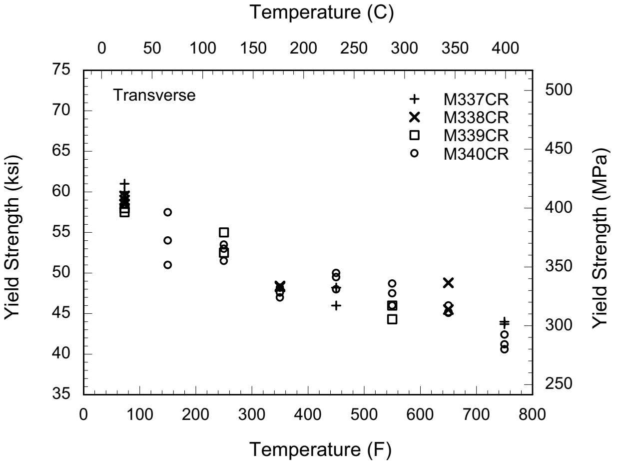

Figure 3. Transverse yield strength

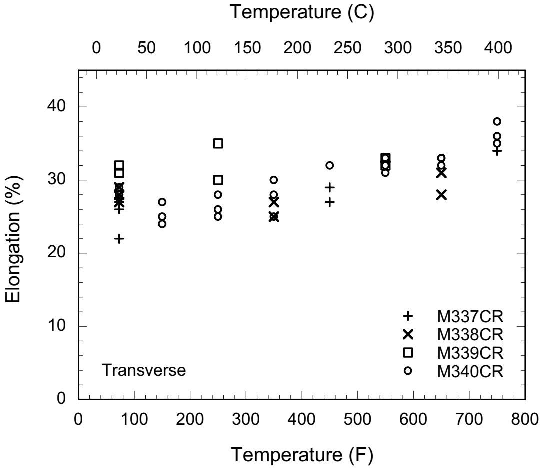

Figure 5. Transverse elongation

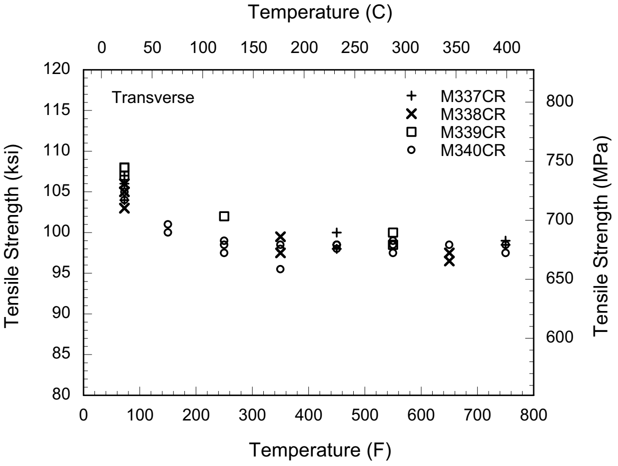

Figure 4. Transverse ultimate tensile strength

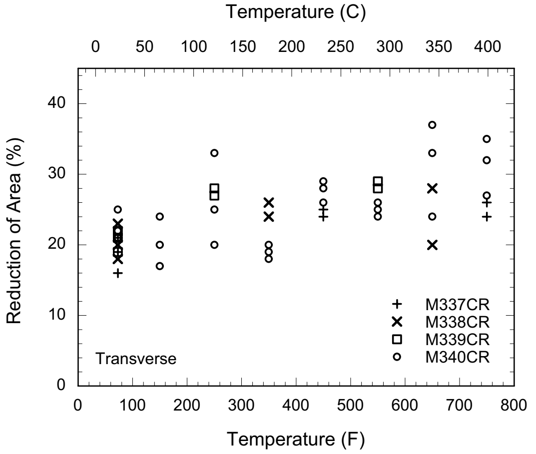

Figure 6. Transverse reduction of area

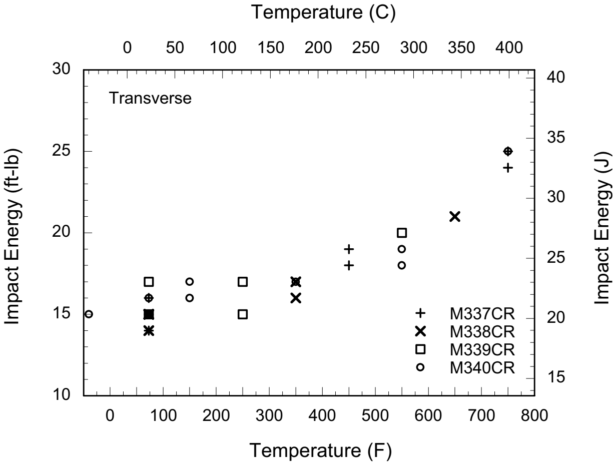

Figure 7. Transverse Charpy Impact energy

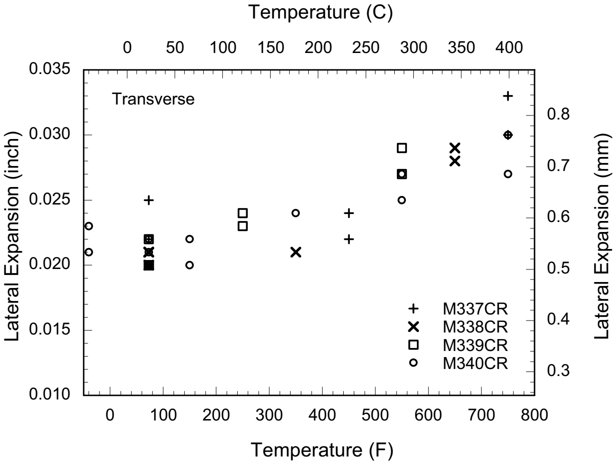

Figure 8. Transverse lateral expansion from Charpy test

The corrosion behavior of the alloy has been extensively investigated. [Ref. 12,13,14,15] The corrosion resistance of these Ni-Cr-Mo-Gd alloys is dependent on the amount of gadolinium addition, which will determine the amount of the gadolinide that will be present in the alloy matrix. The gadolinide that intersects the surface exposed to acidic aqueous solutions and other solutions simulating the Yucca Mountain environment might be preferentially attacked and removed. However, the underlying Ni Cr-Mo matrix will then repassivate, and the corrosion rate will drop off to an extremely low rate.

Preliminary welding investigations [Refs. 9,16] indicate that the solidification temperature range is on the order of 110-130°C and is similar to conventional corrosion resistant Ni-based alloys and the volume fraction of terminal gadolinide is about 6 vol.%. Weld hot cracking resistance is generally acceptable. Mechanical properties of joints welded with Gd-free Ni-Cr-Mo filler metal show reduced ductility relative to the base metal. The reduction is primarily the result of redistribution of the gadolinide in the partially molten heat-affected zone, but properties can be recovered the use of post weld heat treatment. Evaluations of the fitness-for-service of welds in the as-welded condition are being conducted. Additional weldment mechanical properties measurements will be performed to generate the required data for the extension of ASME Code Case N-728 to welded construction.

CONCLUSIONS

This development program has produced a neutron absorbing, corrosion resistant structural material that can be used to fabricate spent nuclear fuel baskets that will provide criticality control in a geologic disposal setting. Future plans will address issues related to commercial scale material production.

ACKNOWLEDGMENTS

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