2.2 Characterization of 14W NFA Micro-alloyed with Y, Ti, Hf and Zr — Y. Wu, V. Ravula[1] and G. R. Odette (University of California, Santa Barbara)

OBJECTIVE

The objective of this work was to explore alternative composition variants for nanostructured ferritic alloys (NFA).

SUMMARY

Nanostructured ferritic alloys (NFAs) have applications in advanced fission and fusion reactors and are strengthened and made irradiation tolerant by a high number density of Y-Ti-O nanofeatures (NFs) that are very stable up to 1000ºC [1]. We briefly report preliminary results on the effects of various additions of Y, Ti, Hf and Zr to a baseline NFA composition of 14Cr, 3W and 0.3 Y_2O_3 (wt.%) on the microstructure and strength of NFAs. These alloys were characterized by microhardness (μH) and transmission electron microscopy (TEM) measurements. Alloys with additions of Ti (≈ 0.47 at.%) plus Hf (≈ 0.13 at.%) or Y(≈ 0.25 at%) had the highest μH and smallest grain sizes after hot consolidation at 1150°C. The corresponding hardness was lower in alloys alloyed with Zr (≈ 0.25 at. %) and Ti. The μH was lowest in alloys with Hf and Zr but without Ti; Hf again resulted in higher μH in this case than Zr. The alloy alloyed with Hf but without Ti had larger grains than those alloyed with either Hf or Y and Ti.

The alloys with Ti and Hf or Y added had extremely small grain sizes, especially for the consolidation temperature of 1150°C. The average NF size (<d>), number density (N) and volume fraction (f) ranged from 2.8 to 3.9 nm, 1.3 to $1.7 \times 10^{23}/m^3$ and 0.7 to 1.8 %, respectively. The NF oxides appear to be consistent with pyrochlore structures observed in reference NFA MA957, which are Y_2Ti_2O7 in this case. The NFs in alloys without Ti appear to contain large quantities of Cr.

BACKGROUND

To date most NFA have been based on micro-alloying Fe-(12-16)Cr-(2-3)W base alloys with small amounts of Y_2O_3 and Ti (< 1%). However, some researchers have explored the use of Hf and Zr which share Group V with Ti [see Ref. 2 as an example]. Thus as part of his work during a 6 month visit to UCSB, Dr. Vijay Ravula from the International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI) in Hyderabad, India, prepared a number of small batch heats of NFA to explore the relative effects of Hf, Zr, Ti and additional Y to a standard base of a 14YWT NFA. Here we report some results of initial characterization studies of these alloys.

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PROGRESS AND STATUS

Experimental Procedure

We fabricated 6 small alloy heats by mechanical alloying with SPEX ball milling for 20h the extra constituents shown in Table 1 (wt. %) with rapidly solidified Fe-14Cr-3W powders with and without Ti (0 and 0.4 wt.%) designated as 14YW and 14YWT, followed by hot pressing at 1150°C for 3 h at 1.3 MPa. Note, an initial study of an alloy with Ti and Hf additions based on milling for 10 h did not completely succeed in fully mixing the solutes, although this may be partly due to problems with the SPEX shaker mill motor at that time. The alloys are labeled as YWXX, where the last letter(s) designate the solute(s) that were added (T = Ti, H = Hf, Z = Zr, Y = Y_2O_3),

Vickers μH measurements were carried out at a load of 500 g on all the alloys. TEM specimen lift-outs were prepared using a FEI Helios FIB. A final lift out cleaning step used a low energy 2 KV, 5.5 pA beam to minimizing gallium ion damage. Small oxides were also extracted on a carbon foil for TEM EDX analysis. The TEM was performed using FEI Titan at 300 kV equipped with energy dispersive X-ray (EDX) spectrometer on YWTH, YWTY and YWH. Further details can be found in [3].

RESULTS

The μH results are shown in Table 1. Table 2 summarizes the TEM observations in terms of the NF oxide number density, N ($10^{23}/m^2$), average diameter. <d> (nm), and volume fraction, f (%), along with the μH and average grain diameter, d_g (nm) of the three alloys examined.

Table 1 Alloy Compositions (wt. %) and μH (kg/mm^2).

Alloy ID	14YWT	14YW	Zr	Hf	Y	Y_2O_3	μH
YWTH	99.93	-	-	0.4	-	0.3	522
YWH	-	99.93	-	0.4	-	0.3	455
YWTZ	99.93	-	0.4	-	-	0.3	425
YWZ	-	99.93	0.4	0.4	-	0.3	415
YWTZH	99.89	-	0.4	0.4	-	0.3	522
YWTY	99.93	-	-	-	0.2	0.3	533

Table 2. Hardness and TEM Data for Three Alloys.

