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Development and Property Evaluation of Nuclear Grade Wrought FeCrAl Fuel Cladding for Light Water Reactors

Y. Yamamoto*, B.A. Pint, K.A. Terrani, K.G. Field, Y. Yang, L.L. Snead

Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37831-6115, USA

*Corresponding author: yamamotoy@ornl.gov , +1-865-576-7095

Abstract

Development of nuclear grade, iron-based wrought FeCrAl alloys has been initiated for light water reactor (LWR) fuel cladding to serve as a substitute for zirconium-based alloys with enhanced accident tolerance. Ferritic alloys with sufficient chromium and aluminum additions can exhibit significantly improved oxidation kinetics in high-temperature steam environments when compared to zirconium-based alloys. In the first phase, a set of model FeCrAl alloys containing 10–20Cr, 3–5Al, and 0–0.12Y in weight percent, were prepared by conventional arc-melting and hot-working processes to explore the effect of composition on the properties of FeCrAlY alloys. It was found that the tensile properties were insensitive to the alloy compositions **studied**; however, the steam oxidation resistance strongly depended on both the chromium and the aluminum contents. The second phase development focused on strengthening Fe-13Cr-5Al with minor alloying additions of molybdenum, niobium, and silicon. Combined with an

optimized thermo-mechanical treatment, a thermally stable microstructure was produced with improved tensile properties at temperatures up to 741°C.

Keywords: nuclear grade, wrought, FeCrAl, accident tolerant fuel cladding, LWR

1. Introduction

During severe nuclear reactor accidents that result in loss of coolant, the core becomes exposed to a high-temperature steam environment that results in a multitude of physical and chemical degradation phenomena in the core [1]. Zirconium base alloys typically burst at 700-1100°C due to high internal pressure [2] and continues to experience an increase in temperature due to decaying heat generation inside the core as well as the heat generated due to their oxidation with steam. The reactor design requirements have been put in place such that maximum fuel temperature does not extend beyond 1204°C to avoid excessive zirconium-steam reaction and preserve core geometry once a quench sequence is initiated [3]. Under a beyond design basis accident (BDBA), the fuel temperature can exceed well beyond this limit resulting in rapid oxidation of fuel cladding that is accompanied by significant heat production and hydrogen gas generation [1, 4]. Rapid heat and hydrogen generation in the core due to steam oxidation of the cladding as well as other core constituents [5] greatly exacerbate the degradation phenomena in the core and results in melting and relocation of the core inside the reactor pressure vessel (RPV). In order to enhance safety margins and reduce the critical heat removal limit from the core during these severe accident scenarios, substitution of zirconium alloys with materials that exhibit significantly slower oxidation kinetics in high temperature steam environments is necessary [6,7,8].

The FeCrAl alloy class has been widely used with success in many industries where high temperature oxidation resistance is needed including water-vapor containing environments in fossil fuel energy plants [9,10]. An initial evaluation on the FeCrAl alloy system for nuclear energy production was conducted by

General Electric in the 1960's (for example see Refs. [11,12,13] and those within), focusing on corrosion resistance, radiation response, and fuel-cladding chemical interaction. Even prior to that, air oxidation studies on FeCrAl alloys were carried out at Westinghouse research laboratories [14]. Although the reports of these programs provide insight into the performance of simple FeCrAl and FeCrAl+Y model alloys, it does not provide sufficient foundation for a truly optimized, nuclear-grade FeCrAl alloy which exhibits exceptional normal operation performance combined with enhanced accident tolerance for nuclear power generation applications. Therefore, recent work has been initiated to develop FeCrAl alloys deemed 'nuclear grade.' The nuclear grade designation is used here to describe alloys with several important features for nuclear applications including good mechanical properties for extended periods of elevated temperature, oxidation resistance, radiation tolerance, long-term aqueous corrosion resistance, compatibility with the prototypical UO₂ fuel and optimal neutronic behavior (including minor alloying additions) which do not significantly penalize the overall nuclear reactor operation. Furthermore, nuclear grade FeCrAl alloys should be weldable and formable including the ability to make thin-walled tubes for LWR fuel cladding.

The FeCrAl cladding development strategy has used high temperature oxidation resistance in steam as the initial assessment. The oxidation rate is a key for enhancing safety margins under severe accident conditions since it is directly proportional to the heat generation and hydrogen production rate [6], which occurs when the fuel cladding reacts with steam during a severe accident. Combined with superior high temperature strength compared to zirconium alloys, utilization of this class of alloys is expected to enhance burst margins during BDBA scenarios. Additional assessments of mechanical properties, radiation resistance and fabricability are needed followed by the development of a commercial-based processing route for thin-wall LWR fuel cladding. Initial work on this strategy identified FeCrAl as a leading candidate and began to explore some initial effects of composition on high-temperature steam oxidation behavior [15,16]. Subsequently, model ferritic FeCrAl alloys were evaluated which exhibited

oxidation kinetics >2 orders of magnitude below that of zirconium alloys at high temperatures (<1500°C) thereby satisfying the primary requirement of the alloy development strategy [17,18].

Among the various reactor physics related aspects of utilization of this class of cladding in LWRs, neutron economy was initially evaluated. The results of this evaluation have been documented extensively [19,20,21,22,23]. Briefly, the higher thermal neutron absorption in the Fe-based alloys may be rendered inconsequential on the reactor cycle length by reducing the thickness of the cladding. This is the main strategy that was used in the past for austenitic stainless steel cladding used in LWRs [24]. For instance, in case of PWRs, the ~600µm-thick Zr-based cladding may be replaced with a ~350µm-thick FeCrAl alloy. The new cladding internal volume, made available by this reduction, may now be filled with additional fuel (UO₂). In this manner, the reactor cycle length will not be penalized.

This paper summarizes the current complementary efforts aimed at developing nuclear-grade FeCrAl alloys for LWR fuel cladding with potential enhanced accident tolerance, including evaluation of properties of the candidate alloys such as fabricability and mechanical properties which would be correlated with the oxidation resistance and the irradiation resistance of the series of the alloys that have already been discussed elsewhere [18,25]. The results are segmented into two phases: the first was an evaluation of the effect of major alloying constituents (namely Cr and Al) on mechanical properties and steam oxidation resistance and the second focused on optimizing mechanical properties via computationally-guided minor alloying additions and thermo-mechanical treatments within the composition space defined in the first phase. A parallel project is optimizing oxide dispersion strengthened (ODS) FeCrAl for this application [17]. By focusing on wrought FeCrAl, the ultimate goal is to utilize commercial seamless tube fabrication processes for production of fuel cladding tubes using simple drawing techniques that are even simpler than the pilgering methods needed for current Zr-based cladding production [26,27].

2. Experimental procedure

2.1. Phase I alloy processing

It was postulated that the higher Cr content in these alloys would be beneficial for corrosion resistance in the high temperature water of LWRs and also high-temperature steam oxidation resistance ($>1000^{\circ}\text{C}$) to support the stability of the protective α -alumina-scale in high temperature oxidizing environment such as those seen during a LOCA [28]. On the other hand, it was expected that higher Cr content would result in potential embrittlement of these alloys at typical LWR operating temperatures ($288\text{-}320^{\circ}\text{C}$) due to the formation of either Cr-rich α' or σ -FeCr phases given the specific ageing or irradiation temperature [29,30,31,32,33,34]. The higher Al content is also beneficial for high-temperature steam oxidation resistance because of promoting external alumina scale formation at elevated temperatures, but it may raise the ductile-brittle transition temperature (DBTT) which could affect the room temperature fabricability [35]. Kobayashi et al. [32] reported a composition range of potential Cr-rich α' formation in Fe-Cr-Al ternary alloy systems at 475°C , which indicated that more than 6 at% (~ 3 wt.%) of the Al addition would be effective in reducing the stability of Cr-rich α' , and further Al addition would result in increasing the solution limit of Cr in BCC-Fe matrix. Similar trends in the Fe-Cr-Al have been recently proposed by other authors [33,34]. Yttrium was added to enhance the oxidation resistance at elevated temperatures. Addition of such reactive elements is known to reduce the growth rate of the alumina scales and improve the adherence resulting in improved oxidation resistance compared to that of base alloys which do not contain yttrium [36,37].

Based on these considerations as well as known oxidation and phase stability composition spaces, model FeCrAl alloy heats in a nominal composition range of Fe-(10-20)Cr-(3-5)Al-(0-0.12)Y in weight percent were selected, as summarized in **Table 1**. It should be noted that yttrium can easily be oxidized or evaporated during arc-melting process and therefore the yield of yttrium was not consistent among the alloys. Three commercial FeCrAl alloys, APMT (Kanthal, Fe-22Cr-5Al base, an extruded bar), Alkrothal

14 (Kanthal, Fe-15Cr-4Al base, a rolled and annealed plate), and Aluchrom YHf (ThyssenKrupp VDM, Fe-20Cr-6Al base, a rolled and annealed plate), were also used to serve as basis for comparison of their properties with the model FeCrAl alloys.

Table 1. Compositions of Phase I model FeCrAl alloys and commercial FeCrAl alloys.

