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Information depth in backscattered electron microscopy of nanoparticles within a solid matrix

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ABSTRACT

Measuring the dimensions and number density of nanoparticles dispersed in a solid matrix is usually accomplished via transmission electron microscopy (TEM) which suffers from high cost, low throughput, and small analytical volume. In comparison, scanning backscattered electron microscopy is inexpensive, requires little sample preparation, and allows for the analysis of large sample areas. However, the information depth is usually not known precisely and depends on several factors such as the composition of the nanoparticles and the matrix as well as the size of the nanoparticles, hindering the reconstruction of the actual size distribution and three-dimensional number density. Here we present a method to estimate the information depth for spherical nanoparticles of different sizes in order to accurately determine size distribution and number density. The approach is based on Monte Carlo simulation of electron trajectories in the material and analysis of the obtained backscattered electron signal-to-noise-ratio. Our experimental results are compared to those obtained via TEM and good agreement is demonstrated; this shows that TEM can be replaced by scanning electron microscopy for studying nanocomposites in many cases.

1. Introduction

The determination of the size distribution and number density of nanoparticles dispersed in a solid matrix is a challenge in many different fields of research. Examples include Au nanoparticles in cells [1,2], soil ecotoxicity studies [3], and sol-gel processing [4,5].

In metals, the size and density of nanoscale second phase particles can have a dramatic influence on recrystallization behavior [6], resistance to deformation [7,8] and fracture [9]. The ability to quantify such nanoparticles is therefore crucial for the development of reliable mechanistic models for predicting materials' mechanical properties.

An example of such nanoscale second phase particles are α-$Al_{12}(Fe,Mn)_3Si$-dispersoids in Al-Mg-Si wrought alloys (6xxx series Al alloys) [8,10,11]. These dispersoids form during the homogenization heat treatment which, in industrial practice, is usually performed after casting of the billets. Since 6xxx series Al alloys are the most commercially important class of Al wrought alloys, the characterization of the dispersoids is of great interest to the industry. Furthermore, other important types of Al wrought alloys such as the 5xxx and 7xxx series exhibit similar dispersoids.

The standard method for counting and measuring the dimensions of dispersoids is transmission electron microscopy (TEM) combined with a method providing the thickness of the foil, usually electron energy loss spectroscopy (EELS). Since particles cut at the surface can appear with reduced dimensions in the micrographs, the acquired dimensions can be corrected with the help of statistical methods [12]. However, the analytical volume in TEM is very small, yet the number density of dispersoids can vary significantly over the sample [10,13,14]. Therefore, a sufficiently high number of micrographs has to be analyzed to acquire representative data. Additionally, such analyses require sensitive instrumentation such as EELS and time-consuming sample preparation, thus limiting throughput.

The investigation of nanoparticles in solid matrices can also be done using a focused ion beam (FIB) coupled with secondary electron (SE) imaging [2,15], or even high resolution X-ray imaging methods [16]. Although these methods can provide real three-dimensional information in high resolution, they suffer from similar constraints as TEM, especially with regard to experimental effort and instrumentation.

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The use of backscattered electron (BSE) micrographs acquired by scanning electron microscopy (SEM) is a promising approach for the quantification of dispersoids and similar nanoparticles as it can overcome the aforementioned limitations, greatly reduce the experimental effort, and allow for the survey of large sample areas [14]. However, in order to obtain the three-dimensional number density and a correct size distribution of dispersoids from two-dimensional BSE images, the escape volume of BSE, which is a function of the accelerating voltage of the beam, has to be taken into account. Under ideal conditions, all dispersoids located in this escape volume or extending into it could be detected. In practice, the signal strength decreases for smaller dimensions of dispersoids and increasing distance from the surface (i.e., depth z). When the signal-to-noise-ratio (SNR) falls below a certain threshold, the dispersoids cannot be detected any more. Since smaller dispersoids yield a weaker increase in BSE signal than larger dispersoids, the maximum depth for which they can still be reliably detected (z_{info}) is also smaller. Therefore, when dispersoids are counted and measured on a BSE micrograph, the size distribution will be skewed towards large particles. Furthermore, it is not easily possible to convert the areal number density to a volume number density because z_{info} is unknown and, as mentioned, it is a function of particle size.

Although the use of SE for imaging would greatly reduce the interaction volume, SE provide topographical contrast and less compositional contrast. It is therefore difficult to distinguish between nanoparticles and surface features or contaminations, while the use of BSE imaging allows for distinguishing structures with different composition within the sample, practically irrespective of the surface topography.

Here we present Monte Carlo (MC) simulations of the interactions of electron beams with nanoscale dispersoids in an Al matrix for different electron beam energies. Based on the results of the simulations, a function for z_{info} in BSE imaging was derived. For experimental validation, dispersoids were counted and measured on BSE micrographs and the volume number densities for different size ranges of dispersoids were calculated. The results are compared to size distributions acquired by TEM and good agreement is demonstrated. The method can be readily adapted to other nanoparticle matrix systems.

