The role of processing route on the microstructure of 14YWT nanostructured ferritic alloy

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Abstract

Nanostructured ferritic alloys have outstanding high temperature creep properties and enhanced tolerance to radiation damage over conventional ferritic alloys. To achieve these properties, NFAs are fabricated by mechanical alloying of metallic and yttria powders. Atom probe tomography has demonstrated that milling times of at least 40 h are required to produce a uniform distribution of solutes in the flakes. After milling and hot extrusion, the microstructure consists of α -Fe, high number densities of Ti-Y-O-vacancy-enriched nanoclusters, and coarse $Y_2Ti_2O_7$ and Ti(O,C,N) precipitates on the grain boundaries. In contrast, the as-cast condition consists of α -Fe with 50-100 μm irregularly-shaped $Y_2Ti_2O_7$ pyrochlore precipitates with smaller embedded precipitates with the $Y_3Al_5O_{12}$ (yttrium-aluminum garnet) crystal structure indicating that this traditional processing route is not a viable approach to achieve the desired microstructure. The nano-hardnesses were also substantially different, i.e., 4 and 8 GPa for the as-cast and as-extruded conditions, respectively. These variances can be explained by the microstructural differences and the effects of the high vacancy content introduced by mechanical alloying, and the strong binding energy of vacancies with O, Ti, and Y atoms that retard diffusion.

Keywords: nanostructured ferritic alloys, atom probe tomography, vacancy, nanoclusters

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1. Introduction

The microstructure of nanostructured ferritic alloys (NFAs), such as 12YWT and 14YWT, results in excellent creep and radiation tolerance properties, due to a high density of ultrafine intragranular Y-Ti-O-enriched nanoclusters (NCs), nanosize grains ($< 500\text{nm}$) as well as precipitation on and solute segregation to grain boundaries (GBs) [1-5]. However, the formation of this unique microstructure is highly dependent upon the processing path [6]. This uniqueness is because of synergies between the Ti, Y, O, and vacancy species in non-equilibrium arrangements within the matrix resulting from mechanical alloying. Although the 12YWT and 14YWT NFAs [7-10] were developed prior to the first-principals calculations of Fu et al. [11-12], these calculations indicated the potential of yttrium additions for further improving the bonding energy of Ti-O-vacancy clusters, and are supported by experiments [13].

As yttrium is almost insoluble in iron, yttrium-doped iron alloys cannot be produced by traditional casting methods [14, 15]. In addition, the liquid phase cannot be used to homogenize the distribution of solutes. Therefore, mechanical alloying [16-18] is a viable processing route for such alloys. This alternative route introduces new parameters on the optimization of the alloy design. In particular, the milling time will have a strong influence on the initial distribution of the solutes, particularly yttrium and oxygen [19]. The tensile properties of a 14Cr NFA are directly associated with the microstructural changes that arise during mechanical alloying, such as the attrition time [19], which provide the starting structure for thermomechanical treatment (extrusion, rolling, etc.). Short milling times may not be sufficient to redistribute the solute atoms in all the yttria particles within the solid solution, whereas overly long milling times add unnecessary expense to the fabrication, and introduce additional elements, such as carbon, from wear of the components of the attritor mill [16, 20]. Microstructural studies of these alloys for long milling times (i.e. > 20 hours) have been reported [6, 21-25] however, only limited 3-dimensional visualizations of the size and distribution of the NCs and coarse precipitates in the microstructures have been reported for short milling times (i.e. < 20 hours) [25]. The purpose of this

study is to explore the solute distribution in consolidated bars of 14YWT produced from mechanically alloyed 14YWT flakes with different milling times, and compare to a melted (non-NC-bearing) condition of the same alloy, in order to determine the underlying atomistic processes that result in the extruded product's excellent final properties.

