

# Development of Alumina-Forming Austenitic Stainless Steels

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**AUTHOR's NOTE:** This report is based on results presented in references 1-3.

## **ABSTRACT**

This paper presents the results of the continued development of creep-resistant, alumina-forming austenitic (AFA) stainless steel alloys, which exhibit a unique combination of excellent oxidation resistance via protective alumina ( $\text{Al}_2\text{O}_3$ ) scale formation and high-temperature creep strength through the formation of stable nano-scale MC carbides and intermetallic precipitates. Efforts in fiscal year 2009 focused on the characterization and understanding of long-term oxidation resistance and tensile properties as a function of alloy composition and microstructure. Computational thermodynamic calculations of the austenitic matrix phase composition and the volume fraction of MC, B2-NiAl, and  $\text{Fe}_2(\text{Mo},\text{Nb})$  base Laves phase precipitates were used to interpret oxidation behavior. Of particular interest was the enrichment of Cr in the austenitic matrix phase by additions of Nb, which aided the establishment and maintenance of alumina. Higher levels of Nb additions also increased the volume fraction of B2-NiAl precipitates, which served as an Al reservoir during long-term oxidation. Ageing studies of AFA alloys were conducted at 750°C for times up to 2000 h. Ageing resulted in near doubling of yield strength at room temperature after only 50 h at 750°C, with little further increase in yield strength out to 2000 h of ageing. Elongation was reduced on ageing; however, levels of 15-25% were retained at room temperature after 2000 h of total ageing.

## **BACKGROUND AND DISCUSSION OF CURRENT ACTIVITIES**

Recent efforts at Oak Ridge National Laboratory have identified austenitic alloy composition ranges that have the potential for both creep-resistance and alumina scale formation in the 600-900°C temperature range [1-5], at estimated alloy raw material cost comparable to existing advanced austenitic stainless steel families. Components of interest range from super heater tubes in steam boilers to gas-to-gas heat

exchangers and hot-section gas-turbine components with potentially higher operating temperatures and increased environmental durability compared to conventional chromia (Cr<sub>2</sub>O<sub>3</sub>)-forming stainless steels and Ni-base alloys. Efforts in fiscal year (FY) 2009 focused on evaluation of long-term oxidation resistance and tensile properties as a function of alloy composition and microstructure. Compositions for select AFA alloys studied in FY09 are listed in Table 1. The alloys are referred to in shorthand form in the text and figures by their nominal levels of Al and Nb additions, respectively. For example, alloy 2-0.2 refers to an alloy in the 2.5 wt.% Al series and a nominal Nb level of 0.2 wt.%.

Table 1- Analyzed compositions of select developmental AFA alloys. Ni rounded to nearest 1 wt.%, Al, Cr, Cu, Mo, Mn, and W rounded to nearest 0.1 wt.%, and C rounded to nearest 0.01 wt.%.

Alloy	Ni	Cr	Al	Nb	Ti	Mo	W	Cu	Mn	Si	Other
2-0.2	20	14.2	2.4	0.16	0.01	2.4	-	-	2	0.15	0.07C
3-0.4	20	14.3	2.9	0.41	0.11	2	1	0.5	1.7	0.13	0.08C
3-0.6	20	14.2	2.9	0.60	0.11	2	1	0.5	1.9	0.13	0.1C
3-1	20	14.2	2.9	1.01	-	2	1	0.5	1.9	0.14	0.1C
3-1.5	20	14.4	2.9	1.48	0.11	2	1	0.5	1.9	0.13	0.09C
3-2.5	20	14.4	2.9	2.48	0.12	2	0.9	0.5	1.9	0.13	0.08C
4-1 <sup>LNi</sup>	20	12	3.9	1.01	-	2	1	0.5	1.9	0.15	0.1C
4-1	25	11.9	3.9	1.02	-	2	1	0.5	2	0.14	0.1C
4-1 <sup>HfY</sup>	25	11.9	3.9	1.02	-	2	1	0.5	2	0.14	0.11C; 0.14Hf; 0.024Y
4-2.5 <sup>HfY</sup>	25	14.87	4	2.5	-	2	-	-	1.9	0.15	0.09C, 0.14Hf; 0.009Y;

## RESULTS AND DISCUSSION

### OXIDATION RESISTANCE

Oxidation resistance was evaluated using test coupons ~10-12 mm x 20-25 mm x 1 mm thick with a 600 grit (USA standard) finish cut from 1200°C solution-treated material. Oxidation exposures were conducted in 100 h cycles at 650, 700, or 800°C in air with 10 volume percent (vol.%) water vapor, with mass changes measured after every cycle. This environment was used to simulate the detrimental effects of water vapor encountered in combustion environments. Oxidation resistance was also evaluated at 900°C in air with 10% water vapor using 10 h cycles, which is an aggressive screening test condition.

