Nanocrystallization in driven amorphous materials

S. Shukla a, D.T. Wu b, H. Ramanarayan b, D. Srolovitz c,d, R.V. Ramanujan a,*

a School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
b Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore
c Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
d Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA

Received 15 November 2012; received in revised form 7 February 2013; accepted 8 February 2013
Available online 13 March 2013

Abstract

The nanocrystallization of mechanically milled amorphous alloys was examined both experimentally and theoretically. Mechanical milling induces the precipitation of nanocrystals in an initially amorphous Nd–Fe–B magnetic alloy. The effects of milling speed and duration on precipitate growth/size were investigated. Milling intensity was found to significantly affect the steady-state precipitate size. Precipitate growth kinetics and steady-state precipitate size were governed by a dynamic equilibrium between defect-enhanced diffusional precipitate growth and impact-induced crystal attrition. A linear decrease in steady-state precipitate size with increasing milling speed was predicted, consistent with our experimental data. Nanocrystallization in many driven amorphous alloys can be understood using the kinetic model developed here.

© 2013 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Metallic glasses; Mechanical milling; Precipitation kinetics; Growth kinetics; Theory and modeling (kinetics, transport, diffusion)

1. Introduction

The excellent mechanical and magnetic properties of nanocrystalline nanocomposites and partially crystallized amorphous structures have led to growing interest in the control of crystallization of metallic glasses (MGs) [1–4]. Crystallization of MGs can be induced thermally or through the input of some form of external energy that helps overcome the energetic barriers associated with crystallization. Partial or full crystallization usually corresponds to a lower energy state compared with their fully amorphous counterparts.

Annealing of amorphous systems above the crystallization temperature is the most common method to induce crystallization. However, it is usually difficult to control the nucleation and growth of the crystallization process through this means. On the other hand, controlled nanocrystallization is feasible via other processes. These include mechanical processing (e.g. milling [5], nanoindentation [6] and high pressure torsional deformation [2]) and electron/ion irradiation [7]. These techniques result in the formation of nanoscale crystalline grains with well-defined morphologies. Hence, the thermodynamics and kinetics of nanocrystallization of amorphous alloys driven by non-thermal effects is of considerable scientific and technological interest.

Melt spinning, splat quenching and condensation from the gas phase are well-established techniques for producing amorphous alloys. Unfortunately, these methods typically produce either films or ribbons and are not readily applicable to the production of industrially interesting bulk materials and/or complex shapes. Since mechanically milled powders can be readily consolidated, mechanical milling of melt-spun ribbons provides an interesting opportunity to induce nanocrystallization in MGs – paving the way for bulk processing of nanocrystalline structures of arbitrary shape.

Unlike thermally induced nanocrystallization, the mechanism and kinetics of deformation-induced nanocrystallization are not well understood [8–13].
steady-state crystal size of nanocrystals produced during mechanical milling (MM) confined to the nanometer range? Why is this steady-state crystal size much smaller than that produced via thermal annealing? In this work, we examine the growth kinetics of nanocrystals via mechanical milling of melt-spun magnetic amorphous Nd_{10}Fe_{85}B_{5} ribbons. We then develop a kinetic model for the crystallization of amorphous alloys during mechanical milling and parameterize using experimental data to explain the experimental observations.

This work focuses on exchange-coupled magnetic nanocomposites in the Nd–Fe–B hard magnetic alloy system. While conventional permanent magnets are commonly rare-earth-based single phase alloys (e.g. Nd_{2}Fe_{14}B and SmCo_{5}) which exhibit high intrinsic coercivity, they typically possess relatively low magnetization. Moreover, diminishing supplies and escalating costs of rare earth elements pose new challenges for the industrial production of such magnets [14,15]. The discovery of novel exchange-coupled hard–soft nanocomposites offers a promising approach to circumvent these limitations [16]. Rather than trying to simultaneously enhance magnetization and coercivity of a single phase alloy, this can be accomplished in a nanocomposite where the soft and hard magnetic properties are carried by different phases. One phase is magnetically hard with large anisotropy constants and high coercivity (e.g. Nd_{2}Fe_{14}B), while the second is magnetically soft with large saturation magnetization (e.g. α-Fe). Previous work has shown that the magnetic properties of such nanocomposites are sensitive to the size of the magnetically soft α-Fe crystals [16,17]; large energy products can only be obtained when the α-Fe crystals are on the nanoscale.