ID	Nominal, wt. %				Analyzed, wt. %				Remarks
	Fe	Cr	Al	Y	Fe	Cr	Al	Y	
B105N	Bal.	10	5	0	85.12	9.64	5.22	0	• Arc-melted + hot-forged/-rolled + annealed (with/without applying 10% cold-roll)
B105Y	Bal.	10	5	0.15	85.15	10.01	4.78	0.038	
B104Y	Bal.	10	4	0.15	86.12	9.99	3.83	0.040	
B125Y	Bal.	12	4.5	0.15	83.56	11.96	4.42	0.027	
B134Y	Bal.	13	4	0.15	83.02	13.01	3.94	0.007	
B155Y	Bal.	15	5	0.15	79.87	14.98	5.02	0.033	• C, N, O and S contents are less than 60, 26, 26, and 31 wppm, respectively
B155Y-2	Bal.	15	5	0.15	79.88	15.21	4.83	0.063	
B154Y	Bal.	15	4	0.15	81.18	14.86	3.85	0.012	
B154Y-2	Bal.	15	4	0.15	80.99	15.03	3.92	0.035	
B184Y	Bal.	17.5	4	0.15	78.39	17.51	3.91	0.043	
B183Y	Bal.	17.5	3	0.15	79.27	17.53	2.95	0.019	+ 2.75Mo, 0.18Ni, 0.47Si, 0.17Hf, 0.11Zr, 0.04C
B183Y-2	Bal.	17.5	3	0.15	79.52	17.51	2.93	0.017	
B203N	Bal.	20	3	0	77.05	20.01	2.91	0	
APMT	Bal.	22	5	0.2	69.75	21.18	4.77	0.212	
Alkrothal 14	Bal.	15	4	0	80.31	14.73	4.23	0	
YHf	Bal.	20	6	0.06	72.85	20.31	6.1	0.0626	+ 0.19Mn, 0.14Ni, 0.19Si, 0.05Zr, 0.02C

The model alloys were cast by arc-melting in a back-filled argon gas atmosphere with pure element feedstock and pre-alloyed Al-Y to button ingots. The ingots were flipped and melted several times to avoid any potential inhomogeneity in the ingots. Then the ingots were drop-cast in a back-filled argon gas atmosphere to a water-cooled copper mold with a size of $13 \times 25 \times 125$ mm to make bar-shape ingots, or 36 mm diameter $\times$ 100 mm length to make a columnar ingot. The ingots were homogenized at 1200°C for more than 2 h, and then thermo-mechanically processed by using hot-forging at 1200°C , followed by rolling in a wide temperature range from 700 to 1050°C to make plate specimens with a final nominal sheet thickness of 0.85 mm. Some of the cast ingots were hot-rolled without pre-forging. Subsequent annealing in a temperature range from 700 to 1050°C after the rolling process was applied to control the

recrystallized grain structure. In order to evaluate the effect of grain size on mechanical properties, two different thermo-mechanical processes were applied to several alloys. For the specimens with large grain sizes (LG), the homogenized ingots were hot-rolled at 1050°C with 40% total thickness reduction, followed by annealing at 1050°C for 10 min. The average grain sizes of these samples were in a range of 250-900 μm . For the specimens with small grain size (SG), the homogenized and forged ingots were hot-rolled at 700°C with more than 90% total thickness reduction, followed by annealing at 700°C for 1 h, which gave uniform, fully recrystallized grains in a range of 20-35 μm . Additional cold rolling with 10% thickness reduction was applied for selected plate specimens with small grain size, which simulated a potential cold-shaping of industrial tube products after annealing process.

2.2. Phase II alloy processing

In Phase II, Fe-13Cr-4.5Al + Y was selected as the base composition for further optimization. Minor alloying additions such as Mo, Si, Nb, and/or C were added in order to introduce either solution-strengthening and/or precipitate-strengthening together with minimizing negative impacts on the other properties such as fabricability and oxidation resistance. The alloys were prepared by arc-melting in a back-filled argon gas atmosphere to make 25 $\times$ 25 $\times$ 100 mm size ingots or by a vacuum induction melting (VIM) with pure element feedstock to make 86 mm diameter $\times$ 300 mm columnar ingots (~20 kg). The nominal and analyzed alloy compositions of the Phase II FeCrAl alloys are summarized in **Table 2**. Note that T35Y2 in the table is a Phase I alloy used as a reference material. The cast ingots were homogenized at 1200°C for more than 2 h. The arc-melted ingots were hot-forged at 1200 or 800°C to make ~8 mm thick pancake-shape samples, followed by hot-rolling at 1200 or 800°C with more than 90% total reduction to ~0.89 mm thickness. The sheets were subsequently annealed at the hot-rolling temperature for up to 24 h for recrystallization and grain size control. The VIM ingots of T35Y2 and C35MN5 were extruded at ORNL at 1050 and 800°C, respectively, and then annealed at 700 and 800°C, respectively. In the case of C35MN5, more than 97% total area reduction was applied by conducting the extrusion twice in order to control the microstructure. To study thermal stability, warm-rolling and

annealing were applied to two selected alloys (C35M and C35MN5). They were hot-rolled at 800°C and 1150°C, respectively, and then warm-rolled at 300°C with more than 80% total thickness reduction, in order to obtain a heavily deformed microstructure. The warm-rolled plates were annealed in a temperature range of 600-700°C for C35M and 700-800°C for C35MN5 for various periods of time up to 504h.

Table 2. Nominal and analyzed compositions of Phase II FeCrAl alloys.

IDs		Fe	Cr	Al	Y	Mo	Si	Nb	C	Remarks
T35Y2	Nominal	82.35	13	4.5	0.15	-	-	-	-	Phase I, VIM + extrusion
	Analyzed	82.26	13.15	4.44	0.12	<0.01	0.01	<0.01	0.002	
C35M	Nominal	80.15	13	4.5	0.15	2	0.2	-	-	Arc-melt + hot-roll
	Analyzed	80.88	12.68	4.22	0.031	1.92	0.20	<0.01	0.003	
C35MC	Nominal	80.07	13	4.5	0.15	2	0.20	-	0.08	Arc-melt + hot-roll
	Analyzed	80.96	12.53	4.22	0.026	1.94	0.21	<0.01	0.089	
C35MNC	Nominal	79.83	13	4.5	0.15	2	0.20	0.3	0.02	Arc-melt + hot-roll
	Analyzed	80.41	12.77	4.31	0.065	1.95	0.20	0.24	0.026	
C35MN	Nominal	79.15	13	4.5	0.15	2	0.20	1	-	Arc-melt + hot-roll
	Analyzed	79.96	12.77	4.22	0.032	1.94	0.21	0.81	0.004	
C35MN5	Nominal	78.53	13	5.2	0.07	2	0.20	1	-	VIM + extrusion
	Analyzed	78.68	13.02	5.08	0.032	1.99	0.21	0.97	0.003	

2.3. Alloy characterization

Microstructure of the rolled/extruded samples was characterized by using a light optical microscope (OM) and a JEOL-6500F scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) and electron back-scatter diffraction (EBSD) system. The sectioned samples were prepared for characterization using typical metallography techniques followed by etching with a solution of 50 ml H₂O, 10 ml HNO₃, and 1 ml of HF. Average grain size were determined by using the standardized mean intercept method, counting more than 100 grains [38]. The samples for SEM observation were re-polished by using colloidal silica to eliminate the surface relief, and then observed by using back-scattered electron (BSE) mode. Uniaxial tensile test of the selected alloys was performed in a temperature range from room temperature to 741°C. Sub-sized sheet tensile specimen (a dog-bone shape, designation SS-3) with the gauge size of 0.76 mm thickness, 1.5 mm width, and 7.6 mm length were

prepared by electro-discharge machining. The tensile axis was always parallel to the rolling or the extrusion direction. The test was conducted with a strain rate of 10^{-3} s^{-1} using cross-head control. Only one specimen was evaluated in each test condition. Micro-Vickers hardness test were also conducted with 300g load for thermal stability evaluation study. At least 7 indents were made for each specimen and the averaged data were compared.

3. Results

3.1. Microstructure of model FeCrAl alloys

As expected, the grain size of the alloys was sensitive to the process conditions such as hot-rolling temperatures, thickness reduction, and final annealing temperature and time. For example, **Figure 1** shows the microstructure of B154Y processed at different temperatures using hot rolling and a subsequent annealing. This alloy was hot-rolled with 40% total thickness reduction (TR) at 1050 and 900°C, or 93-94% TR at 800 and 700°C, and then annealed at the same temperatures for 10-15 min (**1a**, **1b**, **1c**, and **1d**) or 1 h (**1e**). Recrystallization was observed at any of the process conditions, although annealing for 15 min at 700°C was not enough time-at-temperature for the alloy to be fully recrystallized. The grain size decreased with decreasing final annealing temperature, from more than 1000 μm at 1050°C to <100 μm at 700°C after 1 h annealing.

