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Effect of boron and carbon addition on microstructure and mechanical properties of the aged gamma-prime strengthened alumina-forming austenitic alloys

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ABSTRACT

The goal of this work was to understand the effects of aging at 800 °C on the microstructures and mechanical properties of two recently-developed AFA stainless steels based on Fe-14Cr-32Ni-3Nb-3Al-2Ti (wt.%), one of which contained small additions of boron and carbon. To that end both the size distributions and growth kinetics of the B2, Laves phase, $L1_2$ precipitates present were quantified. While the lattice parameter, morphology, size and coarsening behavior of the $L1_2$ precipitates was the same in both AFA alloys, the B and C enhanced the grain boundary coverage by both Laves phase and B2-NiAl precipitates, but suppressed their coarsening. These interstitial additions also suppressed the formation of twins and discontinuous precipitation, which were observed in the B and C-free material. It is shown that the yield strength at 700 °C is largely controlled by the size of the $L1_2$ precipitates, with the largest strengthening effect obtained after aging for 2.4 h for both AFA alloys. Longer aging time led to a loss of strength mainly due to the coarsening of the $L1_2$ precipitates.

1. Introduction

In order to reduce environmental pollution, there is an urgent demand to increase the thermal efficiency of fossil fuel power plants by increasing the working temperature and pressure. The key limitation is the creep life of the materials used. To meet the target of operating at 700-760ºC/35 MPa for the next generation of advanced ultra-supercritical power plants, new materials must be developed to withstand this high operating temperature at low cost [1,2].

Alumina-forming austenitic (AFA) stainless steels have potential to meet the requirements for this application due to promising mechanical properties and oxidation resistance [3–5]. AFA steels are designed to have a single-phase austenitic matrix with MC carbide and/or $L1_2$-Ni_3(Al, Ti) as the main strengthening precipitates. They can provide better oxidation resistance than conventional heat-resistant stainless steels due to alumina scale formed on the material's surface [3,4].

Recently, it has been shown that the addition of carbon and boron to AFA stainless steels improves the creep life dramatically. Interestingly, the addition of carbon alone did not show any improvement in the creep life time, while boron addition is associated with significant improvement in the creep performance [5].

Boron addition has been reported to increase creep rupture strength in AFA stainless steels, but the reasons are not well explained [4,5]. It is widely believed that the addition of boron increases creep rupture life and ductility through the increase in creep cavitation resistance of the steel by grain boundary (GB) strengthening. The mechanism for strengthening of the GB is not precisely known. In most instances, it has been suggested that the segregation of boron to the GBs fills the vacancies, resulting in a decrease in GB diffusivity and, consequently, the rate of void formation [6,7].

It has also been proposed that addition of boron increase the creep life by decreasing the agglomeration of $M_{23}C_6$ carbides at the GBs [8]. In a type 316 stainless steel, Fujiwara et al. attributed the increase in creep strength from boron to the enhanced precipitation of $M_{23}C_6$ carbides at dislocations [9]. Abe et al. [10] examined the effect of boron on the fine distribution of $M_{23}C_6$ carbides in tempered martensitic 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel containing boron with concentrations of 0, 48, 92 and 139 ppm. He found that boron reduces the Ostwald ripening rate of $M_{23}C_6$ carbides near austenitic GBs at elevated temperatures. With increasing boron concentrations, the time to rupture significantly increased at low stresses during creep tests [10]. Takahashi et al. studied the addition of 120–370 ppm boron to improve the creep strength of 0.2C–10.5Cr-1.5Mo-0.2V-0.2Nb-0.02N steel and found that the $M_{23}C_6$ carbides were enriched with boron with the

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resulting carbides finer than in the steel without boron [11].

Recently, Tarigan et al. [12,13] examined the effect of boron (0.03%) on the creep strength of Fe-20Cr-30Ni-2Nb (at.%). Both the boron-doped and boron-free alloys contained Ni_3Nb precipitates within the grains and Laves phase precipitates at the GBs. The boron addition decreased the creep rate and increased the creep rupture life by almost a factor of four. The role of boron appeared to increase the extent of the Laves phase precipitation at the GBs. However, simply aging the boron-free alloy increased the extent of GB coverage by the Laves phase from 52% to 89% and also both increased the creep rupture life and decreased the creep rate to a similar extent as the boron containing alloy [13]. In other words, the boron addition did not appear to enhance the creep properties compared to a boron-free alloy aged for a longer time.

Chen et al. [14] also studied Fe-20Cr-30Ni-2Nb with and without 0.03% boron and found that boron both increased the number density and produced finer Laves phase precipitates on the GBs. GB segregation of boron in the alloy was observed using an Electron Probe Micro-analyzer (EPMA). This segregation may have promoted precipitation of Laves phase on GBs, and enhanced the creep resistance of the alloy.

The current study investigated the effects of boron and carbon additions on the ageing behavior and mechanical properties of recently-developed, AFA stainless steels, based on Fe-14Cr-32Ni-3Nb-3Al-2Ti. The key difference from the earlier studies containing Laves phase precipitates is the addition of both aluminum and titanium [15].

