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On the remarkable thermal stability of nanostructured ferritic alloys

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ABSTRACT

We explore the high-temperature thermal stability of a class of potentially transformational materials for high temperature applications that we call nanostructured ferritic alloys (NFAs). NFAs manifest unprecedented properties including outstanding strength and irradiation tolerance that are primarily enabled by an ultrahigh concentration of Y–Ti–O nanoscale features (NFs). One significant challenge is to understand and control the stability of the NFs under extreme high temperature and long-time aging conditions. Thermal aging was carried out between 800 °C and 1000 °C for times up to 32.4 kh. A toolkit of characterization techniques shows that the NFAs and NFs are stable below 900 °C, while experiencing slow, but systematic coarsening at 950 °C and especially 1000 °C, accompanied by small reductions in strength. Other microstructural changes are also described.

1. Introduction and background

This paper investigates the thermal stability of the nanostructured ferritic alloy (NFA) MA957. NFAs are often called oxide dispersion strengthened (ODS) steels, but it is useful to distinguish them from alloys like INCO MA956 and Plansee PM2000, since the latter contain coarser (>5 nm) oxide phases and are generally not as strong or radiation damage tolerant as NFAs. This investigation describes the microstructural characterization of MA957 aged for up to 32 kh at temperatures from 800 °C to 1000 °C. A complementary analysis, that combines these data with those from past studies performed at higher temperature and shorter times to develop an aging model, will be reported in a separate publication.

NFAs manifest remarkably high strength and radiation damage resistance due to the presence of an ultrahigh density of nanoscale features (NFs) [1,2]. Thus a significant challenge is to understand and control the formation and stability of the NFs and the balance of the NFA microstructure. NFAs are ferritic stainless steels that typically contain 12–16 wt% Cr, ≤ 1.0 wt% Mo or ≤ 3 wt% W (for solid solution strengthening) and small additions of Y, Ti and O that form 1–5 nm-scale Y–Ti–O NFs. The NFs provide dispersion strengthening and help stabilize dislocation and fine grain structures. They also reduce excess concentrations of irradiation-induced displacement defects by enhancing vacancy-interstitial recombination, and trap helium in fine, relatively harmless (or, indeed, potentially beneficial) bubbles [1–4].

NFAs are typically processed by ball milling pre-alloyed, rapidly-solidified metal alloy and yttria (Y_2O_3) powders [1]. Proper milling effectively dissolves the Ti, Y and O solutes that then precipitate as NFs during hot consolidation by isostatic pressing (HIPing) or extrusion. Powder consolidation is usually followed by a series of deformation processing and shaping treatments.

Since coarsening may reduce their beneficial contributions to alloy function, the thermal and irradiation stability of the NFs are extremely critical issues. The results reported here focus on the thermal stability of International Nickel Company (INCO) MA957 that was developed as the first commercial vendor 14Cr NFA in the late 1970s for use in liquid-metal fast breeder reactors [5]. Although no longer in production, research continues of the remaining stock of MA957, which serves as a reference material for a number of small-heat model NFA variants typically called 14YWT [6–9].

Not surprisingly, past anneals at 760 °C and below for 10 kh on alloy MA957 produced no microstructural or hardness changes [10], and annealing at 1000 °C for 1 h showed no significant change in the NFs of a 14YWT alloy [11]. However, aging an MA957 alloy at 1300 °C coarsened the NFs from a radius of 1.2 ± 0.4 nm to 1.7 ± 0.4 nm after 1 h and 4.6 ± 1.1 nm after 24 h [12]. This aging resulted in partial recovery of the dislocation structure and some solute segregation to dislocations and grain boundaries. However, no recrystallization or significant grain growth was observed [13]. Transmission electron microscopy studies following 1200 °C, 1 h anneals of MA957 showed that while most of the NFs were stable, some grew with increasing Y content and the largest precipitates coarsened by an Ostwald ripening mechanism [14]. The limits of NF stability were explored by aging studies on a French heat of MA957 for times of up to

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480 h at temperatures from 1150 °C to 1400 °C [6,7]. The heat was fabricated at CEA/Saclay in France by center drilling an extruded U. S. MA957 bar followed by an extrusion or pilgering process (HBB-0127). Small angle neutron scattering (SANS) showed coarsening at and above 1150 °C. A coarsening model derived from these data suggested that the NFs would remain stable for very long times ($\geq 10^5$ h) at operating temperatures below 1000 °C [1,7]. Finally, in the same French heat of MA957 also aged at 850–1000 °C for times up to 3 kh, the grain and dislocation structures remained stable, while the NFs coarsened slightly without significantly reducing the hardness [15].

A number of researchers have concluded that Ti increases both the number density and resistance to coarsening of the smallest NFs [7,8,16,17]. However, a recent atom probe study by Williams compared oxides with and without Ti and concluded that the coarsening rates are unaffected by Ti and the details of the corresponding oxides [18]. However, if the Williams data are analyzed in a more rigorous way, the coarsening rates are found to be a factor of 1.8–2 times higher for larger Y_2O_3 oxides compared to smaller Y–Ti–O NFs.

A primary objective of this research is to examine the very long-term NFA stability at temperatures below those in previous studies at conditions closer to those experienced in service. Specifically we report the results of long-term thermal aging (LTTA) of a reference NFA, a U.S. heat of MA957, at temperatures from 800 °C to 1000 °C for aging times up to 32.4 kh. The techniques used to characterize the NFA and NFs included Vickers microhardness (H_v), small angle neutron scattering (SANS), transmission electron microscopy (TEM) and atom probe tomography (APT). Spatial and time-dependent composition changes as a function of the distance from the aged specimen surfaces and the redistribution of Ti were also characterized by electron probe microanalysis (EPMA) along with dislocation and grain structures.

