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# Atom probe study of radiation induced grain boundary segregation/depletion in a Fe-12%Cr alloy

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ABSTRACT

Ferritic steels are important candidate structural materials for future fission and fusion reactors. However, the effect of radiation induced segregation/depletion (RIS/RID) of Cr in grain boundaries and its effect on microstructures and properties are still not clear. Therefore, a systematic approach is shown in this paper, combining electron backscattered diffraction, focused ion beam specimen preparation and atom probe tomography for analysing a single grain boundary in a Fe-12wt%Cr from the point of grain boundary orientation, microchemistry and impurities. Several samples have been prepared from the same grain boundary and consistent 3D reconstruction with quantitative calculation of segregation demonstrates the high reliability and repeatability of this approach.



## 1. Introduction

Ferritic steels are receiving increasing interest as structural materials for future nuclear fission and fusion reactors due to their advantages over traditional austenitic steels, including low swelling rates, better thermal fatigue resistance and lower thermal expansion coefficients (Takahashi et al., 1982; Ohnuki et al., 1982). Point defects can be introduced in the alloys by ion or neutron irradiation. If not recombined, these point defects will diffuse to sinks such as grain boundaries. The interaction between point defect fluxes and solute atoms will cause coupled transport of solute atoms, giving rise to the non-equilibrium solute concentration gradients near the grain boundaries. This mechanism does not occur during thermal aging at similar temperatures. This phenomenon is recognized as radiation induced segregation (RIS) or depletion (RID) which can strongly affect grain boundary chemistry and furthermore mechanical properties. In particular, RIS/RID has raised significant interest because of its role in irradiation assisted stress corrosion cracking (IASCC) and corrosion of structural materials (Busby et al., 2002; Faulkner, 1997; Was and Bruemmer, 1994).

Okamoto et al. (Okamoto and Rehn, 1979) summarised theoretical models which link solute segregation in irradiated alloys to the formation of mobile solute–defect complexes and/or inverse Kirkendall effects resulting from differences in the diffusion rates of free solvent and solute atoms when migrating via an interstitial or vacancy mechanism. The authors also suggested that undersized solute atoms were built-up near point defect sinks while oversized solutes tend to be depleted from sinks by vacancy migration. Such composition changes could likely influence a number of properties such as ductility and may enhance stress corrosion cracking (Okamoto and Wiedersi, 1974). Many studies (Allen et al., 1998; Nakata and Masaoka, 1987; Sakaguchi et al., 2005) focused on RIS/RID have reported the depletion of Cr from grain boundaries in austenitic steels. However, both segregation and depletion of Cr in grain boundaries have been reported in ferritic steels with no clear dependency on irradiation condition or alloy type, and the mechanistic understanding is far from complete. Lu et al. suggested that whether Cr should be considered as an undersized, or oversized, atom depends on alloy chemistry and pre-existing precipitation. This may provide a possible explanation for the discrepancies among the data in the literature (Lu et al., 2008).

RIS/RID at grain boundaries have been previously studied by Auger Electron Spectroscopy (AES) and more recently by using a Scanning Transmission Electron Microscope coupled with an Energy Dispersive X-ray Spectrum (EDS) capability (STEM/EDS). (Was and Bruemmer, 1994) STEM/EDS involves collecting spectra at discrete points across the grain boundary which are used to build a 1D composition profile normal to the boundary plane. This technique provides information on the chemistry of the grain boundary and the width of segregation or depletion. The most accurate results can be obtained if a field emission gun is used to provide enough intensity in small electron probes (<1 nm), the

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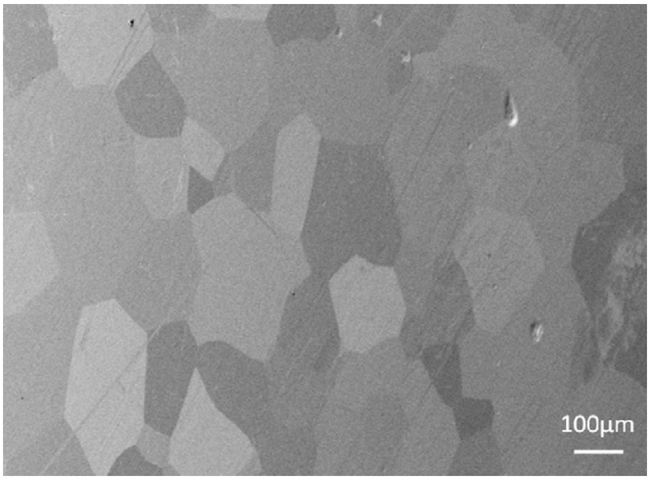


