

**MULTI-PHASE HIGH TEMPERATURE ALLOYS:
EXPLORATION OF ALUMINA-FORMING, CREEP-RESISTANT
AUSTENITIC STAINLESS STEELS**

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ABSTRACT

Work in 2007 focused on the development of a new class of heat-resistant austenitic stainless steel alloys which achieved a unique combination of high-temperature creep strength and excellent oxidation resistance via protective Al₂O₃ scale formation. Strengthening is achieved via the formation of stable nano NbC carbides with/without Fe₂Nb and related intermetallic phase dispersions, with controlled levels of Al to enable Al₂O₃ scale formation in both air and air + water vapor environments up to ~800-900°C. The developed alloys exhibit comparable creep resistance to that of the best commercial heat-resistant austenitic stainless steels, and the protective Al₂O₃ scale formation provides oxidation resistance superior to that of advanced Cr₂O₃-forming heat-resistant austenitic alloys. Preliminary screening also indicated that the developed Al-modified alloys were amenable to welding.

INTRODUCTION

The efficiency of boiler/steam turbine power plants is a strong function of steam temperature and pressure [1]. Consequently, it is attractive to operate at higher temperatures and pressures to increase energy efficiency. However, under such conditions, high-temperature creep strength is a major issue for hot components in advanced fossil energy conversion and combustion systems. For example, current goals for advanced fossil energy power plants call for ferritic steels capable of operation above 600°C, and austenitic steels capable of operation at greater than 700°C. Components of interest range from superheater tubes to industrial gas turbine components. A key need is the concurrent development of strength and oxidation resistance.

Conventional heat-resistant stainless steels rely on Cr₂O₃ scales for protection from high-temperature oxidation. However, the oxidation resistance of Cr₂O₃-forming alloys in the presence of aggressive species such as water vapor, carbon, sulfur, etc. is compromised [2], inhibiting increases in operating temperature to achieve improved efficiencies. Alumina scales grow at a slower rate than Cr₂O₃, offer superior thermodynamic stability, and thus provide protection to higher temperatures than Cr₂O₃ in many aggressive, industrially-relevant environments [2]. Modification of the creep-resistant, austenitic face-centered cubic (fcc) form of Fe to form Al₂O₃ protective oxide scales has the potential to solve these problems, and permit higher operating temperatures in water vapor and other aggressive environments. A fundamental problem is that Al stabilizes the weaker body centered cubic (bcc) form of Fe, such that levels of Al typically added to achieve alumina scale formation result in bcc phase formation, and a loss of creep resistance at service temperature.

We recently reported the development of a creep-resistant, Al₂O₃-forming austenitic stainless steel, HTUPS 4 (high temperature ultrafine precipitate strengthened) [3]. The basis for achieving both Al₂O₃ scale formation and creep resistance in this alloy was a compositional modification to maintain a single-phase, face-centered cubic (fcc) matrix in the presence of the strong bcc-stabilizing effects of Al, and the avoidance of Ti and V microalloying additions. Additions of Ti and/or V have been used to aid formation of nano-MC (M = Nb, Ti, V, etc.) carbide dispersions to improve creep strength, but those additions also result in loss of the ability to form protective Al₂O₃ scales in these relatively low Al-containing alloys. The new alloy is based on Fe-20Ni-14Cr-2.5Al-0.95Nb weight percent, wt.%, with strengthening achieved via the formation and stability of nano-NbC carbides during creep.

DISCUSSION OF CURRENT ACTIVITIES

Efforts in 2007 focused on detailed characterization of the oxidation resistance and mechanical properties of the HTUPS 4 alloy. Systematic study of the effects of alloy additions on properties was also explored in order to provide a scientific basis for alloy optimization. This progress report is compiled from findings from this work, originally reported in references 3-5.