Figure 1. Light optical micrographs of a model FeCrAl alloy (B154Y: Fe-15Cr-4Al+Y) hot-rolled and annealed at various temperatures; (a) 1050°C and (b) 900°C with 40% total thickness reduction, and (c) 800°C and (d, e) 700°C with 93-94% total thickness reduction, followed by annealing at the hot-rolling temperatures for 10 min - 1 h.

The recrystallization kinetics was also dependent on the amount of thickness reduction, although no significant dependence of alloy compositions on the final microstructure was observed. **Figure 2** shows 4 different alloys hot-rolled at 700°C with 73 and 93% TR, and then annealed at 700°C for 1h. After applying 73% TR at 700°C all the model alloys showed non-uniform grain structure consisting of recrystallized grains and non-recrystallized grains that were elongated to the rolling direction after annealing, as shown in **Fig. 2a**. On the other hand, after application of 93% TR the same alloys exhibited

uniform, fully recrystallized grain structure (**Fig. 2b**), indicating the importance of total thickness reduction on the microstructure control. After various thermo-mechanical treatments (TMTs) were applied to the other model alloys, the optimized process to obtain 20-80 μm grain size was found to consist of hot-rolling at 700°C with more than 90% TR, followed by annealing at 700°C for at least 1h, as shown in **Figs. 2c through 2f**. No significant dependence of grain size on either the Cr or Al contents in the ranges of this study was observed. However, alloys with no yttrium addition (**Figs. 2b or 2d**) showed relatively larger grain size compared to the alloys that contained Y (**Figs. 2c or 2e**), which is consistent with a report by Golightly et al. in 1970's [39]. This could be due to grain boundary pinning effect of Y-rich second-phase precipitate formation (i.e., Fe_{17}Y_2 intermetallic compounds) which would not dissolve into the matrix by solution heat-treatment [40].

Figure 2. Light optical micrographs of various model FeCrAl alloys hot-rolled and annealed for 1h at 700°C; (a,b) B105N, (c) B105Y, (d) B134N, (e) B134Y, and (f) B155Y, which applied either 73% (a) or 93% (b-f) total thickness reduction during hot-rolling.

3.2. Tensile property evaluation of model FeCrAl alloys

The tensile properties of model FeCrAl alloys showed very little dependence of the Cr and Al contents in the range of this study. **Tables 3 and 4** summarize tensile properties of model FeCrAl alloys with the small and large grain sizes, respectively, tested at 24 and 279°C. The results for the commercial FeCrAl alloys are also listed for comparison. **Figure 3** shows the yield and ultimate tensile strengths of the FeCrAl alloys plotted as a function of Cr and Al contents. The model alloys with small grains showed ~400-500 MPa yield strengths (YS) and ~550-600 MPa ultimate tensile strengths (UTS) at 24°C, and ~250-270 MPa YS and 380-430 MPa UTS at 300°C. The large grains in the other heats lowered the strength compared to the SG variants and the magnitude of this strength reduction did not show any compositional dependence. The variation of strengths among the alloys were smaller than the property difference between the SG and LG samples, indicating that grain size is a more significant factor than composition. This is an important observation, suggesting that composition can be tailored to optimize other properties without affecting the mechanical properties. The commercial alloys exhibited relatively higher YS and UTS compared to the model FeCrAl alloys since they (1) contained additional elements providing solution hardening (Mo), precipitate strengthening (zirconium/hafnium carbides and/or yttrium oxide particles), and (2) had smaller grain size (**Table 3**) compared to the SG Phase I variants.

Figure 3. Tensile properties of FeCrAl alloys plotted as a function of Cr and Al contents; (a, b) tested at 24°C and (c, d) at 279°C.

Figure 4. Tensile properties of FeCrAl alloys with and without 10% cold-work tested at 24°C, plotted as a function of Cr and Al contents; (a, b) yield and ultimate tensile strengths, and (c, d) uniform and total plastic elongation.

Table 3. Tensile properties of model FeCrAl alloys (SG) tested at 24 and 279°C, together with those of commercial FeCrAl alloys

ID	Average grain size, μm	Properties at 24°C				Properties at 279°C			
		YS, MPa	UTS, MPa	UL, %	TL, %	YS, MPa	UTS, MPa	UL, %	TL, %
B105N	31	453	546	12.1	26.3	-	-	-	-
B125Y	23	456	566	13.9	26.0	-	-	-	-
B134Y	22	383	470	13.4	25.4	267	387	10.2	21.9
B155Y	20	429	521	13.5	28.5	268	432	13.4	23.7
B155Y-2	26	505	618	13.5	26.3	-	-	-	-
B154Y-2	21	428	541	15.1	28.3	-	-	-	-
B184Y	29	462	568	14.1	26.7	-	-	-	-
B183Y-2	25	354	459	19.5	35.4	253	377	12.1	22.6
B203N	35	424	522	13.8	27.0	-	-	-	-
APMT	36	576	608	0.7	0.9	379	680	19.8	27.3
Alkrothal 14	11	459	595	18.3	32.6	359	520	9.9	19.5
YHf	10	595	799	14.8	25.0	-	-	-	-

YS: yield strength, UTS: ultimate tensile strength, UL: uniform plastic elongation, TL: total plastic elongation

Table 4. Tensile properties of model FeCrAl alloys (large grains) tested at 24 and 279°C

ID	Grain size, μm	Properties at 24°C				Properties at 279°C			
		YS, MPa	UTS, MPa	UL, %	TL, %	YS, MPa	UTS, MPa	UL, %	TL, %
B105N	905	303	366	7.7	15.5	250	336	26.8	30.0
B104Y	304	294	371	6.2	12.3	233	312	6.2	15.0
B154Y	530	337	387	6.6	16.0	246	399	13.1	20.6
B184Y	255	349	395	3.9	8.3	169	350	18.2	23.6
B183Y	402	282	378	8.3	16.2	134	328	18	24
B203N	499	309	381	12.4	23.1	133	337	25.7	34.9

Applying 10% cold-work resulted in a uniform increase in the tensile strength across all the alloys, once again irrespective of the composition. **Table 5** summarizes tensile properties of model FeCrAl alloys with 10% cold-work, tested at 24 and 279°C. **Figure 4** shows strengths and plastic elongations of the FeCrAl alloys tested at 24°C plotted as a function of Cr and Al contents. The introduction of 10% cold working increased the YS of these samples to levels comparable or superior to the UTS of the non-cold-worked samples. On the other hand, the uniform plastic deformation ($UL = \text{plastic elongation at UTS}$) of the cold-worked samples was less than 1%, indicating that there was almost no work hardening. This is reasonable

since the non-cold-worked samples exhibited a UL of ~10 %, so that the additional 10% cold-work should correspond to closely maximizing the work hardening of the alloys and allow almost no uniform plastic elongation. Although the UL was small, the total plastic deformation (TL) of the alloys was higher. Similar trends were observed in the cold-worked samples tested at 279°C.

Table 5. Tensile properties of model FeCrAl alloys (small grains + 10% cold-work) tested at 24 and 279°C

ID	Grain size, um	Properties at 24°C				Properties at 279°C			
		YS, MPa	UTS, MPa	UL, %	TL, %	YS, MPa	UTS, MPa	UL, %	TL, %
B105N	31	636	647	0.4	14.3	519	532	0.6	10.7
B125Y	23	592	604	0.8	14.6	519	525	0.3	9.8
B134Y	22	605	614	0.6	12.5	447	456	1.0	10.4
B155Y	20	551	591	6.6	18.5	417	473	4.7	15.9
B155Y-2	26	772	793	0.6	8.5	602	609	0.4	9.7
B154Y-2	21	627	649	0.6	12.7	478	489	0.9	10.8
B184Y	29	584	597	1.0	11.9	466	476	0.8	9.0
B183Y-2	25	531	537	0.6	15.3	430	434	0.5	11.1
B203N	35	583	592	0.7	13.5	463	464	0.2	8.8

The temperature dependences of tensile properties of the model FeCrAl alloys with 10% cold-work are shown in **Figure 5**. All of the model alloys showed similar trends vs. temperature and almost no trend based on composition. The YS of the model alloys were higher than that for APMT or Alkrothal 14 (K14 in the figure) up to ~400°C which is due to the cold-work effect; such an effect is diminished above 500°C due to recovery or recrystallization. APMT exhibits a higher tensile strength at elevated temperatures compared to the model alloys because of its dominant strengthening mechanism (oxides dispersed by the powder metallurgy processing). The plastic elongation, similar to the YS, shows temperature dependence but no strong composition dependence. The cold-work effect that reduced the ductility was diminished above 500°C. It should be emphasized that the high Al content alloys (B125Y, B155Y, and B155Y-2 alloys) tended to show slightly higher strength values compared to the other model

alloys but still maintained more than ~10% TL at ~200-400°C, indicating that higher Al contents may be preferred in terms of tensile properties above room temperature.

Figure 5. Temperature dependence of tensile properties of the model FeCrAl alloys with 10% cold-work; (a) yield strength, (b) ultimate tensile strength, and (c) uniform plastic elongation. Results of commercial FeCrAl alloys (APMT and Alkrothal 14 [= K14], no cold-work) are also plotted for comparison.