2. Experimental and Methodology

2.1. Materials and Experimental Procedures

Plate material of aluminium alloy (AA) 6082 with a thickness of 10 mm was used. The alloy composition as determined by optical emission spectrometry is Al – 1.10% Mg – 1.02% Si – 0.48% Mn – 0.44% Fe – 0.17% Cr – 0.09% Cu – 0.09% Zn – 0.01% Ni – 0.01% Ti. The material was solution heat treated at 570 °C for 1 h followed by water quenching. Cross sections for SEM analysis were mechanically polished using standard metallographic procedures.

SEM analysis was carried out on a Zeiss Ultra Plus 55 field emission SEM equipped with an angular selective backscattered (AsB) electron detector. The working distance was 2.6 mm, the aperture was set to 60 µm and the accelerating voltage was 20 kV. Images were recorded in a resolution of 1024 by 768 pixels at a scan rate of 9 which corresponds to a frame time of 20.2 s.

Transmission electron microscopy (TEM) thin foils were prepared by ion-milling in a precision ion polishing system (PIPS) at 4.5 V for about 10 h. TEM investigations were carried out on an FEI Tecnai F20, equipped with an extreme field emission gun (X-FEG) operated at 200 kV. More than 600 dispersoids were manually counted and measured in five TEM bright field micrographs; the thickness of the foil in the respective micrographs was measured using EELS. The number density N of dispersoids was calculated as follows: $N = n_{obs}/[A(t + 2\bar{r}_{obs})]$ where n_{obs} is the number of observed dispersoids, A is the area, t is the thickness of the foil, and $\bar{r}_{obs}$ is the mean radius of the observed dispersoids which was added to the foil thickness to account for dispersoids that were visible but whose centers lay outside of the foil. An example micrograph is given in a previous study [17] where the size distribution data was also used.

2.2. Methodology of Monte Carlo Simulations

Monte Carlo simulations were carried out using the Casino v3.2 software which describes electron trajectories by discrete elastic scattering events and inelastic events which are approximated by a mean energy loss model between two elastic scattering events [18,19]. The physical model used for the electron elastic cross section is based on the ELSEPA software [20] and contains the calculation of the Dirac partial wave for scattering by atoms. The mean energy loss model for the inelastic scattering is based on the empirical stopping power relationship of Joy and Luo [21].

The dispersoids of diameters (d) of 100 nm, 250 nm, or 500 nm were introduced in an Al matrix as spheres with the composition $Al_{12}Mn_2FeSi$ (and Au for preliminary simulations). For each diameter, ten dispersoids were created in depths z ranging from $z = r$ to $z = 10r$, with r being the radius, in equal steps as shown in Fig. 1 for dispersoids of 100 nm diameter. For preliminary simulations, beams of 100 or 45 e^- were aimed directly at the particles and the trajectories were plotted for illustrative purposes. For the line scans and 2D scans (i.e., simulated images) 10,000 electrons (e^-) per point were used and the distance between the scanning points was 6 nm which is approximately equal to the pixel size in the experimental BSE images (50,000× magnification) used for measuring the dispersoids. The electron beam was parallel to the z axis. The shot noise of the electron gun was modeled by varying the nominal number of e^- per point based on the noise characteristics of a field emission gun [19]. The noise stemming from the detector and other sources was not taken into account. To derive the signal strength S, the backscatter coefficient of each point was multiplied with a factor of $(0.0267E_0 + 0.2)$ to take into account

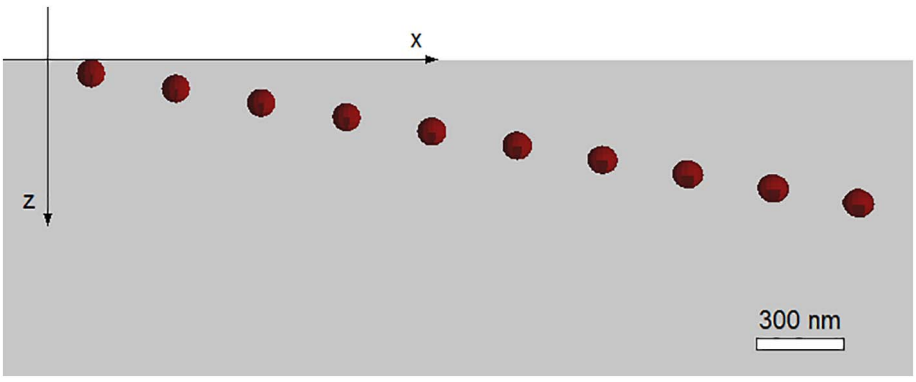

Fig. 1. Placement of the spheres representing the dispersoids in the simulation (d = 100 nm).