Alloy	μH [kg/mm2]	N ($\times 10^{23}/m^2$)	<d> (nm)	f (%)	d_g (nm)
YWTH	522	1.3	3.4	0.7	150
YWH	455	1.5	3.9	1.4	525
YWTY	533	1.7	2.8	1.8	132

The grain structures of YWTH, YWTY, and YWH are shown in Figure 4. The alloys that contain both Ti and either Hf or Y additions have remarkably small grain sizes of less than 150 nm, especially considering the consolidation temperature of 1150°C. There are also small grains in the YWH alloy without Ti, but in this case the average is size ≈ 3.5 to 4 times higher than for the

Ti alloyed heats. Small grains certainly contribute to the higher strength of the YWTH and YWTY alloys [4].

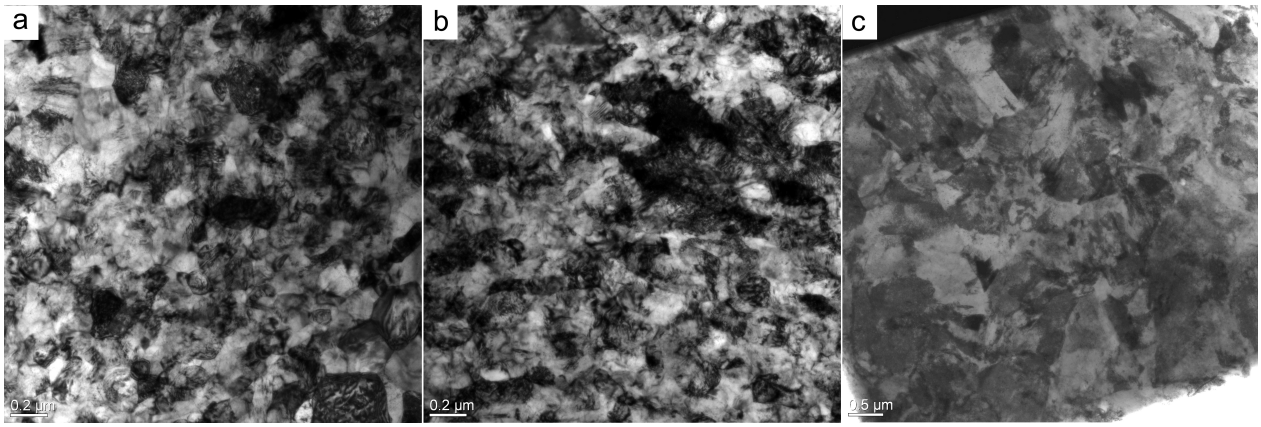

Figure 1. Lower magnification images show the grains in: a) YWTH; b) YWTY; and, c) YWH.

As shown in the extraction replica micrographs in Figure 2, small NF oxides were found in both YWH and YWTH. However, the <d> of the NFs in YWTH is slightly less than that in YWH, reflecting the well known refining effect of Ti [1]. However, the variations in N and <d> are relatively modest for all 3 alloys. The NF f varies from 0.7 to 1.8%. The nominal f is largest in the YWTY alloy with the highest Y + Hf + Ti solute content (≈ 1.1 at.%), but was smallest in the YWTH alloy with an intermediate solute content (≈ 0.98 at.%). The large f in the lowest solute content YWH alloy (0≈0.26 at. %) is not understood; and it is not clear that is consistent with a solute mass balance without the inclusion of a large fraction of Cr (see below).

Figure 3 shows a HRTEM images of small NF in YWTH (a) and the corresponding FFFT diffraction pattern (b) that is consistent with an fcc pyrochlore-type $Y_2Ti_2O_7$ complex oxide structure (b). Table 3 shows the corresponding lattice d-spacings taken from SAD ring patterns for the extracted NF oxides for YWH and YWZ are also consistent with $Y_2Ti_2O_7$, suggesting that he are $Y_2Hf_2O_7$ and $Y_2Zr_2O_7$ in YWH and YWZ, respectively.