3.3. Oxidation resistance

Figure 6 illustrates the effect of Cr and Al contents on the steam oxidation resistance at 1200°C, showing the oxidation behavior of the present model and commercial FeCrAl alloys [18]. Protective behavior under these conditions is the formation of a uniform and adherent α -alumina layer on the surface of a polished metal coupon after 4-24h at 1200°C in 1bar steam. On the other hand, non-protective behavior is associated with the rapid formation of Fe-oxide nodules during the same exposure, implying that the alloy cannot form a protective alumina scale. This figure indicates a critical combination of Cr and Al content in the alloy is necessary for protective behavior and suggest that promising oxidation resistance can be expected in a wide composition range of Cr and Al contents, which would give a wide window for the alloy design to optimize various other properties, such as fabricability, mechanical properties, weldability,

environmental compatibility, and radiation tolerance. For example, the lower Cr (i.e. 10-13 wt.% Cr) would be preferred to avoid potential embrittlement at temperatures below 500°C due to the formation of Cr-rich α' under irradiation [25], but the high temperature oxidation resistance can be expected in the same alloy by including >4% Al .

Figure 6. Effect of Cr and Al content in commercial and model FeCrAl alloys on steam oxidation resistance at 1200°C (after reference 18).

It should be emphasized that the corrosion behavior of ferrous steels and alloys (austenitic, ferritic, duplex, and ferritic/martensitic) in high-temperature water has received ample attention in the past [41,42]. The literature suggests that under high temperature aqueous environments with and without excessive

dissolved oxygen, M_2O_3 or M_3O_4 oxide films (where M is a mixture of Fe and Cr) form on the surface of Fe-Cr alloys, respectively. This was confirmed in a series of recent tests on the Phase I FeCrAl alloys after one year of autoclave testing under various LWR water chemistry conditions [43]. In all cases, corrosion behavior of these alloys appeared very limited (< few micrometers/year).

3.4. Microstructure of Phase II alloy

Based on consideration of the Phase I results, it was determined that the two strongest factors affected by changes in base alloy composition were (1) high Cr content leading to embrittlement at service temperatures due to Cr-rich α' formation [25], and (2) sufficient Cr and Al providing acceptable high temperature steam oxidation resistance [11-14]. The result is a necessary balance between these two factors must be struck. Here, it was determined a Fe-13Cr-4.5Al+Y base composition for Phase II would satisfy the necessary balance for acceptable performance in reactor. This selection was based on preliminary irradiation results showing that compositions between 12-15 wt.% Cr showed the deleterious Cr-rich α' formation, but showed similar ductility parameters after irradiation [25]. The resulting selected base composition with 13 wt.% is therefore expected to behave similar in performance as other known high-Cr Fe-based alloy variants under investigation for nuclear applications such as HT9 or 12YWT, but have slightly improved oxidation kinetics needed for accident tolerant applications.

Minor alloying additions were explored to improve the strength compared to the reference alloy. Amounts of minor alloying additions were selected with the guidance of computational thermodynamics and a design strategy to control stable microstructures in a wide temperature range from room temperature to elevated temperatures, such that stable properties would be expected not only at the service temperature of $\sim 320^\circ\text{C}$ but also under elevated temperatures observed during nuclear reactor accident scenarios. Phase equilibrium of the Phase II alloys was predicted by using computational thermodynamics software Pandat [44] and Fe base alloy database OCTANT [45].

Figure 7 shows the calculated phase equilibrium of the Fe-13Cr-4.5Al-2Mo-0.2Si with or without Nb and C, as a function of temperature. Note that Y is not available in the database, so that the results were from the alloys without Y. In the C35M alloy variant (**Table 2**), only solid-solution strengthening from the Mo addition is expected, however, it is noted that Fe_2Mo Laves phase would form below 640°C as a byproduct. C35MC showed Cr-rich carbides (M_{23}C_6 and M_7C_3) over almost the entire temperature range that could be attributed to the very low carbon solubility in the ferrite matrix. C35MNC showed NbC instead of Cr-rich carbides in C35MC because of the strong C stabilizing effect of Nb. For the C35MN composition, prevalent formation of $\text{Fe}_2(\text{Mo,Nb})$ Laves phase up to 1000°C was expected. All alloy compositions were selected such that complete solid solution was achieved at elevated temperatures in order to control the second-phase precipitate dispersions through various heat treatments at lower temperatures. It should be emphasized that the temperature range of Cr-rich α' formation was predicted to be insensitive to these minor alloying additions, indicating that the effect of alloying additions on the potential embrittlement below $\sim 500^\circ\text{C}$ due to Cr-rich α' formation should be negligible.

Figure 7. Phase equilibrium of the Fe-13Cr-4.5Al base Phase II alloys predicted by a computational thermodynamics tool; (a) C35M: Fe-13Cr-4.5Al-2Mo-0.2Si, (b) C35MC: Fe-13Cr-4.5Al-2Mo-0.2Si-0.1C, (c) C35MNC: Fe-13Cr-4.5Al-2Mo-0.2Si-0.3Nb-0.02C, and (d) C35MN: Fe-13Cr-4.5Al-2Mo-0.2Si-1Nb.

It is also worthwhile to note that for solid solution strengthening, W is considered a more effective addition than Mo [46,47]. In fact, for the developmental of ferritic steels for fast fission and fusion reactors, W additions (~2wt%) are routinely utilized. However, while the high-energy neutron spectrum in those applications is indifferent to the presence of W in the alloy, the thermal spectrum of LWRs is

susceptible to significant absorption by W isotopes. A depletion analysis for LWR fuel cladding applications [20] indicated that after its lifetime in the core, 12% of W atoms in the alloy would have transmuted away. The same analysis for Mo indicated that less than 0.5% of Mo atoms were subject to such a scenario. Due to this analysis, Mo was selected as the strengthening addition for in-core LWR service.

Figure 8 summarizes the microstructure of the Phase II FeCrAl alloys processed at 800 and 1200°C, compared with a model alloy (T35Y2) containing no minor alloying additions (**Fig. 8a**). The alloys processed at 1200°C showed a fully recrystallized microstructure with $> 100\ \mu\text{m}$ grain size and a few Y-rich precipitate dispersions (**Figs. 8b~8d**). As predicted, no second-phases were observed. C35M processed at 800°C showed uniform grain size in a range from 30-50 μm (**Fig. 8e**) which was smaller than that of the T35Y2 processed at a lower annealing temperature, indicating that the Mo addition could retard recrystallization. C35MC and C35MNC (**Figs. 8f and 8g**) were annealed for 24h at 800°C in order to obtain a fully recrystallized microstructure, and resulted in grain sizes of $\sim 100\ \mu\text{m}$ with relatively elongated grains along the rolling direction (parallel to the horizontal direction in the pictures). On the other hand, C35MN did not show recrystallization even after 24h annealing at 800°C but maintained the rolled microstructure macroscopically (**Fig. 8h**).

Figure 8. Light optical micrographs showing the Phase II FeCrAl alloys together with a reference model FeCrAl alloy; (a) T35Y2 extruded at 1050°C, (b) C35MC, (c) C35MNC, and (d) C35MN processed at 1200°C, and (e) C35M, (f) C35MC, (g) C35MNC, and (h) C35MN processed at 800°C. Note that HE and HR stand for hot-extruded and hot-rolled, respectively.

Figure 9 shows SEM-BSE images of the Phase II FeCrAl alloys processed at 800°C. The predicted second-phases such as $M_{23}C_6$ (M: mainly Cr), MC (M: mainly Nb), and Laves phase precipitates were observed in the alloys, based on the SEM-EDS analysis. The size of $M_{23}C_6$ carbides in C35MC was more

than 10 μm which would not provide significant strengthening (**Fig. 9a**). C35MNC showed dispersions of MC and Laves phase precipitates, although the volume fractions of them are too small to expect significant precipitate strengthening (**Fig. 9b**). On the other hand, C35MN exhibited a very fine grain size microstructure with $\sim 1\text{--}3\ \mu\text{m}$ grain size together with a dispersion of sub-micron size Laves phase precipitates on grain boundaries (**Fig. 9c**). SEM-EBSD analysis revealed that the fine grains consisted of sub-grains, indicating that the grains were not formed by recrystallization, but by recovery during final annealing at 800°C.

Figure 9. SEM-BSE images showing the Phase II FeCrAl alloys processed at 800°C; (a) C35MC, (b) C35MNC, and (c) C35MN.

3.5. Tensile properties of Phase II alloy

Tensile properties of the Phase II alloys are summarized in **Table 6**. Results for T35Y2 are shown for comparison. Only slight improvement of the properties in C35M, C35MC, and C35MNC processed at 800°C were observed compared to T35Y2, indicating that the expected solid-solution strengthening or precipitate strengthening were not significant in the case of a fully recrystallized microstructure tested at room temperature. On the other hand, C35MN processed at 800°C showed more than 25% improvement of the yield and tensile strengths together with reasonable ductility. The properties of C35MC, C35MNC and C35MN processed at 1200°C showed slightly improved properties compared with the 800°C processed alloys even with the larger grain sizes, indicating that dissolution of minor alloying elements (C and/or Nb) contributed to the solid-solution strengthening. However, the ductility of C35MC and C35MN were significantly lower than those processed at 800°C. From these comparisons, the sub-grain structure with Laves phase precipitate dispersion in the 800°C processed C35MN seemed most effective for improving the tensile properties of the FeCrAl alloys.