Low specific mass gains, consistent with the slow oxidation kinetics of protective Al₂O₃ scale formation, were observed for HTUPS 4 over the course of ten, 100-h cycles (1000 h total time at temperature) (Fig. 1a, after reference 3). By comparison, ~100 μm thick gas-turbine recuperator foils of NF709 (Fe-25Ni-20Cr wt.% base) and HR 120 (Fe-37Ni-25Cr wt.% base), state-of-the-

art Cr_2O_3 -forming austenitic alloys, showed moderately higher specific mass gains. However, the mass change data reflects both the balance of oxygen uptake to form Cr_2O_3 and the mass loss from volatilization of the Cr_2O_3 , such that the mass change curve under represented the actual rate of oxidation and Cr consumption. For example, at 800°C in air with 10% water vapor, NF709 foil suffers from volatility-driven Cr_2O_3 scale breakdown and extensive Fe-oxide nodule formation after only 5000-7000 h of exposure, depending on foil thickness [6-8]. Even at 700°C in air with 10% water vapor, NF709 alloy foil exhibits the onset of Fe-oxide nodule formation after $\sim 10,000$ h [6-8]. The higher Ni-containing alloys such as HR 120 show longer lifetimes in water-vapor containing environments due to healing of the Fe-oxide nodule formation by NiO [6, 8]. However, the high Ni levels also significantly increase alloy cost. The available data indicate that Al_2O_3 scale forming alloys are not adversely affected in air with water vapor at these temperatures, due to the high stability of Al_2O_3 in water vapor [8-9].

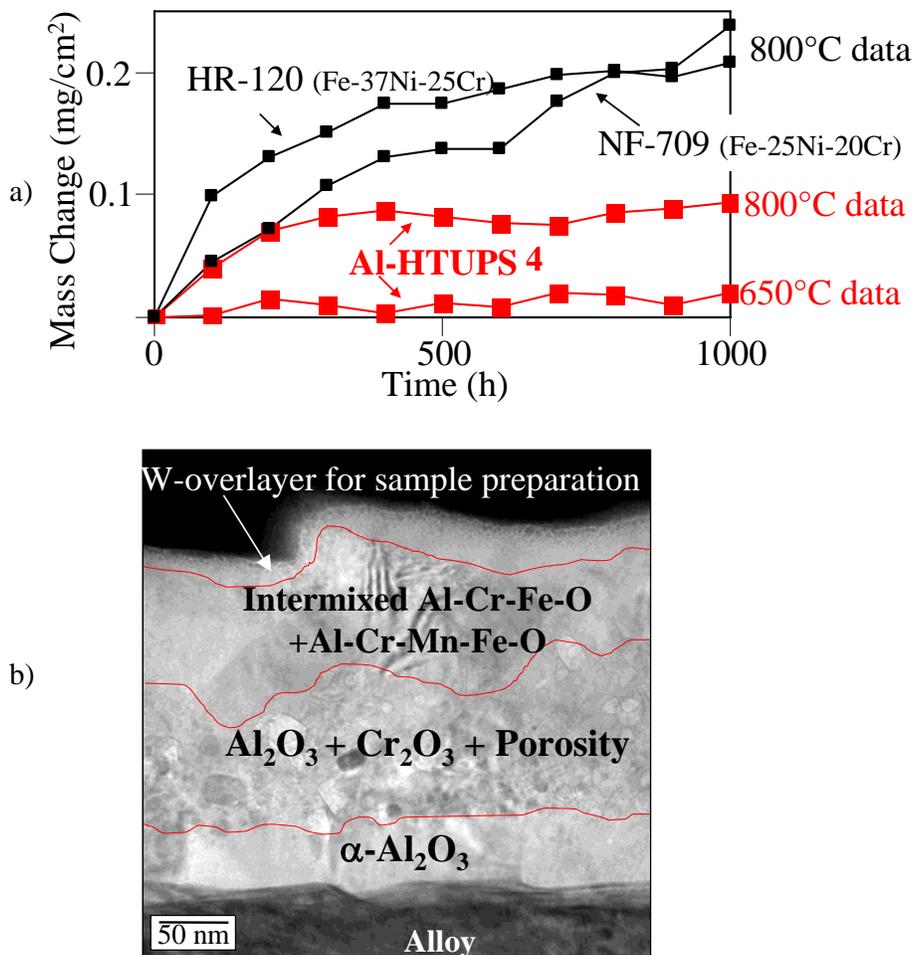


Fig.1- a) Oxidation kinetics in air with 10% water vapor (10-100 h cycles) (NF709 and HR 120 data from references 6,7), b) TEM bright field cross-section of scale formed on HTUPS 4 after 1000 h at 800°C in air with 10% water vapor. Oxidation data and micrograph from reference 3.