It should be noted that the small features in MA957 and other alloys have been reported to be primarily complex oxide $Y_2Ti_2O_7$ pyrochlore phases [16,19]. However, in this paper we will refer to them simply as NFs, except for in the discussion section.

2. Materials and methods

2.1. Material and aging conditions

A heat of US MA957 (DBB0122), originally manufactured by INCO, was acquired from Pacific Northwest National Laboratory in the form of a 25 mm diameter extruded round bar. The alloying and consolidation conditions are proprietary and unknown in specific detail, but the original patent gives the likely processing parameters including: use of −40 and −80 mesh size powders for all of the alloying elements plus Y_2O_3; attritor milling for 24 h at 288 rpm using a 20:1 ball to powder mass ratio; and extruding the canned powder at 1065 °C at a 6:1 ratio [5]. The nominal and measured (method not given) compositions (wt%) of MA957 from a previous study are shown in Table 1 [10].

Long-term thermal aging (LTTA) was carried out in quartz capsules containing a dry He atmosphere in a tube furnace at temperatures between 800 °C and 1000 °C in 50 °C increments for times up to 32.4 kh. The specimens aged at 800 °C, 900 °C and 1000 °C were cut from the original 25 mm round bar into semi-cylinders. The coupons aged at 850 °C and 950 °C were smaller ≈8 mm diameter cylinders. Cr oxide was observed to sublimate significantly from the surface after 3 kh above 900 °C. Subsequently, the higher temperature coupons were tightly wrapped in a 309 stainless steel foil (22–24 wt% Cr) to minimize the loss of this element. Aging was interrupted periodically for microhardness measurements and microstructural characterization studies. Approximately 1–2 mm of the outer surface region was removed after each aging time increment to avoid near surface effects. However, as shown below, at higher temperature and longer times Cr was enriched to a larger depth, requiring the removal of additional material.

Table 1
The nominal and measured composition of MA957.

wt%	Fe	Cr	Ti	Mo	Y	O	Ni, Al, Mn	Si, C, S, P
Nominal	Bal.	14.0	1.0	0.3	0.197	0.053	–	–
Measured[a]	Bal.	13.87	1.05	0.30	0.22	0.22	< 0.15	< 0.05

[a] Average measured composition from several MA957 heats [10].

Vickers microhardness measurements were performed on vibratory polished (0.3 μm) surfaces using a LECO M-400A semi-automated hardness tester at a 500 g load. Between 20 and 40 indents were made in each test. SANS, APT and TEM were used to characterize the microstructures of the aged MA957. EPMA was used to measure compositions of key elements as a function of the distance from the coupon surfaces. Previous work indicated that the grain structure and NFs remain stable up to 900 °C for 3 kh [15], so the major focus here was on the 900–1000 °C aging temperatures.

2.2. Small angle neutron scattering (SANS)

SANS was used to characterize the average size ($\langle d \rangle$), number density (N), and volume fraction (f) of the NFs. The SANS measurements were performed at the NIST Center for Neutron Research in Gaithersburg, MD [20] on the NG7 beam line, using a neutron wavelength of $\lambda = 0.5 \pm 0.03$ nm with a two-dimensional ^{3}He detector located 1.55 m from the sample and offset by ≈20 cm to increase the useful scattering vector ($q = 4\pi \sin\theta/\lambda$ where θ is the scattering angle) range up to ≈3 nm^{-1}. Measurements were made with a 4 mm diameter aperture on ≈2 mm thick coupons in a 1.7 ± 0.1 T horizontal magnetic field applied along the extrusion direction to saturate the magnetic Fe–Cr matrix; separate measurements support the assumption that the matrix magnetization was saturated at these field levels [7,8]. The magnetic field permits separation of the nuclear (n) and magnetic (m) differential scattering cross sections ($d\Sigma(q)/d\Omega$), where the latter depends on the angle from the horizontal magnetic field direction, ϕ as

$$\frac{d\Sigma}{d\Omega}(q,\phi) = \frac{d\Sigma}{d\Omega}(q)_n + \sin^2\phi \frac{d\Sigma}{d\Omega}(q)_m \quad (1)$$

The method for converting raw detector count data to $d\Sigma/d\Omega$ curves is described in detail elsewhere [8,21,22]. The SANS analysis involves subtracting a measured control $d\Sigma/d\Omega$ from that for the sample to isolate the scattering by the NFs. In this case, the control was a Fe–14Cr–0.3Mo–1Ti HIP consolidated alloy that did not contain Y. The $d\Sigma/d\Omega$ is related to the scattering feature size distribution [$N(r')$], number density (N), volume fraction (f) and scattering contrast factor, $\Delta\rho$; the latter is the difference between the feature and matrix scattering length densities. The $N(r')$ can be used to derive the average radius $\langle r^3 \rangle^{1/3}$. Further details of how N, $\langle d \rangle = 2\langle r'^3 \rangle^{1/3}$ and f are determined from the $d\Sigma/d\Omega$ data are also described elsewhere [7,8,22,23].

The magnetic (M) to nuclear (N) scattering ratio, $M/N = (d\Sigma/d\Omega_m)/(d\Sigma/d\Omega_n)$, contains information of the composition and structure of the scattering features. In this study the magnetic scattering $d\Sigma/d\Omega_m$ is independent of the composition of the non-magnetic scattering features embedded in a saturated ferrite matrix. However, the nuclear scattering depends on the composition and atomic density of the scattering feature. The M/N can vary with q if the composition-structure of the feature varies with size,