# Grain boundary diffusion of Fe in ultrafine-grained nanocluster-strengthened ferritic steel

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## Abstract

Grain boundary diffusion of Fe in nanocluster-strengthened ferritic steel (Fe–14Cr–3W–0.4Ti–0.25Y$_2$O$_3$ in wt.%) has been investigated. The steel was produced by mechanical alloying followed by hot extrusion. The final grain size was ∼200 nm. The diffusivity of Fe was measured within the temperature range 423–820 K. The grain boundary penetration at lower temperatures revealed a specific time dependence, which indicates a residual interconnected porosity in the ferritic steel. In order to quantify the percolating porosity, conventional radiotracer ($^{59}$Fe) diffusion measurements were combined with a study of room temperature penetration of liquid $^{110m}$Ag solution to distinguish between solid-state diffusion along boundaries and penetration along the surface of interconnected cavities. The presence of porosity affected the diffusion process, introducing a hierarchy of internal interfaces. The grain boundary diffusion coefficient and the diffusivity along internal surfaces were determined in the so-called type C–C, C–B and B–B kinetic regimes of interface diffusion in a hierarchical microstructure. Using the residual activity method and a $^{65}$Zn tracer, the volume fraction of the percolating porosity was estimated to be 0.6%.

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## 1. Introduction

Ultrafine-grained metals and alloys with grain size in the submicron range exhibit many attractive properties, such as high strength, hardness [1], superplastic behavior at relatively low temperatures and high strain rates [2]. Recently developed nanocluster-strengthened ferritic steels with ultrafine grain sizes are of interest because of their excellent creep strength [3–6]. In addition, such steels are considered as candidate structural materials for fission and fusion power plants, because they exhibit good resistance to irradiation-induced swelling [7–10].

The current study is based on the nanocluster-strengthened 14YWT alloys (where 14 stands for the Cr concentration in weight per cent, and YWT stands for alloying with Y, W and Ti). The alloy was produced at Oak Ridge National Laboratory, Oak Ridge, TN, USA, by mechanical alloying followed by hot extrusion. It displays remarkable creep resistance when compared with conventional oxide dispersion strengthened steels [3]. In the 14YWT alloy, tungsten causes solid solution hardening, whereas Y and Ti form complex mixed oxides and give rise to particle strengthening. Kim et al. [11] showed that the oxide particles in alloys containing only Y and W, but no Ti, are relatively large (∼30 nm), and that additions of Ti are crucial for obtaining ultrafine 2–4-nm-diameter oxide particles, also called nanoclusters [4]. These clusters have been proposed as the reason for the outstanding creep resistance of 14YWT alloy [3,4,12,13]. Because of the nanoclusters, the grains in 14YWT are usually ultrafine, with sizes as small as ∼200 nm [4,6]. Surprisingly, the fine grain size does not result in easy superplastic deformation or diffusional creep at elevated temperatures [6]. Creep rates at

1073 K are up to a factor of $10^8$ times slower than those predicted for diffusional creep by volume diffusion (Nabarro–Herring creep) or grain boundary (GB) diffusion (Coble creep). If the corresponding values of Fe self-diffusion in α-Fe are used, this raises the question of whether diffusion in 14YWT might be significantly affected by alloying and/or nanocluster formation. This paper aims to investigate the GB diffusion in 14YWT steel. The GB diffusion is measured using the classical radiotracer technique with ^{59}Fe and [110m]Ag isotopes.

## 2. Experimental details

The 14YWT alloy with nominal composition Fe–14Cr–3W–0.4Ti–0.25$Y_2O_3$ (wt.%) was prepared by mechanical alloying of a mixture of pre-alloyed metallic and $Y_2O_3$ powders in a static argon environment, followed by hot extrusion [4,5]. Subsequently, disk-shaped specimens with diameter ∼14 mm and thickness ∼2 mm were annealed at 1273 K for 1 h in air, followed by polishing of their faces.

Commercial ^{59}Fe tracer was supplied by NEN Company in the form of iron chloride dissolved in 0.5 mol HCl. The original solution was highly diluted in double-distilled water. The [110m]Ag tracer was produced from the natural isotope [109]Ag by neutron irradiation at the research reactor in Geesthacht (Germany). The irradiated Ag chip was transferred to the radiotracer laboratory, Münster, and dissolved in nitric acid and diluted double-distilled water. The [65]Zn and [63]Ni isotopes used in several experiments were purchased from PerkinElmer and Dupon NEN, respectively.