A bright field transmission electron microscopy (TEM) cross-sectional image of the scale formed on the HTUPS 4 alloy after 1000 h at 800°C in air with 10% water vapor is shown in Fig. 1b (the following description of scale microstructure is from reference 3). The scale consisted of a 40-50 nm inner region of columnar α -Al₂O₃ (diameter: 75-100 nm) adjacent to the alloy, and an overlying 60-100 nm thick, fine-grained (< 20 nm) intermixed layer of transition Al₂O₃ + Cr₂O₃ + porosity. In some scale regions, a 0.05-0.5 μ m columnar-grained surface layer of intermixed Al-Cr-Fe-O + Al-Cr-Mn-Fe-O rich phase was also observed, as were occasional nodules 1-5 μ m thick containing Nb-rich oxide regions. Auger electron spectroscopy profiling indicated that the oxide scale was Al-rich, with generally less than 10 at.% total combined of Cr, Fe, Si [3]. The observed oxide scale microstructure is consistent with the measured oxidation kinetics, which indicated relatively high mass gain during the first few hundred hours of exposure (when the mixed oxides were forming), followed by a transition to slow, protective oxidation kinetics when the α -Al₂O₃ layer developed.

Figure 2 shows creep rupture life data for HTUPS 4 relative to some commercially available heat-resistant alloys. The data indicate that HTUPS 4 exhibits creep resistance comparable to state-of-the-art austenitic stainless steels such as NF709, and approaches the range offered by the Ni-base alloy 617. In addition to the significant advantage of Al₂O₃ scale formation (both NF709 and 617 form Cr₂O₃ base scales), HTUPS 4 has Ni levels lower than NF709 and 617, and therefore has the potential to be lower cost. Figure 3 shows results of an initial weldability assessment of HTUPS 4 via a gas tungsten arc weld pass. No cracking is observed in or near the weld. Much more expansive welding studies will be needed before a definitive conclusion regarding the weldability of HTUPS 4 can be made; however, this initial finding is promising.

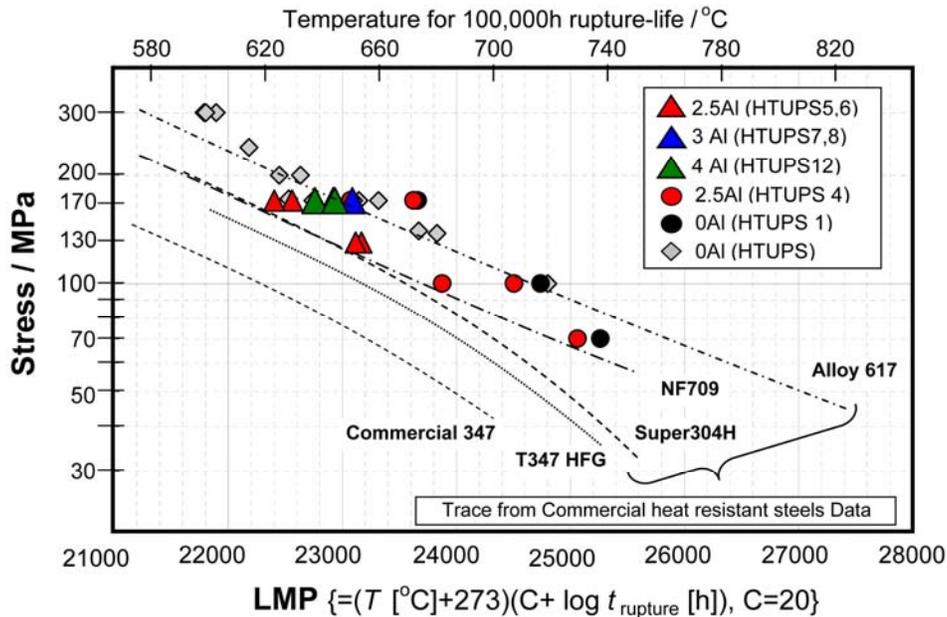


Fig. 2- Comparison of Larson Miller Parameter of the developed alloys in the present study with several commercial heat-resistant austenitic stainless steels and alloys. Figure modified from reference 3. Data for HTUPS 1 – 12 is for samples with 10% cold work.

One limitation of HTUPS 4 is that it requires cold work to aid nucleation of the nano NbC strengthening precipitates responsible for the excellent creep resistance. Exploration of the effects of Al, Nb, Ti, and V additions was therefore explored, with the ultimate goal of optimizing creep resistance and reducing or eliminating the need for cold work to obtain sufficient creep resistance.