Oxidation data (100 h cycles) at 650°C in air with 10% water vapor is shown in Fig. 1 [1]. Oxidation resistance improved with increasing both Al and Nb content in the range of 2.5-3Al and 0.2-0.6Nb. Visual inspection of the test coupons indicated that the surface was covered with interference colors indicative of a thin, semi-transparent oxide scale and consistent with the slow growth kinetics of Al-rich oxide formation. Similar composition trends and excellent oxidation results were obtained at 700°C in air with 10% water vapor (data not shown) [1]. For the lower-Nb alloys 2-0.2 and 3-0.4, nodular oxide structures dispersed throughout the surface and edges of the coupons were also observed. Such structures were not observed in the alloy 3-0.6, which had the highest Al and Nb levels and lowest mass gains of the alloys shown in Fig. 1. For comparative purposes, oxidation data at 650°C in air with 10% water vapor is also shown for type 347HFG austenitic stainless steel (67Fe-18Cr-12Ni wt.% base). In air with water vapor, the chromia scale formed by the 347HFG stainless steel becomes compromised [6], resulting in rapid Fe-base oxide nodule formation and a transition to oxide scale spallation and mass loss after only 300 total h of exposure. (Advanced austenitic chromia-forming alloys such as alloy 709 (Fe-25Ni-20Cr-0.2 Nb wt.% base) resist oxidation to higher temperatures in water vapor than type 347 and

related austenitics, with the upper-temperature limit dependent upon component thickness, lifetime requirements, and water vapor content and flow rate [7]).

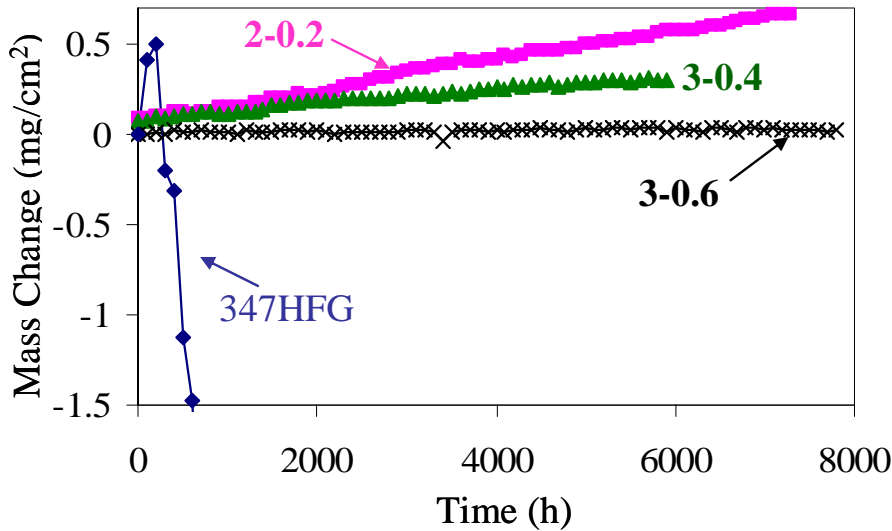


Fig.1- Cyclic oxidation (100 h cycles) at 650°C in air with 10% water vapor (after reference 1).