2. Experimental

2.1. Material

The NFA was fabricated by mechanically alloying a master Fe-Cr-W-Ti alloy powder with Y_2O_3 powder. The alloy was characterized after two different sets of conditions. The first condition, hereafter referred to as the as-cast condition, was a mechanically alloyed and consolidated 14YWT specimen that was melted in a differential scanning calorimeter (DSC) and cooled to room temperature. The melting point of the as-cast specimen was estimated from the DSC data to be $\approx 1515^\circ\text{C}$. The second condition consisted of a series of specimens that were prepared from flakes mechanical alloyed for 5, 20 or 40 h in the attritor mill, consolidated by hot extrusion at 850°C , and aged for 1 h at 1000°C . The composition of the consolidated 14YWT NFA used for this study [21] is given in Table 1. The use of 5, 20 and 40 h as sample name indicates the milled, extruded and annealed sample conditions.

2.2. Nanohardness

A Nanoindenter-XP system with a Berkovich tip was used to measure the hardness and modulus of the specimens. Load (P) and displacement (h) were continuously recorded up to a maximum applied load (P_{max}) of 1.5 mN at a constant indentation strain rate $(dP/dt)/P$ of 0.05 s^{-1} , which resulted in a maximum depth of $\sim 100\text{ nm}$. The hardness and modulus were determined from the P - h unloading curves by the Oliver-Pharr method [26].

2.3. Specimen preparation

The extruded specimens were fabricated into atom probe tomography (APT) needle-shaped specimens by standard electropolishing methods [27-28]. Some electropolished specimens were also refined with an annular Ga ion milling in a FEI Nova 200 dual beam scanning electron microscope (SEM) and focused ion beam (FIB) technique [29-30]. In the as-cast material, site-specific APT specimens were fabricated by a lift-out method from a mechanically-polished surface, the details of which can be found elsewhere [29-30].

2.4. Microstructural characterization methods

Electron microscopy and electron backscatter diffraction (EBSD) was performed in a JEOL JSM6500F field-emission SEM, equipped with an EDAX Hikari EBSD camera and EDAX Apollo 40 silicon drift detector (SDD) energy dispersive spectrometer (EDS). APT was performed in a CAMECA instruments Inc. LEAP™ 4000X HR. All APT specimens were analysed in laser mode (with a focused UV laser beam) with a specimen temperature of 30 K, a pulse repetition frequency of 200 kHz, a pulse laser energy of 100 pJ, and an average ion detection rate of 0.2%. All APT composition estimates are given in atomic percent.

3. Results

3.1. Hardness

The nanohardness of the as-cast alloy was 4.0 ± 0.4 GPa and the modulus was 188 ± 14 GPa. In comparison, the nanohardness of the extruded alloy was 8.2 ± 0.6 GPa (after a short anneal at 75 °C) with modulus of 269 ± 28 GPa. Therefore, the nanohardness and modulus of the as-cast condition decreased by approximately 50% and 30%, respectively, compared to the extruded condition which is indicative of variances in the resulting microstructures of the two processing routes.