Table 6. Room temperature tensile properties of the Phase II FeCrAl alloys.

Name	Remarks	Process*	GS, μm	at 24°C			
				YS, MPa	TS, MPa	UL, %	TL, %
T35Y2	model alloy	HE1050°C + Ann 700°C-1h	50-80	384	536	21.8	37.5
C35M	Mo + Si	HR800°C + Ann 800°C-1h	30-50	451	570	17.9	33.9
C35MC	Mo+Si+C	HR800°C + Ann 800°C-24h	<100	412	549	14.3	23.0
C35MNC	Mo+Si+Nb+C	HR800°C + Ann 800°C-24h	<100	448	592	15.8	27.1
C35MN	Mo+Si+Nb	HR800°C + Ann 800°C-24h	~1	629	811	12.0	21.6
C35MC	Mo+Si+C	HR1200°C+ Ann 1200°C-1h	300-500	589	633	1.7	3.9
C35MNC	Mo+Si+Nb+C	HR1200°C+ Ann 1200°C-1h	100-300	445	562	16.3	27.6
C35MN	Mo+Si+Nb	HR1200°C+ Ann 1200°C-1h	100-300	566	662	7.6	14.1

*HE: hot-extruded, HR: hot-rolled, Ann: annealed

Figure 10 shows the temperature dependence of the tensile properties of T35Y2 and Phase II alloys (C35MN and C35M, processed at 800°C). For comparison purposes, a commercially available FeCrAl alloy (APMT, Fe-22Cr-5Al base alloy) was also plotted. The C35MN specimens were prepared using two different processing routes: hot-rolling and hot-extrusion at 800°C, which exhibited similar microstructures as shown in **Fig. 9c**. The results clearly indicated the improved tensile performance of C35MN superior to the other alloys, regardless of two different processing routes, including total elongation of ~20%.

Figure 10. Temperature dependence of FeCrAl alloys: (a) yield strength and (b) total plastic elongation.

3.6. Thermal stability of sub-grain microstructure

The results in the previous section indicated that the sub-grain microstructure improved tensile strengths of the Phase II alloys with reasonable ductility over a wide temperature range. The fine and dense Laves phase precipitates were observed on the sub-grain boundaries, suggesting that these precipitates pinned the boundaries to maintain the sub-grain structure [48]. Thus, the dual effects from the sub-grain structure

formation and improved microstructural stability appear to be a key for improving the mechanical properties. Based on this assumption, the thermal stability of the sub-grain microstructure was evaluated to understand the mechanism of the property improvement in the C35MN alloy.

C35M and C35MN5 were selected to study the effect of the 1% Nb addition. Both alloys were warm-rolled at 300°C with more than 80% total thickness reduction to obtain the heavily deformed microstructure (similar to the one in **Fig. 8h**) without second-phase formation. The sheet samples were then annealed in a temperature range from 600 to 800°C for various periods of time to observe the recrystallization sequence, in order to evaluate the stability of the microstructures. **Figure 11** shows the cross-sectional microstructure of C35M and C35MN5 before and after annealing at 700°C. The as-rolled microstructure of C35M and C35MN5 (**Figs. 11a** and **11c**, respectively) consisted of a typical, severely deformed features which aligned mostly parallel to the rolling direction (the horizontal axis of the pictures) together with the slip lines along the diagonal axes. After annealing for 24 h, C35M had a fully recrystallized microstructure with ~30 μm grain size (**Fig. 11b**). On the other hand, C35MN5 after 168 h annealing exhibited no recrystallized grain formation but very fine dispersion of dark contrast particles corresponding to the Laves-phase precipitates formed along the grain boundaries or slip lines (**Fig. 11d**). These results clearly indicated that the Nb addition increased the stability of the warm-rolled microstructure, likely due to the pinning effect of Laves phase precipitates.

(a) C35M, as-rolled

(b) C35M, 700°C/24h

(c) C35MN5, as-rolled

(d) C35MN5, 700°C/168h

100μm

Figure 11. Light optical micrographs of the warm-rolled Phase II FeCrAl alloys, before and after annealing at 700°C; (a) C35M, as-rolled, (b) C35M, 700°C for 24h, (c) C35MN5, as-rolled, and (d) C35MN5, 700°C for 168h.

Figure 12 shows micro-Vickers hardness plotted as a function of annealing time for C35M and C35MN5. C35M showed a steep drop in hardness in the early stage of annealing at 650 and 700°C, which was attributed to the formation of recrystallized grains after only 4h and 0.5h annealing, respectively. However, once the materials were fully recrystallized the hardness change during further annealing was minor. The hardness change at 600°C was also minimal because no recrystallization took place in the time-temperature range studied. C35MN5, on the other hand, showed a slower drop in hardness but at

higher annealing temperatures. Recrystallization was observed after annealing for 168h at 750°C or 24h at 800°C. Based on these results, a time-temperature diagram for recrystallization was built as shown in **Figure 13**. Recrystallization of the warm-rolled C35M takes place above 650°C, and fully recrystallized microstructure can be obtained after only 1h at 700°C. On the other hand, the C35MN5 was not recrystallized after 504h at 700°C; but will recrystallize at higher temperatures or after longer annealing times compared to C35M.

Figure 12. Micro Vickers hardness of the warm-rolled (a) C35M and (b) C35MN5 plotted as a function of aging time in the range from 600 to 800°C

Figure 13. Effect of the Nb addition on the recrystallization of Fe-13Cr-5Al base alloys.

Computational thermodynamics predicted that C35M would form Fe_2Mo Laves phase below 650°C as shown in **Fig. 7a**, so that the resistance to recrystallization (i.e. preservation of deformed microstructure) of C35M alloy at 600°C could also be associated with the formation of Laves phase precipitates. Therefore, minor alloying additions (such as Nb) to promote the Laves phase precipitation at higher temperature would be key in improving high temperature microstructural stability.

4. Discussion

4.1. Model FeCrAl alloys

Tensile properties of the model FeCrAl alloys showed very little dependence of Cr and Al contents in the composition range of this study, even in different conditions such as a range of grain sizes, with or without cold-work, and temperatures ranging from room temperature to 600°C. This result makes alloy design easier since small changes in Cr or Al would not have a significant impact on the tensile properties when other properties need to be optimized through chemistry control. In addition, the model alloys exhibited good tensile properties even in the fully recrystallized condition with a grain size of 20-35 μm without any intentional strengthening strategies employed. From a simplistic point of view, their strengths exceeded the minimum tensile property requirements of nuclear-grade zirconium alloys, such as Zircaloy 2 or 4, as described in ASTM B351 [49], and listed in **Table 7**. From a simple structural viewpoint, the model FeCrAl alloys are adequate as the base material for fuel cladding (assuming cladding geometry is unchanged). Furthermore, the elastic modulus of this class of alloys is twice that of Zr-based alloys and therefore provides further margins [6]. However, many other properties of these alloys need to be quantified and optimized (e.g. thermal and irradiation creep) for LWR cladding applications, particularly if significantly thinner cladding designs are needed.

Table 7. Minimum requirement of tensile properties of zirconium alloys (ASTM B351), together with the present results of Fe-13Cr-4.5Al+Y base Phase I and Phase II alloys

Grade	Temperature, °C	YS, MPa	UTS, MPa	Elongation, %
R60802	RT	240	415	14
(Zircaloy 2)	316	105	215	24
R60804	RT	240	415	14
(Zircaloy 4)	316	105	215	24
T35Y2 (current result)	RT	384	536	37.5
C35MN, processed at 800°C (current result)	RT	629	811	21.6

Wukusick and Collins [10] reported the Al dependence of ductility of Fe-25Cr-(0-7)Al-0.7Y alloys, which indicated that alloys containing 5 to 7 wt.% of Al addition would be increasingly brittle and difficult to work. On the other hand, the current model alloys had no difficulty with hot-working even with 5 wt.% of Al, and no apparent dependence of the Al contents below 5 wt.% on the ductility in a wide temperature range. Since Wukusick and Collins did not analyze the detailed mechanism of the embrittlement in the high Al containing alloys, it is difficult to explain the gap between the literature and the current results. Qu et al. [35] reported the effect of grain size on DBTT by using a Fe-20Cr-6Al base alloy with 0.2La and 0.03Zr. It was concluded that larger grains would result in a higher DBTT, although the alloy with 50 μm grains showed a DBTT at -4°C , even with 6 wt.% of Al content. Therefore, FeCrAl alloys with such levels of Cr and Al content would still be allowable in terms of ductility or potentially good workability, and the microstructure control would be the key to control the mechanical properties. The effect of higher Al contents on the mechanical properties is currently being evaluated.