Two methods were used to deposit the ^{59}Fe tracer on the sample disk: (i) ^{59}Fe tracer solution was dropped on the well-polished sample disk as a liquid solution; (ii) ^{59}Fe tracer was deposited in the form of a solution on a "dummy sample" 14YWT disk. Later, when the tracer solution became dry on the dummy disk, it was placed face to face on a fresh, well-polished disk of the same material, so that the tracer was sandwiched between the fresh and dummy disks. After deposition (in both methods), the samples were wrapped in Ta foil and encapsulated under purified Ar atmosphere in silica tubes for diffusion annealing.

Diffusion annealing was done in a resistance furnace. The temperature was measured and controlled to an accuracy of ±1 K with calibrated NiCr/Ni thermocouples. After diffusion annealing, the samples were reduced in diameter to eliminate radial diffusion effects from the sample surface.

Parallel mechanical sectioning by grinding was used in order to assess the diffusion profile of the tracer. The thickness was accurately measured by weighing the sample before and after grinding. Immediately before sectioning, the [110m]Ag tracer was additionally deposited at room temperature as a liquid solution to check the presence of interconnecting porosity in the 14YWT alloy. The activities of the ^{59}Fe and [110m]Ag tracers in the sections were measured by a well-type intrinsic Ge detector equipped with an 8 K analyzer recording the γ peaks at 1099 keV and 657 keV, respectively.

## 3. Results and discussion

Bulk diffusion data are required for analyzing GB diffusion. Since proper measurements of bulk diffusion in 14YWT alloys are absent and owing to limitations in the amount of material available, data on volume self-diffusion in pure α-Fe were used. The diffusion of Cr in α-Fe is faster by a factor of 10 than the Fe self-diffusion in the range 1083–1183 K [14], so an enhancement of the Fe diffusion in 14YWT alloy may be expected with respect to that in pure α-Fe. Simple estimates according to Le Claire's theory [15] of the solute enhancement factor for body-centered cubic alloys predict an increase in the Fe diffusivity by a factor of two to three. Since only a square root of this value enters the corresponding expressions for the determination of GB diffusivity $D_{gb}$, the uncertainty in the $D_v$ value may introduce a 50% error in the derived $D_{gb}$ values. This uncertainty is accepted in the present study. Moreover, the exact $D_v$ values are not important for the measurements performed at low and moderate temperatures, where only a rough estimate of the applicability of the C kinetics according to Harrison's classification [16] (see below) was required. In the current study, the bulk diffusion data are taken from the study of Lübbehusen and Mehrer [17]:

$$D_v = 2.17 \times 10^{-2} \times \exp\left\{\frac{-303 \text{ kJ/mol}}{RT}\right\} \text{m}^2 \text{ s}^{-1} \quad (1)$$

The present measurements were predominantly designed for Harrison's C-type kinetic regime [16] of GB diffusion in a polycrystalline sample. In this case, the tracer atoms diffuse along the grain boundaries and do not penetrate into the grain interiors. In the present case of self-diffusion, these conditions correspond to

$$\alpha = \frac{\delta}{2\sqrt{D_v t}} \gg 1 \quad (2)$$

Here δ is the GB width, and $t$ the diffusion time. In recent computer simulations, the C regime was identified at $\alpha > 5$ [18]. In practice, $\alpha > 1$ may be considered sufficient, taking experimental uncertainties into account. The concentration profile in the C regime is either a Gaussian function (instantaneous source) or an error function (constant source) with the diffusion coefficient $D_{gb}$.

The experiments in the intended C-type regime were performed in the temperature range 373–623 K. In these experiments, ^{59}Fe tracer was dropped as a liquid solution onto the fresh surface of a sample disk, as explained in the experimental details and, after diffusion annealing of the sample disk, the [110m]Ag tracer was additionally deposited at room temperature as a liquid. The penetration profiles of the ^{59}Fe and [110m]Ag tracer at 323 K and 423 K are shown in Fig. 1. The concentration profiles were measured until the background with respect to the ^{59}Fe signal was reliably reached. These profiles show that [110m]Ag is penetrating deep into the material already at room temperature; also the penetration profiles of ^{59}Fe and [110m]Ag are almost parallel to each other. Furthermore, the diffusion profiles