Controlled nanocrystallization via mechanical milling (MM) of Nd–Fe–B ribbons provides a promising method to manufacture such high performance bulk magnetic nanocomposites. Hence, we study the mechanical milling-induced precipitation of the crystalline α-Fe phase in an amorphous matrix. This study provides an understanding of the atomistic processes during mechanically induced crystallization of amorphous alloys and the role that these processes play in determining steady-state crystal size.

2. Experimental procedure

Amorphous Nd_{10}Fe_{85}B_{5} ribbons were synthesized by induction melting of cast buttons in a boron nitride crucible in an argon atmosphere. The molten material was ejected onto a copper wheel rotating at 70 Hz with an ejection pressure of 500 mbar. As-spun ribbons were crushed and milled in a Pulverisette-5 planetary ball mill in argon [18]. Crystallization kinetics were determined for milling speeds of 150, 200, 250 and 300 rpm for several different milling times (intensities). The milling was stopped for 5 min periods after every 10 min of milling and the milling vial was water-cooled in order to control the temperature. All pre- and post-processing of powders was performed in argon in a glove box. X-ray diffraction (XRD) data were collected using a Bruker D8 X-ray diffractometer (Cu Kα radiation) and analyzed using Rietveld refinement via the TOPAS 3.1 program; a pseudo-Voigt function was used to model the experimental diffraction peaks. Cerium oxide (SRM 674 b, NIST) was used as an internal standard for quantitative phase analysis. TEM investigations were performed using a JEOL-2100F transmission electron microscope.

3. Results and discussion

The X-ray diffractograms of as-spun amorphous Nd_{10}Fe_{85}B_{5} ribbons milled at 150, 200, 250 and 300 rpm for several time periods are shown in Figs. 1–4, respectively. The full width at half maximum (FWHM) of all the α-Fe diffraction peaks decreased while the intensity increased with increasing milling time. This indicates the precipitation of α-Fe nanocrystals within the amorphous matrix followed by an increase in crystal size. The FWHM of each of the α-Fe diffraction peaks in the samples milled at lower milling speeds (Figs. 1 and 2) were much lower than in the samples milled at higher speeds (Figs. 3 and 4). These results suggest that the milling-induced increase in crystal size was more pronounced for samples milled at lower milling speeds. Consistent with the XRD data, TEM micrographs of ribbons milled for 12 h (at 300 rpm) showed that α-Fe nanocrystals were dispersed in the amorphous matrix (Fig. 5).

Fig. 6 shows the α-Fe crystal size (determined by Rietveld refinement) as a function of milling speed. The crystal size increases with milling time and subsequently saturates at late times. Increasing milling speed results in saturation at earlier times. At 300 rpm, saturation is evident within 18 h of milling, while more than 70 h are required at 150 rpm. Importantly, milling speed was found to significantly influence crystal size; increasing milling speed resulted in smaller α-Fe nanocrystals.

![Fig. 1. Rietveld refinement analyses of X-ray diffractograms of Nd_{10}Fe_{85}B_{5} ribbons milled at 150 rpm for (a) 24, (b) 30, (c) 36, (d) 45, (e) 57, (f) 72 and (g) 87 h. The symbols identify major peaks associated with crystalline α-Fe and CeO_{2}.](image-url)
Since amorphous alloys are not in thermodynamic equilibrium, partial crystallization of the amorphous phase can occur if the energy input from mechanical deformation is able to overcome the activation barriers associated with nucleation and growth. Mechanical work supplied via milling provides the driving force required for nucleation; subsequent crystal growth provides a path towards equilibrium. We analyze the results assuming that crystal growth is diffusion-controlled and that atomic diffusion is enhanced by defect formation.

We recently reported that deformation induces local density fluctuations in the amorphous Nd–Fe–B ribbons, leading to the formation of free volume–anti-free volume (FV–AFV) pair defects during mechanical milling [8]. The dilated regions have low atomic density (FV regions), while compressed regions have high atomic density (AFV regions), analogous to Frenkel (vacancy–interstitial) pair production in crystals under irradiation [19,20]. These FV and AFV regions migrate with continued milling.

Since amorphous alloys are not in thermodynamic equilibrium, partial crystallization of the amorphous phase can occur if the energy input from mechanical deformation is able to overcome the activation barriers associated with nucleation and growth. Mechanical work supplied via milling provides the driving force required for nucleation; subsequent crystal growth provides a path towards equilibrium. We analyze the results assuming that crystal growth is diffusion-controlled and that atomic diffusion is enhanced by defect formation.