3.2. Microstructure

3.2.1. As-cast condition

As indicated from the nanohardness results, the microstructure of the as-cast condition is substantially different from the as-extruded 14YWT material. APT of the ferrite matrix did not reveal any fine precipitates or NCs ; however the ferrite was significantly depleted in the solutes, i.e., $0.07 \pm 0.01\%$ Ti, $0.03 \pm 0.01\%$ Y and $0.04 \pm 0.01\%$ O, compared to the base alloy bulk chemistry. The grain size of the as-cast condition was considerably larger, i.e., in the mm range, compared to the 40-200 nm grain size of the as-extruded condition. A finer-scale, 3-15 μm , Y-Ti-Al-O phase was evident in the interior of an irregularly-shaped coarse 50-100 μm Ti-Y-O phase, as shown in the 2-dimensional tri-colour multivariate statistical analysis (MVSA) [31] identification of the phases present with EDS X-ray spectra in Fig. 1. EDS analysis indicated that the composition of the pyrochlore-like phase had an approximate $\text{Y}_{1.5}\text{Ti}_2\text{O}_{5.5}$ atomic ratio ($\sim 15\%$ at. % Y, $\sim 20\%$ Ti, and $\sim 65\%$ O), with a trace level of Al, and the YAG-like phase had an $\text{Y}_3\text{Al}_5\text{O}_{12}$ atomic ratio ($\sim 30\%$ at. % Al, $\sim 15\%$ Y and $\sim 55\%$ O) with a trace amount of Ti. A backscattered electron (BSE) image of the as-cast condition reveals a ferrite matrix with isolated islands of coarse oxide precipitates (Fig. 2). The electron backscatter Kikuchi patterns of these Ti-Y-O and Y-Ti-Al-O oxides, Fig. 2, were consistent with the crystal structures of $\text{Y}_2\text{Ti}_2\text{O}_7$ (pyrochlore) and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (yttrium-aluminum garnet - YAG) phases, respectively, but other phases with similar interplanar angles could be possible. In comparison, an APT composition estimate of the interior of the pyrochlore phase was 17.7 ± 0.016 at. % Ti, $11.2 \pm 0.04\%$ Y, $68.9 \pm 0.03\%$ O, and $0.2 \pm 0.01\%$ Al, and that of the YAG-like phase was 19.8 ± 0.1 at. % Al, $15.2 \pm 0.1\%$ Y, $59.1 \pm 0.1\%$ O, and $5.9 \pm 0.02\%$ Ti. These values are in reasonable agreement with the prototypical composition of their respective phases, assuming that the Ti is included in the Al estimate for the YAG phase, as shown in Table 2. Because the Al content of the pre-melted base alloy was assayed as 0.04 at. % Al, it is likely that the high level of Al in the YAG phase arose from the alumina crucible used to melt the alloy.

3.2.2. 5, 20 and 40 h 14YWT milling times

The microstructures of the NFA after the three milling times followed by extrusion and aging for 1 h at 1000 °C are shown in Fig. 3. The 3% Ti concentration isosurfaces reveal the formation of some Ti-O-C-

N-enriched precipitates in all three conditions, but the size of the irregularly-shaped precipitates in the 5 h milled specimen was significantly coarser than the 20 and 40 h milled specimens. The number densities of the precipitates for the 5, 20 and 40 h milled conditions were estimated to be $\sim 7.5 \times 10^{22} \text{ m}^{-3}$, $\sim 2.3 \times 10^{23} \text{ m}^{-3}$ and $\sim 1 \times 10^{24} \text{ m}^{-3}$, respectively. For all three milling times, no evidence was found of any remnants of yttria powder in the matrix. From APT measurements, the compositions of the ferrite phase from different regions of each of the three different milling times are estimated and listed in Table 1. These results indicate marked variations in the solute contents, especially in the shorter milling time conditions. In the 40h volume, the segregation of W atoms to the GBs was observed, Fig 3c . Some C and Cr segregation to the GB was also observed, which has been previously observed for this processing condition [21, 32, 33, 34]. Other volumes of 40, 20, and 5 h specimens showed similar segregation; the 5 h material's grains were so large only a single GB was captured in atom probe, however. This segregation likely occurs during post-mechanical alloying thermomechanical processing (i.e., extrusion and annealing) and is likely a common occurrence.

Proximity histogram across the interfaces of two of the coarse precipitates in the material milled for 5 h, shown in Fig. 3a, are shown in Fig 4. APT results from two additional regions of the alloy milled for 5 h are shown in Fig. 5. In this data, a coarse, $\sim 25 \text{ nm}$ by $\sim 10 \text{ nm}$, Ti-Y-O-enriched particles was revealed, within which the Y and O were found to be concentrated at its center, as shown in the proximity histogram in Fig. 6a. This central Y-enriched region was found to have a composition of $15.7 \pm 1.5 \text{ at. \% Fe}$, $15 \pm 0.5 \text{ \% Cr}$, $12.5 \pm 0.3 \text{ \% Y}$, $1 \pm 0.3 \text{ \% W}$, $20.6 \pm 0.5 \text{ \% Ti}$, $15.4 \pm 0.26 \text{ \% O}$, $0.3 \pm 0.05 \text{ \% C}$, and $7.6 \pm 0.3 \text{ \% N}$. This type of particle, with a Y-enriched core, was only found in $\sim 1\%$ of the precipitates. The other Ti-O-enriched precipitate, shown in Fig. 6b had a composition of $18.5 \pm 1.5 \text{ at. \% Fe}$, $16.4 \pm 0.3 \text{ \% Cr}$, $1 \pm 0.2 \text{ \% W}$, $31.0 \pm 0.4 \text{ \% Ti}$, $13.8 \pm 0.2 \text{ \% O}$, $2.4 \pm 0.1 \text{ \% C}$, and $6.4 \pm 0.2 \text{ \% N}$. Interestingly, this precipitate was not found to contain any Y atoms. The estimated ferrite compositions from several grains for the 5-h-milled condition are listed in Table 1. Marked variations in the solute contents are evident in different grains, indicating that after this short milling time, the solutes were not uniformly distributed.

