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Estimation of volume-weighted average grain size in Fe-based nanocrystalline soft magnetic materials by autocorrelation function

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ABSTRACT

The coercivity of Fe-based nanocrystalline soft magnetic materials depends critically on the grain size of bcc-Fe grains. Accurately estimating the volume-weighted mean grain size is extremely important to develop new Fe-based nanocrystalline soft magnetic materials with low coercivity. This article shows that autocorrelation analysis of dark-field transmission electron microscope (TEM) images provides a very good estimation of bcc-Fe grain size in nanocrystalline soft magnetic materials. This method can be used to efficiently estimate the volume-weighted average grain size from multiple TEM images with much less inherent bias than manual measurement techniques. The estimated grain sizes show good consistency to the grain sizes estimated by X-ray diffraction (XRD) and manual measurement. In contrast to XRD, this method can also reveal the differences in grain size from different micron-sized regions of a sample.

1. Introduction

Since the first Fe-based nanocrystalline soft magnetic alloy (commercial name 'FINEMET') was reported [1], much effort has been made to understand its excellent soft magnetic properties and to develop new nanocrystalline soft magnetic alloys with improved magnetic properties. The nanoscale grain size (~10 nm) of FINEMET was achieved by crystallization of an Fe-Si-B amorphous precursor containing Cu as a nucleating agent and Nb as a grain growth inhibitor [2–6]. Following Yoshizawa et al., many new Fe-based nanocrystalline soft magnetic alloys have been developed to date [7–13]. The random anisotropy model (RAM) links the nanostructure to the low coercivity [2,3,14,15]. According to RAM, if there is no hard magnetic phase nor induced magnetic anisotropy, the coercivity of Fe-based nanocrystalline soft magnetic materials depends on the 6th power of the mean grain size. This 6th power dependence is brought about by a reduction of the energy density of the magneto-crystalline anisotropy (K_1) by the exchange interaction. This exchange-softening effect depends on the number of bcc-Fe grains (N) in a volume defined by the interplay between the anisotropy and exchange energies, i.e. the exchange coupled volume and $\langle K_1 \rangle$ is inversely proportional to the square root of N. Hence, the soft magnetic properties in nanostructures is governed by the volume-weighted average of the grain size (D). Due to the steep D^6 dependence, a small reduction in the mean grain size can cause a significant change in the coercivity. Correctly estimating the volume-weighted average grain size of bcc-Fe phase is thus vital to the development of Fe-based nanocrystalline soft magnetic materials.

In the vast majority of previous studies, the mean grain size of bcc-Fe was estimated either from X-ray diffraction (XRD) patterns or from transmission electron microscope (TEM) images. The estimation of volume-weighted average grain size from x-ray line broadening in diffraction patterns based on the Scherrer equation [16] can be a reliable method when the results are processed carefully. This method requires the removal of the instrumental broadened profile g from the observed broadened profile h [17] followed by fitting a pseudo-Voigt model to the physically broadened profile f [18]. The mean particle size and lattice imperfections can then be determined from a pseudo-Voigt model fitted to the physically broadened profile [19]. However, the process has some inherent potential for error, such as the neglected asymmetry of f and g [19,20] which introduces uncertainty in the estimated mean grain size [21]. For Fe-based nanocrystalline soft magnetic materials prepared from amorphous precursors, error can also arise from the inaccurate removal of the diffuse peaks from the residual amorphous matrix phase. Since the residual amorphous phase of annealed nanocrystalline products has a different chemical composition to the original amorphous precursors, its contribution on the baseline cannot be predicted unequivocally from the profile of the precursors. Hence, accurately separating the contribution of the residual amorphous phase to the line broadening profile is a challenge. It is worth mentioning here that the volume fraction of the residual amorphous

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phase could be as large as 50% in Fe-based nanocrystalline soft magnetic materials.

TEM images provide a direct view of the microstructure and grain size distribution in a micron-sized area and have been employed to estimate grain size. However, manual measurement methods possess a large potential for systematic error. For example, for granular two-phase structures like nanocrystalline Fe-based materials, the line-intercept method is not appropriate since the volume fraction of amorphous grain boundaries is not negligible. The line-intercept method will not only count the size of bcc-Fe grains but also include the thickness of grain boundaries. Manually measuring the grain size of each grain in a particular area is a method that can provide an accurate estimation of the volume-weighted mean grain size and the grain size distribution within this area. Measuring mean grain sizes of multiple areas would improve the accuracy and show any difference in microstructure in different regions in the same sample. However, this method is very time consuming and could incorporate many biases. For example, larger grains may be measured more frequently. Here we present a technique to accurately estimate the volume-weighted mean grain size of bcc-Fe grains in Fe-based nanocrystalline soft magnetic materials from multiple dark-field TEM image in a time efficient way using the autocorrelation function.

2. Method

The autocorrelation function (ACF) is widely used in multiple fields to estimate the size of particles or clusters [22–25]. The normalized ACF of a 2-D signal $f(x, y)$ can be written in the following form:

$$C(m,n) = \frac{\int\int (f(x,y) - \mu_f)(f(x+m,y+n) - \mu_f)dxdy}{\sigma_f^2} \qquad (1)$$

[26,27] which naturally varies between +1 and −1. Here μ_f is the average image intensity and σ_f is the standard deviation in the intensity. The subscript f represents the intensity distribution $f(x, y)$ of the image.

