Journal of Nuclear Materials 500 (2018) 192–198

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

On α′ precipitate composition in thermally annealed and neutron-irradiated Fe- 9-18Cr alloys

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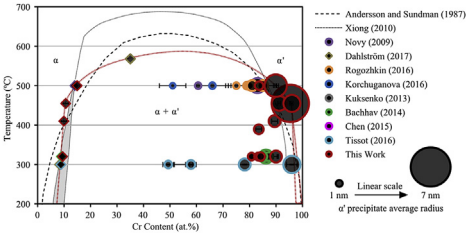
HIGHLIGHTS

- Neutron irradiation accelerates Cr-rich α′ precipitation in Fe-Cr alloys.
- α′ precipitate Cr composition measured by APT depends on precipitate size.
- For small α′ sizes, APT technique artifacts affect composition measurements.
- α′ precipitates reach a thermodynamically stable composition at high temperatures.
- Cascade ballistic mixing likely lowers α′ precipitate compositions at lower temperatures.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 June 2017
Received in revised form
7 December 2017
Accepted 24 December 2017
Available online 28 December 2017

Keywords:
Fe-Cr
Irradiation
α'
Atom probe tomography

ABSTRACT

Ferritic-martensitic steels are leading candidates for many nuclear energy applications. However, formation of nanoscale α′ precipitates during thermal aging at temperatures above 450 °C, or during neutron irradiation at lower temperatures, makes these Fe-Cr steels susceptible to embrittlement. To complement the existing literature, a series of Fe-9 to 18 Cr alloys were neutron-irradiated at temperatures between 320 and 455 °C up to doses of 20 dpa. In addition, post-irradiation annealing treatments at 500 and 600 °C were performed on a neutron-irradiated Fe-18 Cr alloy to validate the α-α′ phase boundary. The microstructures were characterized using atom probe tomography and the results were analyzed in light of the existing literature. Under neutron irradiation and thermal annealing, the measured α′ concentrations ranged from ~81 to 96 at.% Cr, as influenced by temperature, precipitate size, technique artifacts, and, possibly, cascade ballistic mixing.

1. Introduction

Commercial ferritic/martensitic alloys are widely used in the nuclear industry because of their favorable properties that include swelling, creep, and corrosion resistance [1]. However, alloys containing over 9 at.% Cr are subject to the precipitation of the bcc Cr-rich α′ phase [2,3]. Hardening due to α′ precipitation, for example as in so-called "475 °C embrittlement" [4], remains a concern for long-term nuclear applications and has motivated a large number of experimental and theoretical studies. Under thermal aging

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https://doi.org/10.1016/j.jnucmat.2017.12.036
0022-3115/

conditions, Cr diffusion in bcc Fe is extremely slow [5–7] at temperatures below ≈ 400 °C. As a result, most aging studies focused on α-α′ phase decomposition at 500 °C to establish the miscibility gap location and establish the kinetics of spinodal decomposition or precipitation [8–12]. Atom probe tomography (APT) measurements on alloys aged at 500 °C for times ranging from 100 to 1200 h reported high number densities of nanoscale α′ precipitates with compositions increasing from 63 to 87 at.% Cr with longer annealing times [9,13,14]. Mossbauer spectroscopy results from Dubiel and Inden confirmed the trend with a measured α′ composition of 88 at.% Cr after aging at 500 °C for up to 11 years [15].

At lower temperatures (290–400 °C), α′ precipitation under thermal aging is extremely sluggish in steels with less than 20 at.% Cr. However the presence of α′ precipitates has been reported in several commercial and model Fe-Cr model alloys after neutron irradiation using transmission electron microscopy [16–19], small angle neutron scattering [8,20,21], and atom probe tomography [22–28]. In this temperature range, even at low neutron fluxes and displacement per atom (dpa) rates, the increase in point defect concentration results in radiation-enhanced diffusion and accelerated α′ precipitation kinetics [29]. At service relevant dose rates, Cr solubility in α-Fe is not expected to be affected by irradiation [8,20,30], and the equilibrium thermodynamic composition of the α′ phase below 500 °C is >85% Cr [31]. However previous APT analyses yielded a range of average α′ precipitate compositions, from 58.5 at.% Cr after 0.6 dpa [24,32] to 84–86 at.% Cr at a slightly higher dose of 2 dpa [23], while a small-angle neutron scattering (SANS) study on binary Fe-Cr alloys measured α′ precipitate compositions in excess of 80 at.% Cr [20]. In addition to binary alloys, an APT study of Fe-Cr-Al alloys irradiated at 320 °C to 7 dpa reported small ~1.5 nm radius α′ precipitates with measured compositions ranging from 55 to 65 at.% [26]. Approximate corrections, based on excess precipitate atomic density adjustments, only increased the Cr content to ≈60 to 89 at.%. Comparing alloys with different Al content, Briggs et al. proposed that Al may have an effect on lowering the Cr content of α' [26]. While this may be the case, irradiations to different doses also showed that both the Cr composition and size of α′ precipitates increased with increasing dose.