In the 20 h condition, the Ti-O-enriched particles were significantly finer-scaled. Proximity histograms across the interfaces of the precipitates with two different sizes in the material that was milled for 20 h, shown in Fig. 3b, are shown in Fig 7. The compositions of 2-4 nm Ti-Y-O NCs were found to be of 57.7 ± 1.7 at. % Fe, 25.6 ± 1.4 % Cr, 0.9 ± 0.2 % Y, 0.7 ± 0.2 % W, 3.8 ± 0.2 % Ti, 8.2 ± 0.3 % O, 0.5 ± 0.2 % C, and no N . The 4-10 nm Ti-Y-O NCs had a composition of 50.7 ± 0.7 at. % Fe, 21.0 ± 0.7 % Cr, 3.8 ± 0.06 % Y, 2 ± 0.9 % W, 4.8 ± 0.1 % Ti, 10.7 ± 0.05 % O, 0.7 ± 0.2 % C, and 4.6 ± 0.2 % N. However, some larger precipitates were also found, indicating that this 20h intermediate milling time was still not sufficient to produce a homogenous solute distribution.

A proximity histogram from one of these larger precipitates is shown in Fig. 8. The coarser precipitate was found to have a composition of 27.0 ± 0.2 at. % Fe, 23.7 ± 0.1 % Cr, 1.0 ± 0.02 % Y, 1 ± 0.05 % W, 9.7 ± 0.02 % Ti, 28.3 ± 0.05 % O, 0.05 ± 0.01 % C, and 0.3 ± 0.02 % N. The estimated ferrite compositions from several grains of the 20-h-milled condition are also included in Table 1. As observed for the 5-h milled condition, marked variations in the solute contents are evident in different grains of the 20-h milled alloy indicating that the milling times up to 20 h were too short to fully homogenize the solute distributions in the milled flakes and take full benefit of the alloying additions.

The smaller (2-4 nm) precipitates show comparatively high Fe and Cr contents (e.g., 58% Fe, 25% Cr); this is likely an artefact of trajectory aberration in APT [35], which is unavoidable where oxide nanoparticles in a metal matrix are examined. With larger precipitates (> 10 nm) the lower Fe contents (e.g., 27%) are probably more accurate, owing to a very small influence of trajectory aberration as the particle sizes increase; cation substitutions are common in ceramics, so the Fe content is possible but certainly not proven. The quantitative nature of trajectory aberration and its influence on composition measurements is still not well known [36], but the trends for solute are what is important to understand NC evolution.

The results presented here and previous APT and transmission electron microscopy (TEM) studies, have demonstrated that the 14YWT powder milled for 40 h does not generally exhibit any coarse (i.e., greater than 100 nm) precipitates [21]. After consolidation by extrusion and thermal aging of these flakes, three main populations of fine scale precipitates are present in the microstructure. The largest (20 - 50 nm) precipitate is a cubic TiX, where X is a combination of N, O and C, and is predominantly found on GBs. Owing to their low number densities, few of these precipitates have been characterized by APT. The solute content is uniform within each precipitate, but the non-metal content (O, N, and C) varies considerably. The Y content is typically <1 at. % in these precipitates and they contain a significant level of Fe. A second population of smaller (approximately 5–10 nm diameter) and higher areal density precipitates was found decorating the GBs [37-38]. In addition, a third dense population of ultrafine scale $\sim 2.0 \pm 0.2$ nm diameter NCs was observed in the grain interior and on GBs. The APT data also indicate that the majority of the Cr and W additions are in solid solution in the ferrite matrix, and there are strong enrichments of Cr and W between the precipitates on the GBs [21]. Low levels of C, P and Si segregation to the GBs have also been observed in APT data [21].