In a dark field TEM image of a nanocrystalline material with an amorphous matrix phase, different phases have significantly different intensity levels. We can threshold the image to remove the contribution from the amorphous phase to analyse the size distribution of the nanocrystalline phase using ACF analysis [23].

In this paper, ribbons of Fe-B-(Cu) alloys were prepared by planer flow casting using a single-roller melt spinner. As-spun ribbons were confirmed to be “diffraction” amorphous by XRD using a BRUKER D8 ADVANCE diffractometer, but some could have quenched-in nuclei observable in the TEM. Ribbons with different compositions were annealed at their optimum annealing temperatures with different heating rates up to 9200 K/s to get different grain sizes. TEM samples of these ribbons were prepared using a precision ion polishing system (Gatan 691 PIPS). The micrographs shown in this paper were acquired using a FEI TECNAI T20 TEM operating at 200 keV. Eight centred dark-field (DF) images from each sample were acquired using a 40 μm objective aperture to select different spots on the ⟨110⟩ ring of its diffraction pattern and/or from different area.

The normalized ACF function was calculated using the Wiener-Khinchin theorem from a processed on-axis dark field (DF) image using Interactive Data Language (IDL). In the DF images such as Fig. 1, there are three main intensity levels from bright and dark grains that are diffracted into and outside the objective aperture and an intermediate level from the amorphous matrix. Images were processed to include intensities from bright grains only by applying intensity thresholds, thus reducing the contribution of the amorphous phase in the calculated ACF function. The threshold used was equal to $\mu_f + 3\sigma_f$. A plot of the grain size estimated by ACF as a function of the threshold used is in Fig. 2. The plot shows several drops of estimated grain size as threshold increases. The first drop is attributed to the loss of contribution of the grey amorphous phase to the ACF. The following drops are attributed to the reduction of grain size as threshold level increases. By making this plot for many different dark-field images, we came to the phenomenological conclusion that the threshold should be $\mu_f + 3\sigma_f$. This threshold removed pixels with an intensity level corresponding to the amorphous matrix in the dark-field image. The 2D ACF was radially averaged to produce a one-dimensional curve.

A library of simulated ACF curves was generated assuming different size distributions of spherical grains (as would be expected from diffusion-limited and stress-free growth [28]) and matching the experimental resolution and magnification. These were employed in a least-squares fitting routine to determine the grain size distribution that most closely matched experiment. A lognormal distribution was assumed for the grain sizes. The grain size distribution of a polycrystalline microstructure developed from amorphous precursors by nucleation and growth has been reported to show a log-normal distribution [29]. This

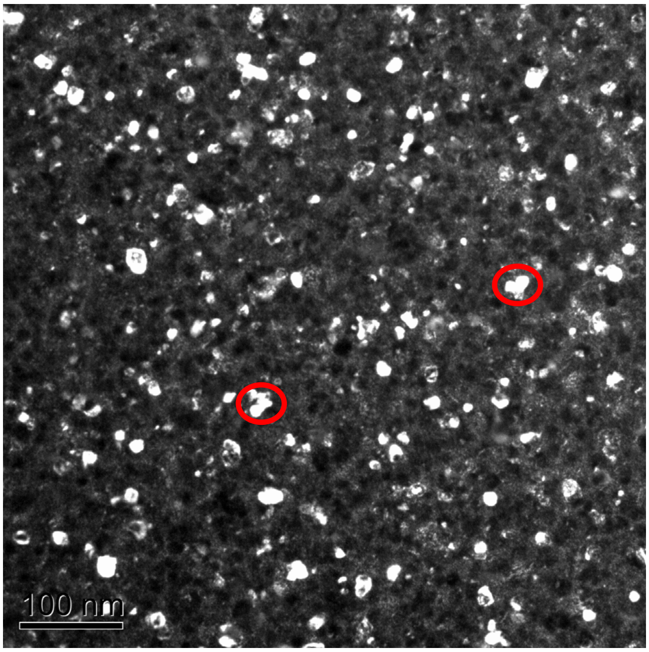

Fig. 1. Dark-field image of $Fe_{85.5}B_{13}Cu_{1.5}$ ribbon annealed at 758 K for 3 s with a 9200 K/s heating rate. In this image, the bright and dark features are bcc-Fe grains. The grey matrix is amorphous grain boundary. The number of bright grains in this image is 150–200.

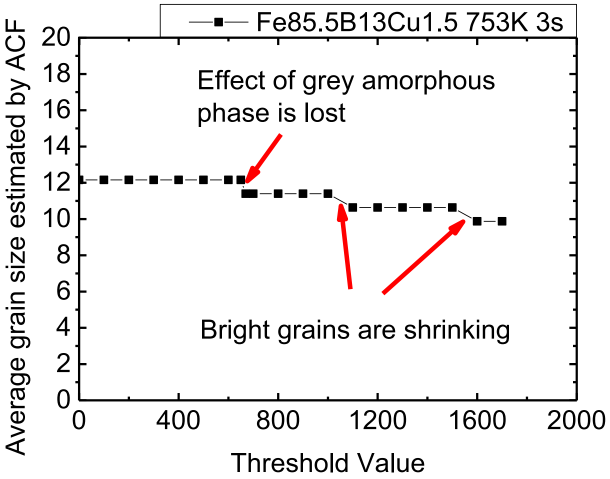

Fig. 2. Average grain size of $Fe_{85.5}B_{13}Cu_{1.5}$ rapid annealed at 753 K for 3 s measured using the ACF vs. the threshold value used to threshold the darkfield image.