**Fig. 1.** Optical microstructure of Fe-12wt%Cr alloy.

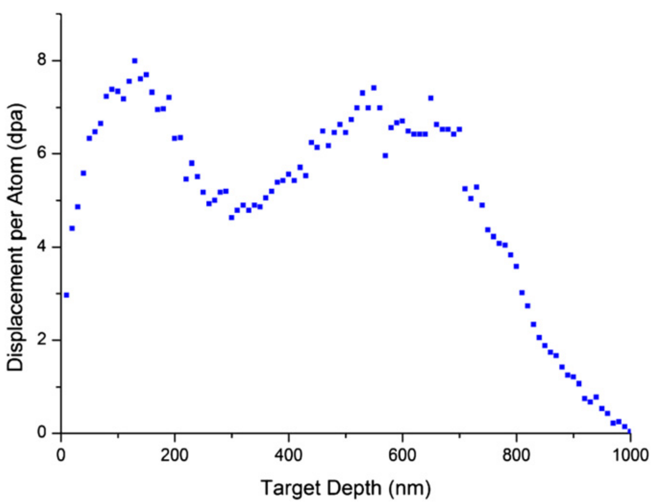


**Fig. 2.** SRIM calculation shows displacement damage as function of depth.

sample is thin and the grain boundary is positioned to be parallel to the beam. However, high angle scattering of the electrons occurs in the specimen and this will broaden the effective probe and complicate deconvolution of the real concentration profile. Furthermore, low-atomic-number elements such as B and C which cannot be easily detected by EDS, could form complexes with elements such as Cr and consequently affect segregation or depletion (Titchmarsh and Dumbill, 1996). Multivariate statistical analysis and other methods that take into consideration beam broadening have been applied during data processing to optimise the accuracy of quantitative measurements (Titchmarsh, 1999). However, most publications on RIS/RID do not study all the contributing factors which could explain the Cr variation at grain boundary after irradiation, such as chemistry before irradiation, grain boundary orientation, existence of impurities and precipitates. Kano et al. (1998) studied the effect of different concentrations of C on the radiation induced depletion of Cr in SUS 304 and SUS316L stainless steels and found that C can suppress the Cr depletion. But the distribution of C at grain boundaries was not discussed possibly due to the difficulty of detecting C using TEM-EDX because of the build up of C on the sample in the TEM column. Another report is provided by Ohnuki et al. (1982) who observed Cr segregation after irradiation in Fe-13%Cr. However the authors applied $C^+$ ion irradiation and introduced large amount of excess C, and also explained that the segregation phenomenon could be caused by the interaction of Cr-C complexes with vacancy flow and migration towards sinks.

In order to develop understanding of the mechanism of irradiation behaviour of Cr in the grain boundaries in ferritic steels, a systematic approach (Marquis et al., 2011) has been developed combining Electron Backscatter Diffraction (EBSD), Focused Ion Beam (FIB) (Miller et al., 2007) specimen preparation and Atom Probe Tomography (APT) (Miller et al., 1996) analysis. To avoid variations between different grain boundaries and demonstrate repeatability of this systematic approach, several results need to be obtained from the same grain boundary and this method has not been reported before. Therefore, in this paper, we present APT analysis of Cr concentration profiles on a chosen grain boundary in a Fe-12Cr alloy after irradiation as well as examining C effects.

## 2. Experimental

The material selected for the research is a ferritic Fe-12wt%Cr (12.8at%Cr) alloy of high purity. A thin square-shaped sample ($10 \times 5$ mm with 2 mm in thickness) was cut using a slow speed diamond saw and then pre-annealed at 800 °C for 1 h in vacuum followed by water quench. The annealing resulted in the recrystallisation of the grain structure and produced large grains ($\sim$100 μm across) with long straight grain boundaries as shown in Fig. 1.

The sample was polished by sand paper 600grit, 800grit 2500grit and 4000grit, diamond suspension and finished by electro-polishing for 15 s in a solution of 5% perchloric acid in

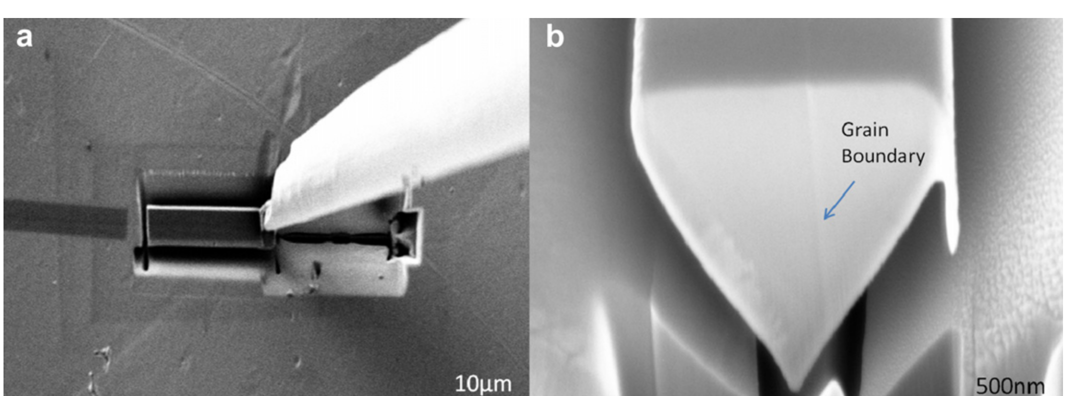


**Fig. 3.** (a) A beam lift-out by built-in-micro-manipulator from the selected grain boundary, (b) the same beam containing the grain boundary.