4. Discussion

A comparison of the as-extruded and as-cast NFAs reveals that traditional casting does not produce the desired fine-scale and uniformly distributed precipitate population necessary to produce a highly stable microstructure in 14YWT and related NFAs with excellent properties. Instead, the coarse-grained microstructure consists of a low-solute ferrite phase devoid of any fine-scale precipitates but with a low number density of irregularly shaped precipitates consisting of a 50-100 μm $\text{Y}_2\text{Ti}_2\text{O}_7$ (pyrochlore) phase embedded with a fine-scale $\text{Y}_3\text{Al}_5\text{O}_{12}$ (yttrium-aluminum garnet) phase.

Mechanical alloying followed by extrusion and annealing can produce the desired nanoscale grains and finely distributed NCs. However, to achieve this goal, milling times of at least 40 h are required. When shorter milling times of ~ 5 h are used (recall that "5 h" denotes 5 h-milled flakes, then consolidated and

annealed into the examined specimens), the microstructure contains a relatively low number density of coarse precipitates. This distribution consumes the alloying elements in a few coarse precipitates, and thereby prevents the formation of the high number density of NCs as the solute content of the ferrite is no longer supersaturated. In the case of 20h sample, instead of coarser Ti-Y-O precipitates formed like in the 5 h sample, finer-scale precipitates are present, presumably due to a more uniform solute distribution within the as-milled flakes prior to the high-temperature consolidation, extrusion, and annealing. After milling for 40 h, this process results in a predominantly uniform dispersion of 2-nm-diameter NCs in the ferrite, and slightly coarser precipitates along the GBs, where the diffusion rate of solutes is likely to be higher due to pipe-diffusion type processes [21]. Milling time, and its concomitant effects of changing the nature and size of the NCs, is likely to heavily modify the NCs ability to serve as beneficial sinks against radiation damage, so optimization of the microstructure is vital for not just mechanical but also irradiation properties, especially considering that many different types of NCs are present even in a single alloy [39]. Milling also has the beneficial effect of refining and maintaining the ultrafine grain size. Longer milling times are anticipated to have limited returns on improving the microstructure, as the precipitate size and number density appears to be near optimal for producing the desired mechanical properties, and longer milling will only serve to increase the production costs, and may result in the introduction of more contaminants [16, 20].

This study has revealed that progressively longer milling times were found to produce a more uniform dispersion of the solutes and a more uniform precipitate size and distribution within the ferrite matrix. Empirical observations have also indicated that long milling times of the precursor material [19, 40] are needed to achieve a uniform as-milled microstructure. This was also supported by producing 14YWT with additions of Fe_2O_3 and YH_2 powder instead of Y_2O_3 powder [41]. Extended ball milling up to 96 h improved oxide dispersion, microstructural refinement and mechanical properties as shown by Romanoski et al [42]. Milling times with different mill technologies (i.e., SPEX rather than attritor mills) can be shorter (e.g., 8 h [6] or 20 h [Ref. 43]) due to the high energy density in the processing, but the

trend to determine a minimum necessary milling time remains due to cost concerns. Studies of high- Y_2O_3 (3-15%) model alloys have revealed that diffraction peaks of Y_2O_3 disappear after milling times of 48-100 h [44-45]. The mechanism becomes more complex with the presence of large amount of yttria in the alloy system. Small amount of the yttria particles is dissolved into the matrix to form a supersaturated solid solution, whereas the remaining oxide particles are transformed to an amorphous compound [46]. However, the relationship between these high yttria model alloys to NFAs with less than 1% Y_2O_3 additions is unclear.

