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Defining clusters in APT reconstructions of ODS steels

Ceri A. Williams [a,*], Daniel Haley [a,b], Emmanuelle A. Marquis [c], George D.W. Smith [a], Michael P. Moody [a]

[a] Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK
[b] Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, D-40237 Düsseldorf, Germany
[c] Department of Materials Science and Engineering, University of Michigan, 2300 Hayward Street, Ann Arbor, MI 48109-2136, USA

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ABSTRACT

Oxide nanoclusters in a consolidated Fe–14Cr–2W–0.3Ti–0.3Y_2O_3 ODS steel and in the alloy powder after mechanical alloying (but before consolidation) are investigated by atom probe tomography (APT). The maximum separation method is a standard method to define and characterise clusters from within APT data, but this work shows that the extent of clustering between the two materials is sufficiently different that the nanoclusters in the mechanically alloyed powder and in the consolidated material cannot be compared directly using the same cluster selection parameters. As the cluster selection parameters influence the size and composition of the clusters significantly, a procedure to optimise the input parameters for the maximum separation method is proposed by sweeping the d_{max} and N_{min} parameter space. By applying this method of cluster parameter selection combined with a 'matrix correction' to account for trajectory aberrations, differences in the oxide nanoclusters can then be reliably quantified.

1. Introduction

Understanding the path to formation of stable oxide nanoclusters in oxide dispersion strengthened (ODS) steels is necessary n order to produce material with a high density of second phase particles that provide high temperature strength and creep resistance. These particles also provide a means of trapping radiation-induced helium and point defects [1]. As such, these materials are suitable candidates for use in fusion reactors and the next generation of nuclear reactors [2].

Quantification of cluster size and composition at various stages during the processing of an ODS alloy gives insight into the cluster formation process, but the clusters can be smaller than 1 nm which makes characterisation difficult. The three-dimensional chemical and spatial information provided by atom probe tomography (APT) makes it an invaluable tool to investigate the oxide nanoclusters; however there are differences in the published literature on how to interpret the results.

1.1. Defining clusters in APT data

Extracting quantifiable differences in clustering from APT data is non-trivial, and there is a wide variety of methods available [3–5]. These range from the analysis of composition frequency distributions [6–8], proximity histograms [9], radial distributions [10] or statistical nearest neighbour analysis [11] to the application of Delaunay tessellations [12].

Numerous approaches to cluster identification algorithms have been developed to define and characterise clustering in reconstructions of dilute alloy systems [13–17]. One of the most widely used techniques for cluster identification in APT is the maximum separation method [13].

In the maximum separation method, a distance d_{max} is chosen and a pair of solute atoms separated by less than this distance is deemed to be clustered. If the clustered solute atoms have neighbours that are also recursively clustered by the above definition, those solute atoms are defined as a single cluster. This method relies on the assumption that there is a bimodal separation in the distribution of nearest neighbour distances such that upon examination of their separations one can neatly discriminate between pairs of clustered and unclustered solutes. In reality this is not the case. Further, even in a random solid solution, some solute atoms are expected within the distance d_{max} of each other. However, the probability of observation decreases rapidly with increasing cluster size in the random case. A cut-off limit for the minimum size of a cluster N_{min} is therefore defined. This cut-off reduces apparent clustering that is solely due to solute couplings within the random distribution.

Various extensions to the maximum separation method have been developed to associate other atoms not defined as 'solute atoms', and a recent review describes several such extensions [5]. For the purpose of this study only the 'double maximum separation and erosion'

* Corresponding author.
E-mail address: ceri.williams@materials.ox.ac.uk (C.A. Williams).

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method developed by Vaumousse et al. will be considered in detail [14], but other methods may be equally valid and the methods to select appropriate cluster selection parameters described in this work could be readily adapted and applied to other situations. Vaumousse et al. proposed that a second maximum distance referred to as the surrounds distance d_{sur} should also be defined such that once the clusters have been defined any atom within this distance of a clustered solute atom will be incorporated in the cluster [14]. This method will lead to the inclusion of a shell of matrix atoms that lie less than the distance d_{sur} from the cluster interface. Hence an 'erosion' process is subsequently implemented to remove these matrix atoms based upon their distance away from their nearest solute atom (d_{er}).

The characteristics of the clusters identified using this method are known to be strongly dependent upon the algorithm's input parameters [18]. It is therefore critical that there is a logical justification for the choice of input parameters. However, this is not straightforward and numerous methods have been proposed to optimise parameter selection, in particular the choice of d_{max}. For example, a method developed by Cerezo and Davin derived a theoretical approach to predicting the cluster–size frequency distribution in a corresponding random solid solution. The value of d_{max} is then selected such that it reproduces this theoretical cluster distribution in a mass-randomised atom probe dataset [19]. (Mass randomisation involves randomly swapping the mass-to-charge-ratio values between atoms in the dataset but retaining their original spatial coordinates. It provides an effective means of removing spatial–chemical correlations from the dataset.) Kolli and Seidman proposed a method whereby the total number of clusters is plotted as a function of d_{max} [16]. A local minimum on this graph indicates a compromise whereby the selected d_{max} is large enough to not break up large clusters into smaller disparate clusters; however it is small enough not to erroneously link solutes in the matrix.