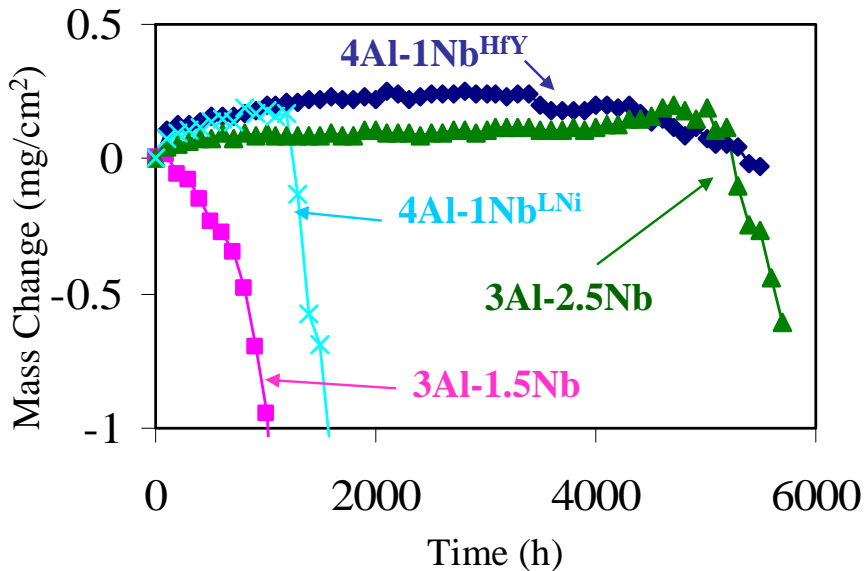


Fig.2- Cyclic oxidation (100 h cycles) at 800°C in air with 10% water vapor (after reference 1).

Cyclic oxidation resistance (100 h cycles) at 800°C in air with 10% water vapor also generally improved with increasing Nb content (Fig. 2) [1]. Higher levels of Nb than that observed at 650°C were needed to obtain the improved oxidation resistance, ~2.5 Nb at 800°C (Fig. 3) vs. ~0.6Nb at 650°C (Fig. 1). However, all alloys evaluated at 800°C in air with 10% water vapor eventually showed a transition to mass loss, with the less oxidation-resistant compositions exhibiting this transition in less than ~1000-2000 total h of exposure. The 3-2.5 alloy did not begin to show a loss of oxidation resistance until after ~5000 total h of exposure (Fig. 2). As with the 650°C exposures, loss of oxidation resistance resulted from Fe-rich oxide nodule formation. A significant improvement in oxidation resistance with Hf and Y reactive

element additions was observed for the alloy 4-1<sup>HY</sup> (Fig. 2), which exhibited oxidation resistance comparable to the 3-2.5 alloy despite its 1 wt.% Nb content.