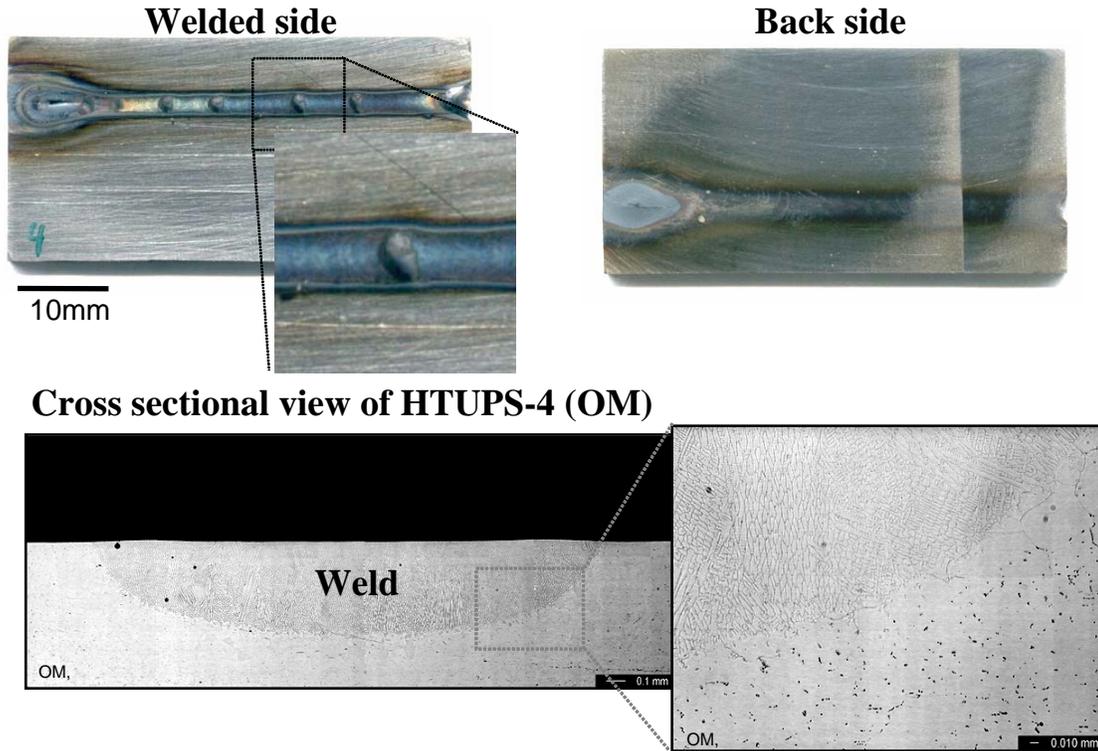


Fig. 3- Preliminary gas tungsten arc-weld screening of HTUPS 4 (OM = optical microscopy).

Fig. 4 shows short term oxidation behavior (from reference 4) for a Fe-21Ni-14Cr-2.5Al-1.7Nb wt.% base alloy with additions of Ti, V, and Ti + V, at the levels of 0.3Ti and 0.5V wt.% utilized in the original (Cr_2O_3 -forming) HTUPS alloys, from which the Al_2O_3 -forming HTUPS 4 alloy was derived [10]. Slow oxidation kinetics, consistent with Al_2O_3 scale formation, were initially observed for the base alloy, and for the alloys with individual additions of 0.3 Ti or 0.5V wt.%. However, the addition of both 0.3Ti and 0.5V resulted in a marked acceleration in oxidation kinetics, consistent with that observed in reference 3 for the development of the HTUPS 4 alloy. As shown in Fig. 5, the faster oxidation kinetics for the alloy with 0.3Ti and 0.5V were caused by the formation of an external Fe-Cr rich oxide scale, with internal oxidation of Al, rather than a continuous, external Al_2O_3 scale. These results suggest that small additions of Ti or V, individually, to improve creep resistance can be tolerated from an oxidation standpoint. For example, an Al_2O_3 -forming austenitic alloy containing 0.2 wt.% V and strengthened by both nano MC carbides and Fe_2Nb Laves phase precipitates (alloy designation FNC 31 in the present work) resulted in a creep rupture life of over 800 h at 750°C and 100 MPa in air in the solution treated condition (no cold work). Subsequent cold work increased the creep rupture life to nearly

1800 h [5]. This alloy also exhibited mass gain kinetics consistent with Al_2O_3 scale formation at 800C in air and air with 10% water vapor [4].