On the other hand, steam oxidation resistance of the model FeCrAl alloys strongly depended on the Cr and Al contents, as shown in **Figure 6**. Since high Cr and Al contents assist in forming a protective alumina scale, the role of Cr often referred to as the “third element effect” [50]. However, for most of the other properties, the high Cr and Al contents would be problematic for potential issues, such as radiation induced hardening and embrittlement due to Cr-rich α' formation during service conditions [25], or potentially high deformation resistance due to excess Al which may hinder thin-wall seamless tube fabrication. Detailed studies of oxidation resistance [15], irradiation resistance [25], fabricability [48], and weldability [51] of the model alloys are currently in progress as parallel efforts, and they will be utilized for further optimization of the FeCrAl alloys.

4.2. Phase II FeCrAl alloys

The original alloy design strategy of the Phase II FeCrAl alloys was to introduce solution-hardening and precipitate strengthening, although they were not as effective as originally expected. Instead of this, the

stable deformed sub-grain structure was found to be the most effective for improving the tensile properties of FeCrAl alloys in a wide temperature range. The properties of C35MN with such a microstructure were even superior to those of the commercial FeCrAl alloy (APMT), at least up to ~600°C. The thermal stability evaluation study indicated that the formation of the second-phase precipitates on the sub-boundary are key in improving the stability of the deformed structure, and thus potential higher temperature tensile strength compared to the model alloys or the alloys with no second-phase precipitates.

The tensile properties of the alloys were evaluated along the rolling direction in the present study. Although no test was conducted perpendicular to the rolling direction, it can easily be imagined that the elongation would be very limited, especially for the alloy C35MN hot-rolled at 800°C, since the elongated grains could be susceptible to be “delaminated” during tensile deformation. Chao et al. [52] reported the strong anisotropy of room-temperature tensile ductility of hot-rolled FeCrAl ODS alloys, showing that the reduction of uniform plastic elongation (UL) in the transverse direction was significant (up to ~78% reduction) compared to the UL along the rolling direction. Therefore, the evaluation of property anisotropy of the present alloys would also be important in order to address potential property issues.

One of the commercial seamless-tube fabrication processes is tube drawing utilizing a die and mandrill at the same time to reduce the tube diameter and wall thickness when the master tube is drawn [53]. Because of the upper temperature limit of the die material for maintaining a consistent size, the drawing process would be performed below ~320°C. Thus, the 300°C warm-rolled plates in the current study should have a microstructure similar to the tube drawn material. Preliminary tensile test results indicated that the yield strength of the warm-rolled C35MN5 exceeded 1 GPa, as listed in **Table 8**. Additional annealing at 650°C resulted in improving the ductility without losing the advantage of improved strength. Although the detailed microstructure characterization of the annealed samples is not complete, it is suggested that the stability of the warm-rolled microstructure is the key to maintaining the very high

tensile strength of the materials. The C35MN5 and C35M alloys have been down-selected as materials for trial tube fabrication via a warm-drawing process with a target wall thickness of 350 μ m.

Table 8. Room temperature tensile properties of warm-rolled C35MN5 alloys before and after annealing at 650°C, together with that of C35MN hot-rolled and annealed at 800°C.

Condition*	YS, MPa	UTS, MPa	UL, %	TL, %	Remarks
As warm-rolled	1362	1380	0.4	5.4	C35MN5
WR + 650°C/1h	1200	1376	5.4	8.9	C35MN5
WR + 650°C/24h	1027	1202	7.2	12	C35MN5
HR@800°C + 800°C/1h	629	811	12	22	C35MN

*WR: warm-rolled

Although the Phase II study focused on microstructure stability and tensile properties, the third element additions should have an impact on the oxidation and irradiation resistance. **Figure 6** shows that the first Phase II alloys were near the protective/non-protective composition border with <4.5%Al, thus the C35MN5 alloy was made with a higher Al content. For irradiation, the formation of Laves phase precipitates is a major concern since the acceleration of the precipitate coarsening is expected under irradiation and could lead to subpar fracture toughness performance. Another concern is weldability since welding can easily affect the deformed microstructure resulting in a coarse grain structure [51], which could result in lowering the tensile properties drastically. Therefore, it is also important to evaluate the weldability and cross-weld properties as a function of the third elements, and these evaluations are also in progress.

5. Conclusions

Development of nuclear grade, iron-based wrought FeCrAl alloys has been pursued as candidate materials for accident tolerant fuel cladding, replacing current Zr base alloys in LWRs. In Phase I, model FeCrAl alloys with minor Y additions, Fe-(10-20)wt.%Cr-(3-5)Al-(0-0.12)Y were evaluated. It was found that the

tensile properties were insensitive to alloy composition and the properties were comparable or superior to commercially available FeCrAl alloys (after controlling for grain size effects). In contrast, the 1200°C steam oxidation resistance strongly depended on both the Cr and Al contents of the alloy. Based on these results, Fe-13Cr-4.5Al+Y was down-selected as a base alloy composition for further development efforts in Phase II. Minor alloying additions such as Mo, Nb, C, and Si together with optimized thermo-mechanical treatment were utilized. One of the Phase II FeCrAl alloys with Mo and Nb additions (C35MN) showed non-recrystallized, deformed microstructure with sub-grains together with the formation of fine $\text{Fe}_2(\text{Mo,Nb})$ Laves phase precipitates after hot-rolling and annealing at 800°C, which successfully achieved improved tensile properties together with good thermal stability. Such a stabilized deformed microstructure is an attractive candidate for further development for this application.

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References

1. P. Hofmann, J. Nuclear Materials, 270 (1) (1999) 194-211.
2. D. Powers, R. Meyer, NUREG-0630; U. S. Nuclear Regulatory Commission: 1980.
3. M. Billone, Y. Yan, T. Burtseva, R. Daum, NUREG/CR-6967; U.S. NRC, Office of Nuclear Regulatory Research: 2008.
4. M. Moalem, D.R. Olander, J. Nuclear Materials, 182 (1991) 170-194.
5. M. Steinbrück, M. Große, L. Sepold, J. Stuckert, Nuclear Engineering and Design 240 (7) (2010) 1714-1727.
6. K.A. Terrani, S.J. Zinkle, L.L. Snead, J. Nuclear Materials, 448 (2014) 420-435.
7. L.J. Ott, K.R. Robb, D. Wang, J. Nuclear Materials, 448 (2014) 520-533.
8. S. J. Zinkle, K. A. Terrani, J. C. Gehin, L. J. Ott, and L. L. Snead, J. Nuclear Materials, 448 (2014) 374-379.
9. E. A. Gulbransen and K. F. Andrew, J. Electrochemical Society, 106 (1959) 294-302.
10. C.S. Wukusick and J.F. Collis, An Iron-Chromium-Aluminum Alloy containing Yttrium, Materials Research and Standards, December 1964, pp. 637-646.
11. High-Temperature Materials Program Progress Report No. 59, Part A, in, General Electric, Cincinnati, Ohio, 1966.
12. J.F. Collins, F.C. Robertshaw, Advanced Long-Life Reactor Fuel Cladding and Structural Materials Development, in: Sixth Annual Report - High Temperature Materials Programs: Part A, General Electric, Cincinnati, Ohio, 1967, pp. 143-174.
13. M. Kangilaski, The Effects of Neutron Radiation on Structural Materials, in, Radiation Effects Information Center, Columbus, Ohio, 1967.
14. E. A. Gulbransen and K. F. Andrew, Journal of the Electrochemical Society, 106 (1959) 294-302.
15. B.A. Pint, K.A. Terrani, M.P. Brady, T. Cheng, J.R. Keiser, J. Nuclear Materials, 440 (2013) 420-427.
16. T. Cheng, J.R. Keiser, M.P. Brady, K.A. Terrani, B.A. Pint, J. Nuclear Materials 427 (2012) 396-400.
17. B. A. Pint, S. Dryepondt, K. A. Unocic, and D. T. Hoelzer, JOM, 66 (2014) 2458-2466.
18. B. A. Pint, K. A. Unocic and K. A. Terrani, Materials at High Temperature, 32 (2015) 28-35.