5. Conclusions

The microstructure of the as-cast NFA consists of coarse grains of $\alpha\text{-Fe}$ with 50-100 μm irregularly shaped $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore precipitates containing smaller embedded precipitates 3-15 μm YAG crystal structure; these YAG particles may be an artefact of melting in an alumina crucible, given the low bulk-Al level in the starting specimen. In contrast, the microstructure of the 40-h-milled as-extruded and aged condition consisted of ultrafine grains of $\alpha\text{-Fe}$ with three distributions of precipitates, ~2-nm-diameter Ti-Y-O-vacancy-enriched NCs, 5-10 nm $\text{Y}_2\text{Ti}_2\text{O}_7$, and 20-50 nm $\text{Ti}(\text{O,C,N})$ precipitates. The nano-hardnesses of the as-cast and as-extruded and aged conditions were also substantially different, i.e., 4 and 8 GPa, respectively, due to the different microstructures produced.

These results confirm that the milling time is an important parameter to optimize particle size distribution and number density within the NFA microstructure. At shorter milling times (5-20 h), the Ti, Y, and O atoms are consumed in lower number densities of coarse precipitates and there are large variations in the solute contents of the ferrite matrix. After a longer milling time (40 h), a uniform distribution of ultrafine precipitates with high number densities are present in the ferrite. Hence, an optimized long milling time upto 40h is needed to achieve desired fine structure, milling time longer than this is not necessary whereas less than 40 h milling time will produce material with inferior properties.

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Table 1. Composition of the 14YWT nanostructured ferritic alloy [21], the ferrite phase in the as-cast alloy, and for the different milling times. The balance is iron.

Element		Cr	Y	W	Ti	O	C	Si	N
Bulk	at. %	13.93	0.14	0.16	0.24	0.39	0.24	0.16	0.15
	wt. %	13.13	0.22	0.54	0.19	1140 ppm	530 ppm	0.08	385 ppm
Ferrite									
As-cast	at. %	15.9 ± 1.6	0.03 ± 0.01	0.52 ± 0.5	0.07 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.07 ± 0.01	0.02 ± 0.01
5h	Grain								
	1	14.8 ± 0.4	0.06 ± 0.01	0.20 ± 0.01	0.06 ± 0.01	0.20 ± 0.002	0.004 ± 0.004	0.05 ± 0.002	0.042 ± 0.01
	2	15.5 ± 0.1	0.04 ± 0.01	0.80 ± 0.03	0.03 ± 0.01	0.30 ± 0.01	0.02 ± 0.01	0.09 ± 0.01	0.003 ± 0.002
	3	14.9 ± 0.1	0.01 ± 0.01	0.90 ± 0.02	0.02 ± 0.01	0.60 ± 0.003	0.004 ± 0.002	0.04 ± 0.01	0.007 ± 0.002
	4	14.4 ± 0.1	0.01 ± 0.01	0.14 ± 0.01	0.11 ± 0.01	0.17 ± 0.01	0.01 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
	5	14.7 ± 0.1	0.01 ± 0.01	0.04 ± 0.01	0.42 ± 0.01	0.35 ± 0.001	0.005 ± 0.01	0.03 ± 0.002	0.30 ± 0.01
20 h	1	14.0 ± 0.04	0.10 ± 0.002	0.13 ± 0.01	0.03 ± 0.003	0.5 ± 0.002	0.04 ± 0.001	0.07 ± 0.004	0.10 ± 0.001
	2	14.2 ± 0.05	0.08 ± 0.002	0.14 ± 0.01	0.30 ± 0.01	0.44 ± 0.002	0.05 ± 0.002	0.02 ± 0.01	0.70 ± 0.01
	3	15.2 ± 0.05	0.30 ± 0.003	0.70 ± 0.01	0.50 ± 0.01	1.00 ± 0.01	0.1 ± 0.004	0.25 ± 0.01	0.34 ± 0.002
	4	14.4 ± 0.05	0.14 ± 0.003	0.10 ± 0.01	0.30 ± 0.01	0.84 ± 0.001	0.05 ± 0.002	0.06 ± 0.003	0.16 ± 0.001
	5	15.9 ± 0.04	0.10 ± 0.002	0.80 ± 0.01	0.20 ± 0.01	0.30 ± 0.01	0.13 ± 0.004	0.24 ± 0.01	0.10 ± 0.001
40 h	1	15.5 ± 0.01	0.06 ± 0.003	0.75 ± 0.01	0.07 ± 0.01	0.30 ± 0.01	0.03 ± 0.003	0.11 ± 0.01	0.03 ± 0.001
	2	13.6 ± 0.06	0.06 ± 0.002	0.63 ± 0.01	0.10 ± 0.01	0.40 ± 0.01	0.06 ± 0.004	0.14 ± 0.01	0.02 ± 0.001
	3	16.0 ± 0.02	0.04 ± 0.002	0.08 ± 0.002	0.14 ± 0.002	0.54 ± 0.003	0.33 ± 0.003	0.44 ± 0.003	0.04 ± 0.001
	4	15.7 ± 0.04	0.02 ± 0.003	0.03 ± 0.002	0.08 ± 0.003	0.32 ± 0.004	0.31 ± 0.01	0.40 ± 0.01	0.02 ± 0.002
	5	15.6 ± 0.04	0.01 ± 0.003	0.005 ± 0.01	0.08 ± 0.003	0.21 ± 0.004	0.30 ± 0.01	0.35 ± 0.01	0.02 ± 0.003