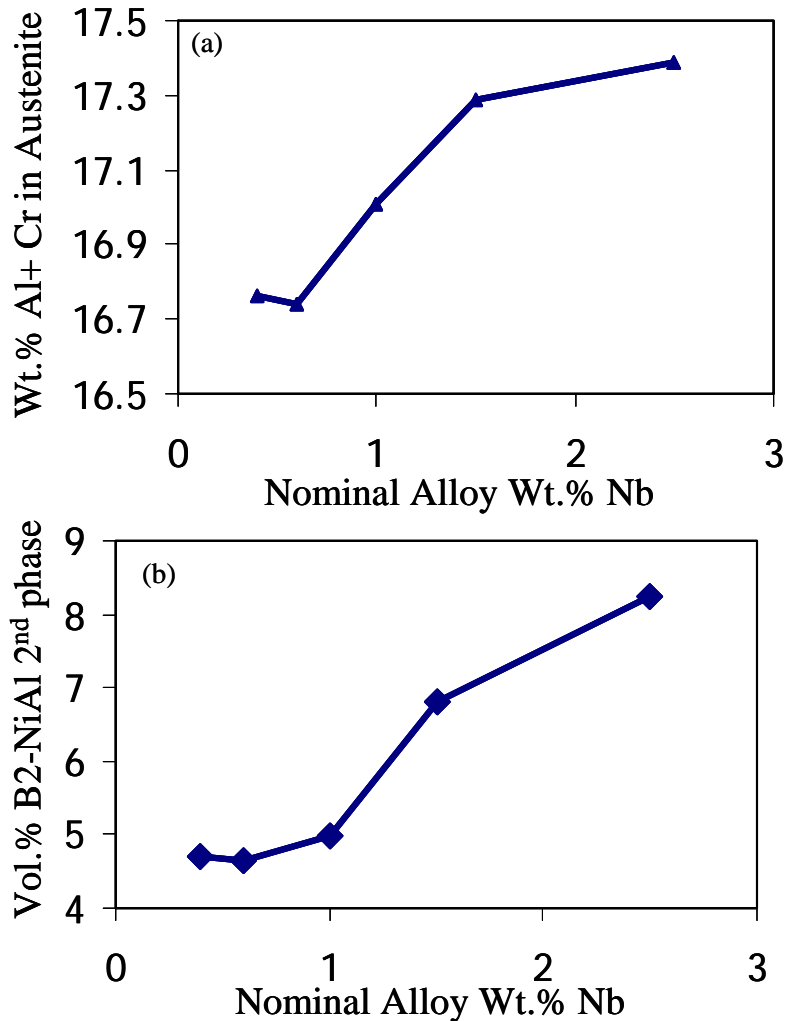


Fig. 3- Computational thermodynamic predictions for Fe-20Ni-14Cr-3Al-xNb-0.1C wt.% base alloy at 750°C data (after references 1 and 8). (a) wt.% Al+Cr in the austenitic matrix phase; (b) vol.% B2-NiAl base phase

Insights into the beneficial effects of Nb on oxidation in AFA alloys were obtained from computational thermodynamic analysis of the equilibrium phases in the AFA alloys [1,8]. The solubility of Al and Nb in austenite decreases significantly with decreasing temperature from the 1200°C solution treatment temperature used for AFA alloys. This results in the formation of nanoscale MC (primarily NbC) and submicron/micron size Fe<sub>2</sub>(Mo,Nb) based Laves phase and B2-NiAl base phase precipitates on exposure at the ~600-900°C range service temperatures (minor amounts of other B, C, Cu, P, etc containing precipitates may also be formed) [4,8,9]. Computational thermodynamic predictions for Fe-20Ni-14Cr-3Al-xNb-0.1C wt.% base alloys at 750°C are shown in Fig. 3. Increasing the alloy Nb content had two unexpected but significant effects. First, increased Nb content resulted in higher levels of Cr in the austenite matrix phase, which was offset slightly by decreased Al levels (total Al + Cr content was plotted in Fig. 3a). Second, increased Nb content resulted in an increased volume fraction of the B2-NiAl base second phase precipitates (Fig. 3b).

In multi-phase alloys, the composition of the matrix phase and the prevalence of second phase reservoir precipitates are critical in determining whether a protective scale can be formed and maintained [10,11]. Specifically for AFA alloys, the matrix phase is austenite with a relatively low maximum Al solubility of ~1.5-2 wt.% in the 600-900°C oxidation temperature range of interest. As such, it is dependent on the beneficial third-element effect of Cr [12] to establish a protective alumina scale, with increased levels of Cr in the austenite matrix phase a key benefit. The B2-NiAl precipitates act as the Al reservoir to maintain alumina scale formation. Increased B2-NiAl phase precipitate volume fraction with increasing levels of Nb provides a more effective Al reservoir, which can assist the alloy in maintaining alumina scale formation. Additional factors may also play a role in the beneficial effects of Nb on oxidation resistance of AFA alloys and are discussed in reference 1.

Based on the aforementioned analysis, alloy 4-2.5<sup>HfY</sup> was designed in an attempt to maximize AFA alloy oxidation resistance. Relative to alloy 4-1, the Cr content in alloy 4-2.5<sup>HfY</sup> was increased from 12 wt.% nominal to 15 wt.%, and the Nb content was increased from 1 to 2.5 wt.%. Reactive element additions of Hf and Y were also added to further improve the quality of the alumina scale. Studies of this alloy from 650-800°C in air with 10% water vapor are in progress, but likely need to accumulate ~10,000 total h data before a definitive assessment of their effects can be made. An accelerated test protocol using 10 h cycles at 900°C in air with 10% water vapor for a total of 1000 h was therefore adopted in order to gain insight regarding the effectiveness of the alloy modifications attempted in alloy 4-2.5<sup>HfY</sup>.