-
19. N. M. George, K. Terrani, J. Powers, A. Worrall, and I. Maldonado, *Annals of Nuclear Energy*, 75 (2015) 703-712.
 20. N. M. George, K. A. Terrani, and J. J. Powers, "Neutronic analysis of candidate accident-tolerant iron alloy cladding concepts, ORNL/TM-2013/121," Oak Ridge National Laboratory (ORNL) 2013.
 21. X. Wu, T. Kozlowski, and J. D. Hales, *Annals of Nuclear Energy*, 85 (2015) 763-775.
 22. J. J. Powers, N. M. George, G. I. Maldonado, and A. Worrall, "Report on Reactor Physics Assessment of Candidate Accident Tolerant Fuel Cladding Materials in LWRs, ORNL/TM-2015/415," Oak Ridge National Laboratory 2015.
 23. K. R. Robb, "Analysis of the FeCrAl Accident Tolerant Fuel Concept Benefits During BWR Station Blackout Accidents," presented at the Proceedings of the 16th International Topical Meeting on Nuclear Reactor Thermal Hydraulics (NURETH-16), Chicago, IL, USA, 2015.
 24. A. Strasser, J. Santucci, K. Lindquist, W. Yario, G. Stern, L. Goldstein, et al., "An Evaluation of Stainless Steel Cladding for Use in Current Design LWRs, NP-2642," Electric Power Research Institute, Palo Alto, CA1982.
 25. K.G. Field, X. Hu, K.C. Littrell, Y. Yamamoto, L.L. Snead, *J. Nuclear Materials*, 465 (2015) 746-755
 26. J. Schemel and R. McKenzie, *ASTM STP*, 551 (1974)169-178.
 27. J. L. Aubin, P. Montmitonnet, and S. Mulot, *ASTM SPECIAL TECHNICAL PUBLICATION*, 1354 (2000) 460-481.
 28. F. Stott, G. Wood, J. Stringer, *Oxidation of Metals*, 44 (1-2) (1995), 113-145.
 29. M. Courtnall, F. Pickering, *Metal Science* 10 (8) (1976) 273-276.
 30. P. Grobner, *Metallurgical and Materials Transactions B*, 4 (1973) 251-260.
 31. M. Mathon, Y. De Carlan, G. Geoffroy, X. Averty, A. Alamo, and C. De Novion, *J. Nuclear Materials*, 312 (2003) 236-248.
 32. S. Kobayashi and T. Takasugi, *Scripta Materialia*, 63 (2010) 1104-1107.
 33. J. Ejenstam, M. Thuvander, P. Olsson, F. Rave, and P. Szakalos, *J. Nuclear Materials*, 457 (2015) 291-297.
 34. W. Li, S. Lu, Q.-M. Hu, H. Mao, B. Johansson, and L. Vitos, *Computational Materials Science*, 74 (2013) 101-106.
 35. H. Qu, Y. Lang, C. Yao, H. Chen, C. Yang, *Materials Science and Engineering: A* 562 (2013) 9-16.
 36. B.A. Pint, *J. American Ceramic Society*, 86 (2003) 686-695.
 37. B.A. Pint, *Oxidation of Metals*, 45 (1995) 1-37.

-
38. ASTM, "Standard Test Methods for Determining Average Grain Size," in E112-12, ed. West Conshohocken, PA: ASTM International, 2012.
39. F.A. Colightly, F.H. Stoot, and G.C. Wood, *Oxidation of Metals*, 10 (3) (1976) 163-187.
40. ASM Alloy Phase Diagram Database, P. Villars, H. Okamoto and K. Cenzual (eds.), ASM International, Materials Park, OH, 44073, USA (2015)
41. J. Robertson, *Corrosion Science*, 32 (1991) 4433-465.
42. B. Stellwag, *Corrosion science*, 40 (1998) 337-370.
43. K. A. Terrani, Y.-J. Kim, and B. A. Pint, "Uniform Corrosion of Model FeCrAl Alloys In LWR Coolants," in *American Nuclear Society Annual Meeting*, San Antonio, TX, 2015.
44. W. Cao, S-L. Chen, F. Zhang, K. Wu, Y. Yang, Y. Chang, R. Schmid-Fetzer, W. Oates, *Calphad*, 33 (2009) 328–342.
45. Y. Yang and J. T. Busby, *J. Nuclear Materials*, 448 (2014) 282-293.
46. R. L. Klueh, *International Materials Reviews*, 50 (2005) 287-310.
47. R. L. Klueh and A. T. Nelson, *J. Nuclear Materials*, 371 (2007) 37-52.
48. Y. Yamamoto, Y. Yang, K.G. Field, K. Terrani, B.A. Pint, and L.L. Snead, "Letter Report Documenting Progress of Second Generation ATF FeCrAl Alloy Fabrication, FY14 FCRD milestone report," M3FT-14OR0202232, ORNL/LTR-2014/219, Oak Ridge National Laboratory (2014).
49. ASTM, "Standard Specification for Hot-Rolled and Cold-Finished Zirconium and Zirconium Alloy Bars, Rod, and Wire for Nuclear Application," in B351/B351M - 13, ed. West Conshohocken, PA: ASTM International, 2013.
50. F.H. Stott, G.C. Wood, J. Stringer, *Oxidation of Metals*, 44 (1995) 113-45.
51. K.G. Field, M.N. Gussev, Y. Yamamoto, L.L. Snead, *J. Nuclear Materials*, 454 (2014) 352-358.
52. J. Chao, C. Capdevila-Montes, J.L. González-Carrasco, *Materials Science and Engineering A*, 515 (2009) 190-198,
53. Wire, Rod, and Tube Drawing, Metalworking: Bulk Forming, Vol 14A, ASM Handbook, ASM International, 2005, p 448–458

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Figure 1. Light optical micrographs of a model FeCrAl alloy (B154Y: Fe-15Cr-4Al+Y) hot-rolled and annealed at various temperatures; (a) 1050°C and (b) 900°C with 40% total thickness reduction, and (c) 800°C and (d, e) 700°C with 93-94% total thickness reduction, followed by annealing at the hot-rolling temperatures for 10 min - 1 h.

Figure 2. Light optical micrographs of various model FeCrAl alloys hot-rolled and annealed for 1h at 700°C; (a,b) B105N, (c) B105Y, (d) B134N, (e) B134Y, and (f) B155Y, which applied either 73% (a) or 93% (b-f) total thickness reduction during hot-rolling.

Figure 3. Tensile properties of FeCrAl alloys plotted as a function of Cr and Al contents; (a, b) tested at 24°C and (c, d) at 279°C.

Figure 4. Tensile properties of FeCrAl alloys with and without 10% cold-work tested at 24°C, plotted as a function of Cr and Al contents; (a, b) yield and ultimate tensile strengths, and (c, d) uniform and total plastic elongation.

Figure 5. Temperature dependence of tensile properties of the model FeCrAl alloys with 10% cold-work; (a) yield strength, (b) ultimate tensile strength, and (c) uniform plastic elongation. Results of commercial FeCrAl alloys (APMT and Alkrothal 14 [= K14], no cold-work) are also plotted for comparison.

Figure 6. Effect of Cr and Al content in commercial and model FeCrAl alloys on steam oxidation resistance at 1200°C (after reference 38).

Figure 7. Phase equilibrium of the Fe-13Cr-4.5Al base Phase II alloys predicted by a computational thermodynamics tool; (a) C35M: Fe-13Cr-4.5Al-2Mo-0.2Si, (b) C35MC: Fe-13Cr-4.5Al-2Mo-0.2Si-0.1C, (c) C35MNC: Fe-13Cr-4.5Al-2Mo-0.2Si-0.3Nb-0.02C, and (d) C35MN: Fe-13Cr-4.5Al-2Mo-0.2Si-1Nb.

Figure 8. Light optical micrographs showing the Phase II FeCrAl alloys together with a reference model FeCrAl alloy; (a) T35Y2 extruded at 1050°C, (b) C35MC, (c) C35MNC, and (d) C35MN processed at 1200°C, and (e) C35M, (f) C35MC, (g) C35MNC, and (h) C35MN processed at 800°C. Note that HE and HR stand for hot-extruded and hot-rolled, respectively.

Figure 9. SEM-BSE images showing the Phase II FeCrAl alloys processed at 800°C; (a) C35MC, (b) C35MNC, and (c) C35MN.

Figure 10. Temperature dependence of FeCrAl alloys: (a) yield strength and (b) total plastic elongation.

Figure 11. Light optical micrographs of the warm-rolled Phase II FeCrAl alloys, before and after annealing at 700°C; (a) C35M, as-rolled, (b) C35M, 700°C for 24h, (c) C35MN5, as-rolled, and (d) C35MN5, 700°C for 168h.

Figure 12. Micro Vickers hardness of the warm-rolled (a) C35M and (b) C35MN5 plotted as a function of aging time in the range from 600 to 800°C

Figure 13. Effect of the Nb addition on the recrystallization of Fe-13Cr-5Al base alloys.

Table 1. Compositions of Phase I model FeCrAl alloys and commercial FeCrAl alloys.

ID	Nominal, wt.%				Analyzed, wt.%				Remarks
	Fe	Cr	Al	Y	Fe	Cr	Al	Y	
B105N	Bal.	10	5	0	85.12	9.64	5.22	0	Arc-melted + hot-forged/-rolled + annealed (with/without applying 10% cold-roll)
B105Y	Bal.	10	5	0.15	85.15	10.01	4.78	0.038	
B104Y	Bal.	10	4	0.15	86.12	9.99	3.83	0.040	
B125Y	Bal.	12	4.5	0.15	83.56	11.96	4.42	0.027	
B134Y	Bal.	13	4	0.15	83.02	13.01	3.94	0.007	
B155Y	Bal.	15	5	0.15	79.87	14.98	5.02	0.033	
B155Y-2	Bal.	15	5	0.15	79.88	15.21	4.83	0.063	
B154Y	Bal.	15	4	0.15	81.18	14.86	3.85	0.012	
B154Y-2	Bal.	15	4	0.15	80.99	15.03	3.92	0.035	
B184Y	Bal.	17.5	4	0.15	78.39	17.51	3.91	0.043	
B183Y	Bal.	17.5	3	0.15	79.27	17.53	2.95	0.019	
B183Y-2	Bal.	17.5	3	0.15	79.52	17.51	2.93	0.017	
B203N	Bal.	20	3	0	77.05	20.01	2.91	0	
APMT	Bal.	22	5	0.2	69.75	21.18	4.77	0.212	+ 2.75Mo, 0.18Ni, 0.47Si, 0.17Hf, 0.11Zr, 0.04C
Alkrothal 14	Bal.	15	4	0	80.31	14.73	4.23	0	+ 0.20Mn, 0.11Ni, 0.17Si, 0.12Zr, 0.03C
YHf	Bal.	20	6	0.06	72.85	20.31	6.1	0.0626	+ 0.19Mn, 0.14Ni, 0.19Si, 0.05Zr, 0.02C

Table 2. Nominal and analyzed compositions of Phase II FeCrAl alloys.