The discrepancy between APT and SANS measurements, and between expected and measured composition, has been attributed to resolution limits of the APT technique. The lower evaporation field of Cr compared to that of Fe [33] generally results in the α′ phase evaporating at a higher rate than the Fe-rich matrix. This difference in evaporation rates translates into a local change in the surface curvature that can lead to overlapping trajectories of ions coming from the α′ precipitate and the neighboring Fe-rich matrix [34]. This trajectory aberration effect has been observed in a number of systems, including in Fe-Cu alloys forming nanoscale Cu precipitates [35]. It can be expected that the α′ concentration should be somewhat underestimated in APT studies, as also discussed in Ref. [20], and this effect would be exacerbated at small sizes (radius ~1 nm).

Most existing APT data on α′ precipitation in binary Fe-Cr alloys under neutron irradiation is limited to relatively low fluence (0.6 dpa [32], 1 dpa [24] and 2 dpa [23]) where the small α′ precipitate sizes maybe prone to APT measurement artifacts. Anderoglu et al. [28] reported a neutron irradiation experiment for a 12 wt% Cr commercial HT9 alloy, reaching a maximum 155 dpa at 440 °C, that produced α′ precipitates with radius ≈ 4.8 nm, however the compositions of α′ were not reported.

To further clarify the discrepancies in reported α′ precipitate composition and understand the development of α′ under neutron irradiation, binary Fe-Cr alloys containing between 9 and 18 at.% Cr were irradiated for a range of doses (up to 17 dpa) at a range of temperatures (up to 455 °C). A Fe-18Cr alloy was also irradiated to 1.8 dpa at 320 °C, followed by long time annealing treatments at 500 and 600 °C. The resulting microstructures were analyzed using APT, providing further insights into potential compositional limitations as well as additional data on the α/α′ phase diagram.

2. Experimental

A series of model Fe-9, 12, 15, 18 at.% Cr alloys were irradiated at 320 °C and 455 °C to a dose of 7 dpa and a dpa rate of $\approx 3.5 \times 10^{-7}$ dpa/s in the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL). These alloys, hereafter referred to as Fe-9-18Cr-ATR, were originally studied as part of the fast breeder reactor program by Gelles et al. [36]. The cold rolled sheet materials were annealed at 950 °C under an argon atmosphere for 15 min followed by air-cooling. Then the alloys were stress relieved at 750 °C for 60 min, followed by air cooling. Post-irradiation annealing was performed on the Fe-18Cr alloy-ATR, irradiated to 1.8 dpa at 320 °C and previously analyzed by Bachhav et al. [23]. After irradiation, the Fe-18Cr-ATR samples were annealed for 300 and 7200 h at 500 °C or 300 h at 600 °C in an argon environment. In addition, two additional model Fe-9 and 12 at.% Cr alloys, hereafter referred to as Fe-9-12Cr-BOR, were irradiated at 390 °C and 410 °C to 17 dpa at a dpa rate of 7×10^{-7} dpa/s in the BOR-60 reactor. Prior to irradiation, these two alloys had been heat treated at 1000 °C in an inert argon atmosphere, hot rolled at 870 °C, then austenized at 1050 °C for 60 min, air cooled, and tempered at 760 °C for 60 min. The average solute composition of these alloys as measured by APT is listed in Table 1, with Fe as the balance.

APT specimens were prepared by following standard lift-out and milling procedures using a FEI Quanta 3D FEG scanning electron microscope (SEM) and focused ion beam (FIB) instrument. Final atom probe milling was performed using a FEI Helios 650 SEM/FIB. Data collection was performed using a Cameca LEAP 4000XHR instrument operated in voltage pulsing mode with a pulse fraction of 20%, a pulse repetition rate of 200 kHz, and data collection rate of 5 atoms per 1000 pulses. The samples were cooled to a base temperature of 50 K. Data analysis was completed with the CAMECA Integrated Visualization & Analysis Software (IVAS) version 3.6.10. The datasets were reconstructed by adjusting the image compression factor and k-value to reach the accurate d-spacing in visible low index planes. The reconstructions were also confirmed to have a constant matrix atomic density throughout the depth and across the diameter of the sample [37]. The image compression factor ranged between 1.2 and 1.5 and the k-value between 3.1 and 4.9.

The composition of α′ precipitates was measured using proximity histograms, or proxigrams [38], based on iso-concentration surfaces at 40% Cr. The Cr concentration measurements included deconvolution of the Fe and Cr isotope overlaps using natural isotopic abundances. Phase compositions were calculated by averaging portions of the proxigrams where the solute concentrations were uniform. However, in the case of very small precipitates, the

Table 1
Alloy compositions (in at.%) measured by APT after neutron irradiation or after post-irradiation annealing. A background subtraction was applied and overlapping peak of Fe and Cr were deconvoluted using isotopic natural abundances.

Alloy	Cr	Si	Mn	V	N	C	P	Count ($x10^6$)
Fe-9Cr-ATR	9.5	0.05	0.03	0.04	<0.01	<0.01	<0.01	14.7
Fe-12 Cr-ATR	11.3	0.05	0.03	0.02	<0.01	<0.01	0.01	19.5
Fe-15 Cr-ATR	15.6	0.06	0.03	0.03	<0.01	<0.01	<0.01	26.4
Fe-18 Cr-ATR	18.9	0.06	0.02	0.03	<0.01	0.02	<0.01	49.0
Fe-9 Cr-BOR	9.7	<0.01	<0.01	<0.01	0.10	0.05	<0.01	6.7
Fe-12 Cr-BOR	11.6	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	11.2