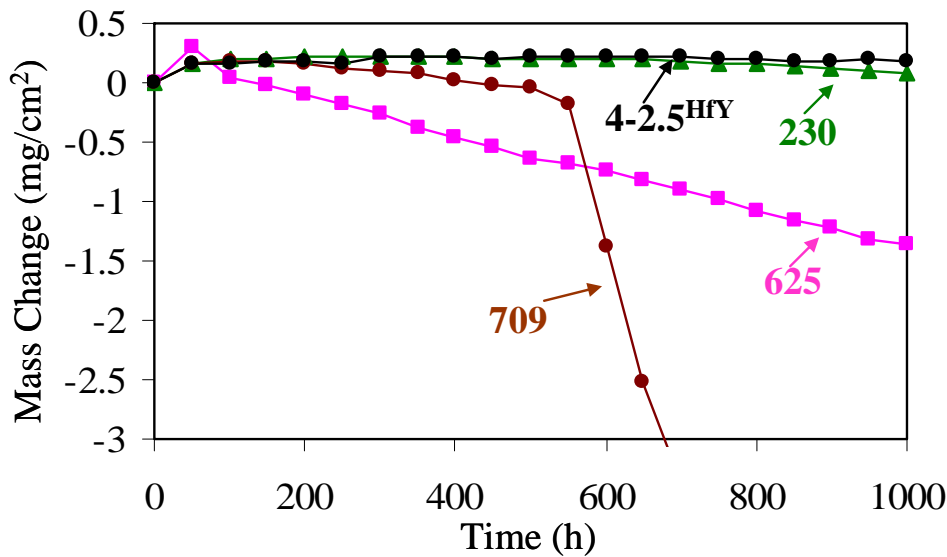


Fig.4- Cyclic oxidation (10 h cycles) at 900°C in air with 10% water vapor (after reference 13).

Fig. 4 shows 900°C oxidation data (10 h cycles, 1000 total h) for alloy 4-2.5<sup>HfY</sup> and several commercial alloys in air with 10 vol.% water vapor [3, 13]. At higher temperatures, oxide reaction products can become susceptible to spallation during thermal cycling. Such spallation results in mass loss, as was observed for the advanced austenitic alloy 709 and the Ni-base alloy 625 (58Ni-21.5Cr-9Mo-5Fe-3.6Nb/Ta wt.% base) after ~200-500 h exposure at 900°C under this accelerated test condition. In contrast, alloy 4-2.5<sup>HfY</sup> showed excellent oxidation resistance, comparable to that of alloy 230 (57Ni-22Cr-14W-2Mo-0.02La wt.% base), which is among the most oxidation-resistant high-temperature alloys available today, but is estimated to be significantly more costly than AFA alloys. Note that the oxide formed on alloy 230 was adherent but experienced some mass loss due to Cr oxy-hydroxide species evaporation [6,11]. Such evaporation may be a limiting factor in some applications, particularly thin-walled components [11]. Overall these results suggest that increased Cr and Nb contents in AFA alloys,

in combination with reactive element additions, hold the potential to increase the upper temperature limit of the AFA alloy family.

## TENSILE AND AGEING BEHAVIOR

Tensile properties were evaluated from solution-treated material using sub-sized dog bone shaped tensile specimens with a thickness of 0.4 - 0.6 mm, a gage length of 12.7 mm and a width of 3.2 mm. Tensile properties were evaluated at a strain rate of  $1 \times 10^{-3} \text{ s}^{-1}$  for as-solution treated and 750°C aged (50, 500, 2012 h) material (test samples were cut from a block of aged material away from the oxidized regions). Strain gages were not attached directly to the specimen gage lengths, and the data should therefore be considered semi-quantitative.