IDs		Fe	Cr	Al	Y	Mo	Si	Nb	C	Remarks
T35Y2	Nominal	82.35	13	4.5	0.15	-	-	-	-	Phase I, VIM + extrusion
	Analyzed	82.26	13.15	4.44	0.12	<0.01	0.01	<0.01	0.002	
C35M	Nominal	80.15	13	4.5	0.15	2	0.2	-	-	Arc-melt + hot-roll
	Analyzed	80.88	12.68	4.22	0.031	1.92	0.20	<0.01	0.003	
C35MC	Nominal	80.07	13	4.5	0.15	2	0.20	-	0.08	Arc-melt + hot-roll
	Analyzed	80.96	12.53	4.22	0.026	1.94	0.21	<0.01	0.089	
C35MNC	Nominal	79.83	13	4.5	0.15	2	0.20	0.3	0.02	Arc-melt + hot-roll
	Analyzed	80.41	12.77	4.31	0.065	1.95	0.20	0.24	0.026	
C35MN	Nominal	79.15	13	4.5	0.15	2	0.20	1	-	Arc-melt + hot-roll
	Analyzed	79.96	12.77	4.22	0.032	1.94	0.21	0.81	0.004	
C35MNS	Nominal	78.53	13	5.2	0.07	2	0.20	1	-	VIM + extrusion
	Analyzed	78.68	13.02	5.08	0.032	1.99	0.21	0.97	0.003	

Table 3. Tensile properties of model FeCrAl alloys (SG) tested at 24 and 279°C, together with those of commercial FeCrAl alloys

ID	Average grain size, μm	Properties at 24°C				Properties at 279°C			
		YS, MPa	UTS, MPa	UL, %	TL, %	YS, MPa	UTS, MPa	UL, %	TL, %
B105N	31	453	546	12.1	26.3	-	-	-	-
B125Y	23	456	566	13.9	26.0	-	-	-	-
B134Y	22	383	470	13.4	25.4	267	387	10.2	21.9
B155Y	20	429	521	13.5	28.5	268	432	13.4	23.7
B155Y-2	26	505	618	13.5	26.3	-	-	-	-
B154Y-2	21	428	541	15.1	28.3	-	-	-	-
B184Y	29	462	568	14.1	26.7	-	-	-	-
B183Y-2	25	354	459	19.5	35.4	253	377	12.1	22.6
B203N	35	424	522	13.8	27.0	-	-	-	-
APMT	36	576	608	0.7	0.9	379	680	19.8	27.3
Alkrothal 14	11	459	595	18.3	32.6	359	520	9.9	19.5
YHf	10	595	799	14.8	25.0	-	-	-	-

YS: yield strength, UTS: ultimate tensile strength, UL: uniform plastic elongation, TL: total plastic elongation

Table 4. Tensile properties of model FeCrAl alloys (large grains) tested at 24 and 279°C

ID	Grain size, μm	Properties at 24°C				Properties at 279°C			
		YS, MPa	UTS, MPa	UL, %	TL, %	YS, MPa	UTS, MPa	UL, %	TL, %
B105N	905	303	366	7.7	15.5	250	336	26.8	30.0
B104Y	304	294	371	6.2	12.3	233	312	6.2	15.0
B154Y	530	337	387	6.6	16.0	246	399	13.1	20.6
B184Y	255	349	395	3.9	8.3	169	350	18.2	23.6
B183Y	402	282	378	8.3	16.2	134	328	18	24
B203N	499	309	381	12.4	23.1	133	337	25.7	34.9

Table 5. Tensile properties of model FeCrAl alloys (small grains + 10% cold-work) tested at 24 and 279°C

ID	Grain size, um	Properties at 24°C				Properties at 279°C			
		YS, MPa	UTS, MPa	UL, %	TL, %	YS, MPa	UTS, MPa	UL, %	TL, %
B105N	31	636	647	0.4	14.3	519	532	0.6	10.7
B125Y	23	592	604	0.8	14.6	519	525	0.3	9.8
B134Y	22	605	614	0.6	12.5	447	456	1.0	10.4
B155Y	20	551	591	6.6	18.5	417	473	4.7	15.9
B155Y-2	26	772	793	0.6	8.5	602	609	0.4	9.7
B154Y-2	21	627	649	0.6	12.7	478	489	0.9	10.8
B184Y	29	584	597	1.0	11.9	466	476	0.8	9.0
B183Y-2	25	531	537	0.6	15.3	430	434	0.5	11.1
B203N	35	583	592	0.7	13.5	463	464	0.2	8.8

Table 6. Room temperature tensile properties of the Phase II FeCrAl alloys.

Name	Remarks	Process*	GS, um	at 24°C			
				YS, MPa	TS, MPa	UL, %	TL, %
T35Y2	model alloy	HE1050°C + Ann 700°C-1h	50-80	384	536	21.8	37.5
C35M	Mo + Si	HR800°C + Ann 800°C-1h	30-50	451	570	17.9	33.9
C35MC	Mo+Si+C	HR800°C + Ann 800°C-24h	<100	412	549	14.3	23.0
C35MNC	Mo+Si+Nb+C	HR800°C + Ann 800°C-24h	<100	448	592	15.8	27.1
C35MN	Mo+Si+Nb	HR800°C + Ann 800°C-24h	~1	629	811	12.0	21.6
C35MC	Mo+Si+C	HR1200°C+ Ann 1200°C-1h	300-500	589	633	1.7	3.9
C35MNC	Mo+Si+Nb+C	HR1200°C+ Ann 1200°C-1h	100-300	445	562	16.3	27.6
C35MN	Mo+Si+Nb	HR1200°C+ Ann 1200°C-1h	100-300	566	662	7.6	14.1

*HE: hot-extruded, HR: hot-rolled, Ann: annealed

Table 7. Minimum requirement of tensile properties of zirconium alloys (ASTM B351), together with the present results of Fe-13Cr-4.5Al+Y base Phase I and Phase II alloys

Grade	Temperature, °C	YS, MPa	UTS, MPa	Elongation, %
R60802	RT	240	415	14
(Zircaloy 2)	316	105	215	24
R60804	RT	240	415	14
(Zircaloy 4)	316	105	215	24
T35Y2	RT	384	536	37.5
(current result)				
C35MN, processed at 800°C	RT	629	811	21.6
(current result)				

Table 8. Room temperature tensile properties of warm-rolled C35MN5 alloys before and after annealing at 650°C, together with that of C35MN hot-rolled and annealed at 800°C.

Condition*	YS, MPa	UTS, MPa	UL, %	TL, %	Remarks
As warm-rolled	1362	1380	0.4	5.4	C35MN5
WR + 650°C/1h	1200	1376	5.4	8.9	C35MN5
WR + 650°C/24h	1027	1202	7.2	12	C35MN5
HR@800°C + 800°C/1h	629	811	12	22	C35MN

*WR: warm-rolled

Figure 1 (modified)

(a) 1050°C-10min (TR: 40%)

(b) 900°C-10min (TR: 40%)

(c) 800°C-10min (TR: 93%)

(d) 700°C-15min (TR: 94%)

(e) 700°C-1h (TR: 94%)

*TR: total thickness reduction

200μm

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

(a) T35Y2 (HE@1050°C + 700°C/1h)

(b) C35MC (HR@1200°C + 1200°C/30min)

(c) C35MNC (HR@1200°C + 1200°C/30min)

(d) C35MN (HR@1200°C + 1200°C/30min)

(e) C35M (HR@800°C + 800°C/1h)

(f) C35MC (HR@800°C + 800°C/24h)

(g) C35MNC (HR@800°C + 800°C/24h)

(h) C35MN (HR@800°C + 800°C/24h)

300μm

Figure 9

(a) C35MC (HR@800°C + 800°C/24h)

(b) C35MNC (HR@800°C + 800°C/24h)

(c) C35MN (HR@800°C + 800°C/24h)

2μm

Figure 10

Figure 11

(a) C35M, as-rolled

(b) C35M, 700°C/24h

(c) C35MN5, as-rolled

(d) C35MN5, 700°C/168h

100μm

Figure 12

Figure 13