Table 2. Compositions of the pyrochlore and YAG phases in the as-cast 14YWT alloy.

At. %	Pyrochlore prototype	Pyrochlore SEM	Pyrochlore APT	YAG prototype	YAG SEM	YAG APT
Ti	18.2	~20	17.7	n/a	trace	5.9
Al	n/a	trace	0.03	25	~30	19.8
Y	18.2	~15	11.2	15	~15	15.2
O	63.6	~65	68.9	60	~55	59.1

FIGURE CAPTIONS

Fig. 1. Multivariate statistical analysis decomposition of SEM EDS X-ray spectrum image. Inset image show false-color score images of three statistically significant components. Loading spectra show the associated elemental response where blue is the Fe-Cr(W) matrix, green is the Ti-Y-O phase, and red is the Ti-Al-O(-Y) phase.

Fig. 2. (a) BSE image of as-cast condition of 14YWT reveals a ferrite matrix with isolated islands of coarse oxide precipitates. EBSD Kikuchi patterns of b) Ti-Y-O-enriched regions, indexed as $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore, and (c) smaller embedded Y-Ti-Al-O oxides, indexed as $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG).

Fig. 3. The microstructures of the 14YWT NFA after milling for 5, 20 and 40 h, extrusion, and aging for 1 h at 1000 °C. The precipitates are shown by a 3% Ti concentration isosurface. The superimposed W atoms indicate the presence of a GB (viewed edge-on) in the 40 h milled specimen.

Fig. 4. APT proximity histograms from the 5 h milled 14YWT NFA showing the solute partitioning of Ti, Y, O, and C between the ferrite phase and 2 coarse precipitates, (a) and (b)

Fig. 5. (a) 1 % Ti (green) and 2.8 % Y (red) concentration isosurfaces of a coarse precipitate from the 14YWT NFA after milling for 5 h with a Y-enriched core region, and (b) a 2 % Ti (green) concentration isosurface of coarse precipitate with no Y-enriched core.

Figure 6. APT proximity histograms from the 5 h milled 14YWT NFA showing the solute partitioning of Ti, Y, O, and C (a) between the ferrite phase and a Y-enriched precipitate, and (b) between the ferrite phase and a TiO- enriched precipitate with no Y enrichment.

Figure 7. APT proximity histograms from the 20 h milled 14YWT NFA showing the solute partitioning of Ti, Y, O, and C between (a) the ferrite phase and the 2-4 nm diameter Ti-Y-O NCs, and (b) between the ferrite phase and 4-10 nm diameter Ti-Y-O NCs.

Figure 8. APT proximity histogram from the 20 h milled 14YWT NFA showing the solute partitioning of Ti, Y, O, and C between the ferrite phase and a large Ti-Y-O-enriched precipitate.