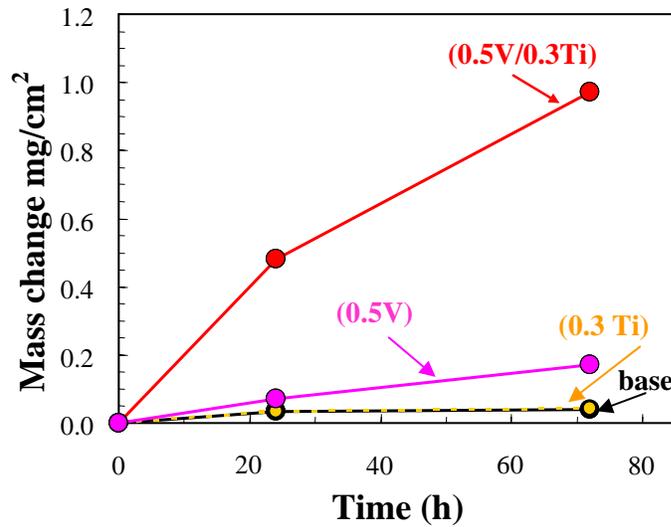


Fig. 4- Oxidation data at 800°C in air for Fe-21Ni-14Cr-2.5Al-1.7Nb wt.% base alloys with additions of Ti and/or V (after reference 4).

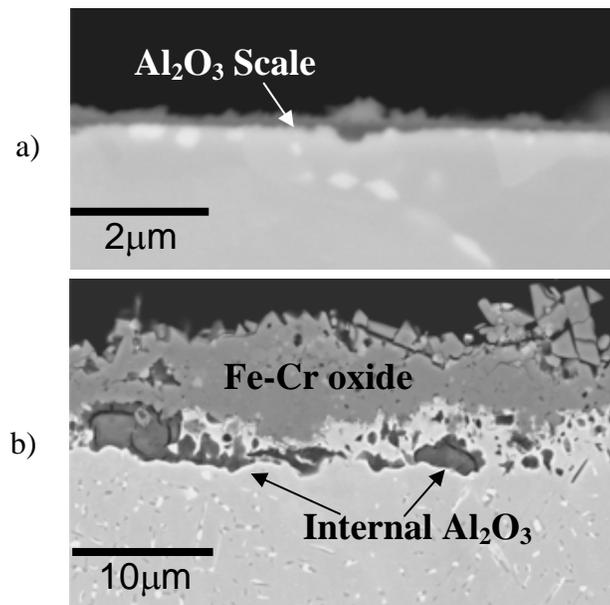


Fig. 5- Secondary electron mode cross-section images of a) 0.3 Ti alloy from Fig. 3 and b) 0.5V + 0.3Ti alloy from Fig. 3 after 72 h oxidation at 800°C (reference 4).

A series of Al₂O₃-forming austenitic alloys with Al contents from 2.5 - 4 wt.%, and Nb contents from 0.1 - 3 wt.%, incorporating small additions of Ti or V, were manufactured for exploration of creep and oxidation resistance (designated HTUPS 5-12, composition details currently proprietary). Initial creep results for some of these alloys are shown in Fig. 2. Creep resistance was generally comparable to, or only moderately lower, than HTUPS 4, indicating the potential viability of higher Al levels in these alloys.

Oxidation behavior was also explored for these alloys at 900°C in air (Fig. 6, microstructures from kinetic data presented in reference 4). HTUPS 4 does not exhibit exclusive, external Al₂O₃ scale formation at 900°C, and areas of internally oxidized Al were clearly observed. This indicates a loss of protective Al₂O₃ scale forming ability between 800 and 900°C for HTUPS 4. Only internal oxidation of Al and external Fe-Cr rich oxide formation were observed for HTUPS 8, which contains more Al than HTUPS 4 (3 vs 2.5 wt.% Al) but less Nb. Alumina scale formation was achieved at 900°C by either increasing Al content, HTUPS 12 with 4 wt.% Al, or increasing Nb content, FNC 31 (Fig. 6).