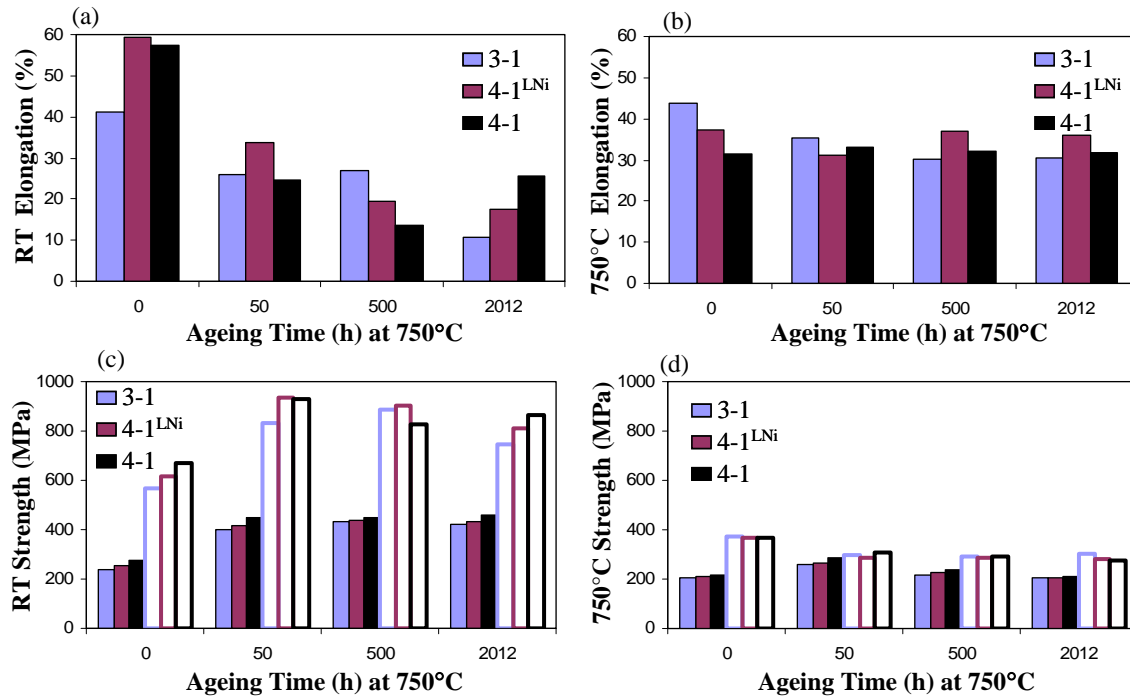


Fig. 5- Tensile properties for alloys 3-1, 4-1<sup>LNi</sup>, and 4-1 after ageing at 750°C (after reference 2). (a) elongation at room temperature (RT); (b) elongation at 750°C; (c) yield strength (filled) and ultimate strength (open) at RT; (d) yield strength (filled) and ultimate strength (open) at 750°C.

Tensile properties for AFA alloys 3-1, 4-1<sup>LNi</sup>, and 4-1 are shown in Fig. 5 [2]. The tensile behavior for all three alloys was similar despite the differences in Al, Cr, and Ni content (Table 1). As solution-treated material exhibited yield strengths in excess of 200 MPa and elongations of 40-60% at room temperature (Fig. 5 a,c). Similar yield strengths were observed at 750°C, with elongations reduced to 30% range (Fig. 5 b,d). On ageing, yield strength at room temperature doubled to 400 MPa range, with a decrease in elongation to 10-25% range. Ageing at 750°C had little effect on yield strength or elongation at 750°C, with 200MPa range yield strength and 30% range elongations. Ageing trends as a function of exposure time at 750°C suggested that the majority of ageing effects emerge after only 50 h of exposure, which is consistent with the relatively rapid precipitation of B2-NiAl and Laves phases at 750°C in AFA alloys [2,8,9].

Preliminary microstructural analysis indicated the formation of small amounts of sigma phase in all the AFA alloys on ageing at 750°C; however, these precipitates remained fine (< 3 micron size range) and did not appear to appreciably degrade mechanical properties. Calculations suggest that, if needed, lower levels of Mo and W than the 2 and 1 wt.% used in these alloys (Table 1), respectively, along with increased C and/or decreased Al and Cr levels would greatly reduce or eliminate this sigma formation. Longer-term ageing studies are planned to better assess whether this sigma phase formation is a liability, and, if so, at what temperature it becomes a liability.

### CONCLUDING REMARKS

The AFA alloy properties achieved to date are considered to be sufficient to merit evaluation for industrial applications up to ~700-750°C. Additional alloy development will be needed for higher-temperature applications (~750-900°C); however, the results obtained for alloy 4-2.5<sup>HfY</sup> under the accelerated screening protocol at 900°C in air with 10% water vapor show good potential to achieve oxidation resistance in this higher temperature range. Future efforts will focus on long-term evaluation of creep, oxidation, and microstructural stability in trial scale heats of AFA alloys made by commercially viable casting and rolling processes. It is anticipated that two to three grades of AFA alloys will be pursued, with compositions dependent on the intended service temperature.

### ACKNOWLEDGEMENTS

The authors thank G. Muralidharan, J.R. Keiser, B.A. Pint, and I.G. Wright for reviewing this manuscript. This work was funded by the United States Department of Energy (USDOE), Fossil Energy Advanced Research Materials program. Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the US DOE under contract DE-AC05-00OR22725. Additional funding and collaboration with the SHaRE User Facility at ORNL is also acknowledged. Notice: This submission was sponsored by a contractor of the United States Government under contract DE-AC05-00OR22725 with the United States Department of Energy. The United States Government retains, and the publisher, by accepting this submission for publication, acknowledges that the United States Government retains, a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this submission, or allow others to do so, for United States Government purposes.

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