Stephenson et al. provide an alternative, rigorous but computationally intensive method of d_{max} selection. They developed a model of complete spatial randomness to estimate the local density of solutes in a cluster, and then derived a formula relating this to a suitable value of d_{max} [15]. Based on the work of Stephenson et al., Marceau et al. adopt a more heuristic approach to d_{max} selection by interrogating the nearest neighbour distances of the solute atoms. The frequency histograms of 5th order nearest neighbour distances are compared to the same distribution generated from mass-randomised datasets to provide an appropriate value of d_{max} [20]. In this case, large solute rich precipitates co-exist with smaller clusters in the APT dataset and therefore the 'correctness' of the d_{max} value is inferred from the accurate selection of the larger precipitates. Alternatively, Ceguerra et al. proposed that d_{max} should be based simply upon the crystallography of the system, in particular the first crystallographic shell nearest-neighbour distance [21].

Hyde et al. investigated the sensitivity of the maximum separation method to the detection of clusters in APT data. They showed that the defined clusters obtained using various values of d_{max} and N_{min} are co-related, and that the value of N_{min} chosen may require amendment if d_{max} is changed to adequately characterise the clusters [18]. Their research suggested that when there are slight changes in cluster composition, or indeed differences in data acquisition conditions (with or without reflectron optics for example), different cluster selection parameters become optimal because the distribution of nearest neighbour distances of the solute atoms may change. In previous studies on clustering found in the literature that employ the double maximum separation and erosion method to define clusters, values for d_{max}, N_{min} and d_{sur}/d_{er} were chosen, but then kept constant when applied across multiple datasets even though the clusters were evolving, and the microstructure was changing.

1.2. Oxide particles in APT data

In addition to the difficulties faced in identifying clusters within APT data, when examining materials such as ODS, complications with the APT data interpretation can also arise due to the differences in the evaporation fields of the matrix and the particles [22]. This has been further demonstrated by field ion microscopy, where it has been shown that atoms from the oxide particles evaporate in preference to matrix atoms [23]. This difference in evaporation fields results in significant local magnification effects [4], and is evident by the distribution of density of hits on the detector, which can be up to three times greater than in regions away from the particles [24]. This leads to the conclusion that a substantial proportion of the atoms detected in the cluster regions are likely due to the trajectory aberrations. Previous studies on oxide particles in ODS steels indicate that the exact quantities of Fe and Cr in the nanoparticles cannot be readily quantified, as it is not possible to distinguish between which Fe or Cr atoms originated from the matrix and which came from the particles [24–26].

Analogous to methods used to account for signal coming from the matrix in EDX analysis [27], and similar to APT data analysis methods for the analysis of carbides in steels [28–31], we have previously proposed a 'matrix correction' to mitigate the influence of the matrix on the measured composition [24–26], which is otherwise not available as a post-processing option in commonly used APT clustering software. The number of Fe ions in the cluster is artificially set to zero, and the proportion of matrix atoms (Cr, W, etc.) expected due to the matrix contribution based on the number of Fe ions are also removed. Oxide particles >10 nm detected at grain boundaries were found to have no Fe at the core, implying that these particles were completely free of Fe. Hence, the Fe level in the clusters was artificially set to zero and, in turn, the number of Fe atoms erroneously detected in the clusters used to estimate the expected quantity of other matrix elements (Cr, W, etc.) introduced by trajectory aberrations. At present, it is unclear how the way the clusters are defined influences the measured composition after the 'matrix correction'. Part of this current work is to address this issue. As the trajectory aberrations will also influence the measured size of a cluster [32], particularly if the cluster size is reported in terms of its radius of gyration or Guinier radius, this required further investigation.

In the earliest stage of oxide nanoparticle formation in ODS steel processing (i.e. in the powder after mechanical alloying), the extent of clustering is very different from that of the consolidated materials. In this study we demonstrate that the cluster selection parameters used to define the clusters in the consolidated material do not adequately define the clusters in the powder and vice versa.

Drawing on the merits of the methods described above to select values of d_{max}, a quick and simple method of selecting the appropriate cluster selection parameters is proposed. The method relies upon the use of mathematical optimisation to construct an objective function which is derived from iterative examination of the outputs of the cluster selection algorithm over a wide range of cluster selection parameters. This method can be readily applied to each dataset using the same objective function, such that parameter selection can be conducted in a consistent manner, hence permitting clustering at different stages of alloy processing to be compared. The impact that changing the cluster selection parameters has on the size and composition of the nanoclusters is then addressed to verify the validity of this approach.

2. Experimental details

The ODS alloy analysed in this study was manufactured by Baluc et al. (Ecole Polytechnique Federale de Lausanne, Switzerland) in a