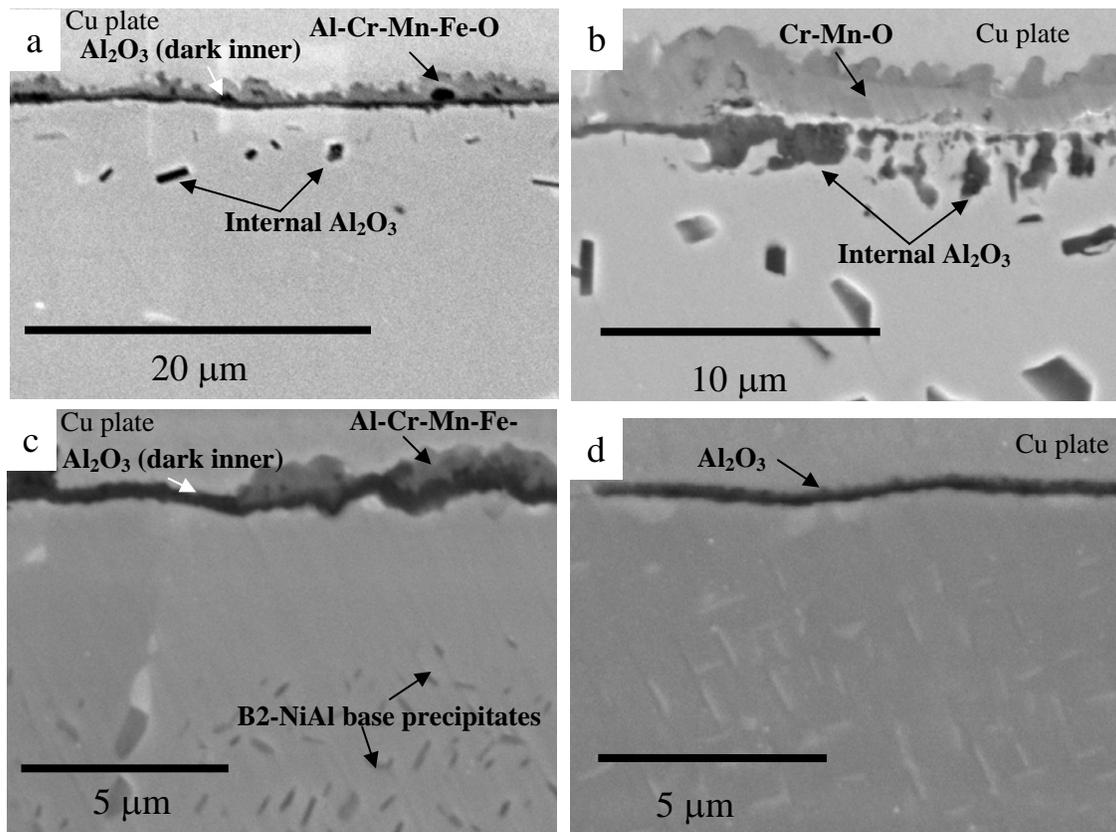


Fig. 6- SEM secondary electron image cross-sections of alloys oxidized for 100 h at 900°C in air. a) HTUPS 4 (2.5Al/0.95Nb); b) HTUPS 8 (3 Al/low Nb); c) HTUPS 12 (4 Al/low Nb); d) FNC 31 (2.5Al/high Nb). The Cu plate was used for sample preparation.

FUTURE WORK

The insights into balancing oxidation and creep resistance gained in this study hold the potential to modify a wide range of existing Fe-base alloy families to form protective Al₂O₃ scales, without loss of creep strength or increase in cost. We plan to explore the range of alloy types and composition threshold limits that this approach can be applied to. We are particularly interested in developing alloys with lower Ni contents to further reduce cost, and alloy modifications for increasing the upper temperature limit of Al₂O₃ scale formation for more demanding applications. Thus far, properties have only been demonstrated from small, laboratory scale arc-castings. The next step is to collaborate with interested alloy manufacturers to produce pilot-scale alloy heats by commercial methods, to provide a basis for scale up and transition to industrial use.

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ACKNOWLEDGEMENTS

This research was sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research Materials (ARM) Program. Oak Ridge National Laboratory is managed by U.T.-Battelle, LLC for the U.S. Department of Energy. The authors thank Joachim Schneibel and Joe Horton for reviewing this manuscript. Extensive discussions and technical input from John Shingledecker, and Ian Wright are also gratefully acknowledged.