2. Experimental

Two recently-developed AFA alloys were used in our studies: DAFA26 and DAFA29 which had been hot-rolled at 1100 °C (80% thickness reduction with ~15–20% thickness reduction per pass) and then annealed at 1100°Cfor 30 min in Ar + 4% hydrogen gas, followed by air-cooling [16,17]. Their compositions are listed in Table 1 [16,17]. The difference between these two AFA alloys is the carbon and boron content: DAFA29 has nominally 0.1 wt% of carbon and 0.01 wt% of boron, whereas DAFA26 has neither carbon nor boron. Both of the alloys were subjected to anneal at 800 °C of 2.4 h, 24 h and 240 h.

Tensile test specimens were milled from annealed material to a dog-bone geometry with a gauge length of 10 mm, width of 2.65 mm, thickness of 0.8 mm, and polished to a mirror finish using 800 grit silicon carbide papers followed by 0.3 μm alumina powder. Tensile tests were performed at 700 °C in air using an Instron 5690 tensile testing machine. A preload force of 50 N was applied before the tensile tests. The initial strain rate for all tensile tests was $5 \times 10^{-4}\ s^{-1}$. Elongations were measured directly from the gauge of the specimens after the tensile tests. All the tensile tests were performed three times for each annealing condition.

Table 1
Nominal and analyzed compositions of as-received DAFA26 and DAFA29.

Alloys	DAFA26		DAFA29	
	Nominal	Analyzed	Nominal	Analyzed
Fe	45.55	45.29	45.44	45.34
Cr	14	14	14	13.83
Mn				0.13
Ni	32	32.47	32	32
Cu				0.12
Al	3	2.95	3	3.02
Si	0.15	0.13	0.15	0.15
Nb	3	2.93	3	2.87
V				< 0.01
Ti	2	1.97	2	2
Mo				0.1
W		0.01		< 0.01
Zr	0.3	0.29	0.3	0.32
C		0.002	0.1	0.11
B		< 0.0003	0.01	0.0085
P		< 0.002		< 0.005
N		0.0004		< 0.0001

Specimens were examined using an FEI XL-30 field emission gun (FEG) scanning electron microscope (SEM) equipped with an electron backscatter detector diffraction (EBSD) system and an energy dispersive X-ray spectrometer (EDS). The EDS system utilizes a lithium-drifted silicon, thin-window detector that detects $Z \geq 4$ with acquisition rates up to 10,000 counts per second. The operating voltage was 15 keV and the working distance was 10 mm for imaging and EDS [18].

The twin density of the alloys was measured: the twin density, defined as the number of twin boundary intercepts per unit length, was calculated using [19,20]:

$$Twin\ density = \frac{L_{tb}}{S} \times \frac{2}{\pi} \quad (1)$$

where L_{tb} is the total length of twin boundaries and S is the corresponding surface area of grains.

The coverage of GBs by precipitates was calculated using [13,21].

$$\rho\ (\%) = 100 \times \frac{[(l_1 + l_2 + l_3...) + (n_1 + n_2 + n_3...)]}{L} \quad (2)$$

where ρ is the area fraction of the Laves phase and B2-NiAl precipitates in the grain boundaries, l and n are the lengths of the Laves phase and B2-NiAl precipitates, respectively, and L is the length of the grain boundaries on 2-D sections. Measurements were performed on 10 BSE images of mechanically polished samples with a total grain boundary length of about 1 mm.

A Tecnai F20 FEG transmission electron microscope (TEM) operated at 200 keV was used to examine annealed specimens. Discs of 3 mm diameter were first produced by electro-discharge machining (EDM), and then ground to ~200 μm thick and twin jet electropolished in an electrolyte of 20% nitric acid, 10% butoxyethanol and 70% methanol using a Streurs Tenupol 5 at a voltage of ~11 V with a current of ~200 mA at ~23 °C. After electropolishing, specimens were washed alternatively in ethanol and methanol for three cycles followed by a final rinse in fresh methanol. The resulting thin foils were examined using a conventional double-tilt holder with a capability of tilting 30° along two axes. A CCD camera with 2048 × 2048 pixels was used to record images. Bright field (BF) images were taken under two-beam conditions with the deviation parameter slightly greater than zero [16].

Thin foil specimens were polished from 200 μm thick discs of annealed specimens to a thickness of 20 μm for synchrotron X-ray diffraction (XRD) measurements. The XRD experiments were performed at the Advanced Photon Source (APS) at Argonne National Laboratory, using the X-ray microdiffraction facility at an undulator beamline 2-ID-D [22]. X-ray photons with energy of 18 keV (wavelength = 0.688 nm) were selected using a Si ⟨111⟩ double-crystal monochromator, and then focused using a Fresnel zone plate to a circular spot of ~400 nm diameter. The diffraction signals were collected using a Rayonix Mar165 CCD detector, with 2048 × 2048 pixels and 80 μm pixel size, located ~58 mm downstream of the sample. The total counting time was 55 s. Over this counting period, the sample was continuously rotated around an axis perpendicular to the incident beam by 110° [16].

3. Results

3.1. Microstructures

Fig. 1a and b shows the microstructures of as-received DAFA26 and DAFA29, respectively. The grain size of DAFA26 was measured to be ~30 μm using the linear intercept method while that of DAFA29 was ~40 μm. The white contrast precipitates in DAFA26 are Laves phase [23]. All the Laves phase precipitates in DAFA26 are aligned in the hot rolling direction and have an elongated shape. No other precipitates were observed in DAFA26. The brighter contrast precipitates in DAFA29 are both Laves phase and MC carbides. The MC carbides