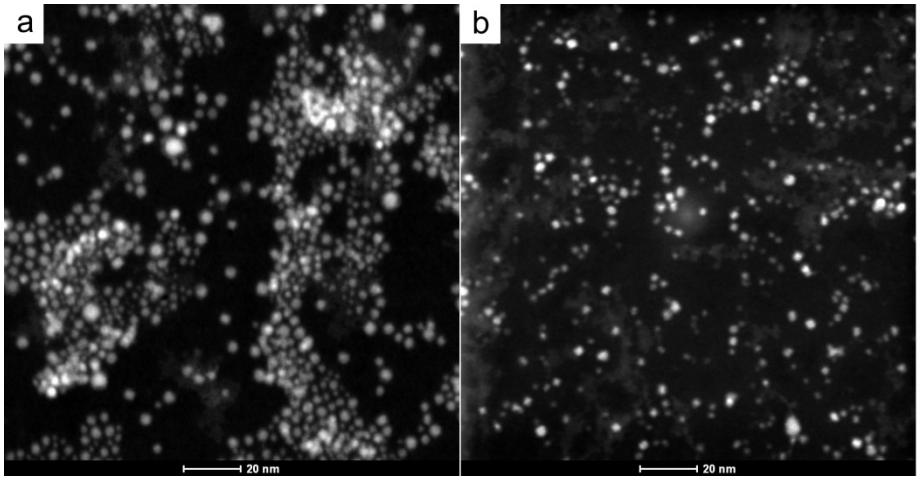

Figure 2. HAADF STEM images showing the NF oxides extracted from: a) YWH; and, b) YWTH.

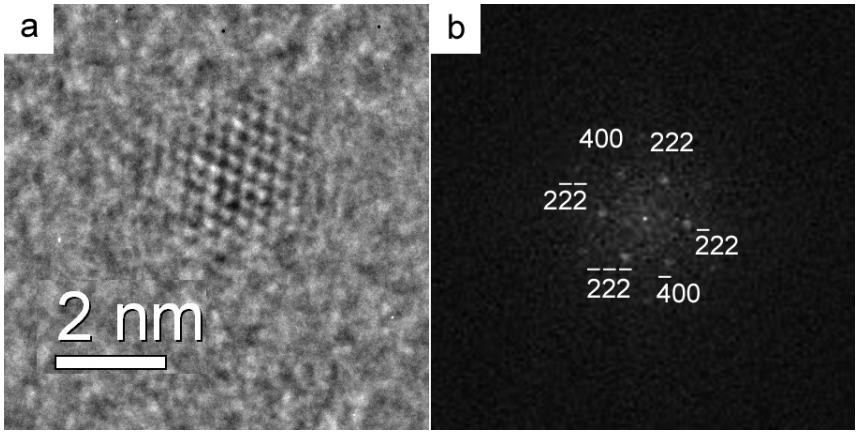

Figure 3. A HRTEM image of a small NF oxide (~2 nm in diameter) extracted on carbon film (a), and the corresponding FFT power spectra (b).

Table 3 gives a summary of d spacings measured from selected area diffraction (SAD) ring patterns (not shown here) in YWH and YWZ. Table 4 shows the results of EDX measurements on small the extracted NF oxides. The alloys without Ti appear to contain a large amount of Cr. Additional measurements will be needed to see is this observation is quantitatively correct; or perhaps partly an artifact of the extraction process. The nominal Zr/Y is ≈ 2.3 and the Hf/Y ≈ 1.2 in the YWZ and YWH alloys respectively. The Cr content of the alloy alloyed with Ti, Y and Hf is much lower; the corresponding Y/Ti = 1, but the Hf/Y and Ti is high at ≈ 4.7. A tentative conclusion is that the NFs are perhaps $(Y,Cr,Ti,Zr,Hf)_4O_7$ oxides, depending on the NFA composition.

Table 3. Measured d-spacings in Three NFA Compared to $Y_2Ti_2O_7$.

Lattice Spacing (Å)	YWZ	YWH	MA957	$Y_2Ti_2O_7$
d_{222}	3.05	3.05	3.0	2.93
d_{400} (Å)	2.60	2.65	2.6	2.56
d_{440} (Å)	1.80	1.8	1.8	1.80
d_{622} (Å)	1.60	1.6	1.6	1.54

Table 4. EDXS Measurements of the NF Compositions (at. %) for d<5 nm.

Alloys	Y	Ti	Hf	Zr	Cr
YWZ	17			39	44
YWH	16		19		65
YWTH	13	13	61		13

DISCUSSION AND FUTURE WORK

This exploratory study showed that alloying YW alloys with Hf and Zr, as well as Ti, would produce NFA and complex oxide NFs. However, the addition of Ti, along with the other Group IV elements resulted in higher alloy strength and smaller grains. Thus this preliminary research will continue. In the near term atom probe tomography (APT) and small angle neutron scattering (SANS) will be carried out on these and other new alloys prepared in the future.

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