We recently reported that deformation induces local density fluctuations in the amorphous Nd–Fe–B ribbons, leading to the formation of free volume–anti-free volume (FV–AFV) pair defects during mechanical milling [8]. The dilated regions have low atomic density (FV regions), while compressed regions have high atomic density (AFV regions), analogous to Frenkel (vacancy–interstitial) pair production in crystals under irradiation [19,20]. These FV and AFV regions migrate with continued milling.
facilitating the atomic redistribution required for diffusion-mediated precipitation.

While crystal growth can be understood on the basis of FV–AFV migration, the saturation of crystal size cannot be explained by this mechanism. Martin [21,22] suggested that the composition and crystal structure of the phases formed during non-equilibrium processes (e.g. mechanical milling and ion irradiation) is the result of two competing processes: ballistic atomic jumps occurring associated with milling/irradiation and equilibrating atomic jumps occurring due to thermal diffusion. Krasnochtchekov et al. [23], Enrique et al. [24] and Bellon et al. [25] used kinetic Monte Carlo simulations to show that this concept may be extended to a variety of driven systems in order to predict precipitate size, composition, stability and morphology at various length scales.

As described above, the crystal size increases with mechanical milling time, followed by saturation (Fig. 6). This suggests that there is a competition between the two atomistic processes. The first is FV–AFV-induced diffusion, which facilitates crystal growth, and the (second) competing process is impact-induced crystal attrition, which tends to lead to smaller crystal sizes.

Thus, if we consider a crystal/amorphous interface, two types of atomic jumps compete:

1. Atomic jumps assisted by FV–AFV migration: Fe atoms from the amorphous matrix jump from the amorphous matrix into the crystal, leading to crystal growth.

2. Atomic jumps due to impacts suffered during milling: Fe atoms from the crystal undergo ballistic jumps from the crystal into the adjoining amorphous matrix, resulting in crystal size reduction.

Crystal growth occurs as long as the diffusional jump processes dominate the ballistic jump processes. When the rate of ballistic atomic jumps becomes equal to the rate of diffusional jumps, a steady-state crystal size is achieved. The steady-state crystal size is a dynamic steady state associated with these competing atomistic effects.

Since crystal growth occurs due to FV–AFV migration, we develop an expression for the crystal growth rate in terms of defect-enhanced diffusion. Also, using the analogy between milling-induced crystal attrition and shrinking of embryos in thermally induced crystallization, we propose an ansatz for the rate of crystal size reduction. Finally, we combine these analyses of crystal growth and crystal size reduction to determine the rate of crystal size evolution.

3.1. Rate of crystal growth

We use an approach similar to that employed to describe defect evolution in irradiated materials [26]. Assuming that defect creation and annihilation occur homogeneously, the time derivative of the net defect concentration resulting from milling-induced deformation \( c_f \) can be written as [27,28]:

![Fig. 6. Comparison of the experimental data with theoretical prediction of crystal size as a function of milling time of Nd_{5}Fe_{85}B_{5} ribbons milled at (a) 150, (b) 200, (c) 250 and (d) 300 rpm.](image-url)
\[
\frac{dc_f}{dt} = \frac{dc}{dt} - \left[ (c_f - c_f^0) k_2^2 \right] k_2 \tag{1}
\]

where \(dc/dt\) is the rate of atomic defect generation per unit volume, \(k_2\) is a rate constant, \(c_f^0\) is the equilibrium defect concentration in the ribbon before milling and \(k_e\) is the strength of available sinks. We assume bimolecular kinetics for defect annihilation (rather than unimolecular kinetics) [29], since the dominant defects created during the mechanical milling of Nd10Fe85B5 ribbons are FV–AFV pairs, rather than only FV regions [8].

At steady state, the time derivative of the defect concentration \(dc_f/dt = 0\). Hence, setting the time derivative in Eq. (1) to zero, we obtain the steady-state atomic defect concentration \(c_f^{ss}\).

If \(c_f^0\) is much smaller than \(c_f^{ss}\),

\[
c_f^{ss} = \frac{1}{\sqrt{k_2 k_v}} \sqrt{\frac{dc}{dt}} \tag{2}
\]

Atzmon et al. [30] applied defect evolution models, originally developed for irradiated materials, to deformed amorphous alloys, and showed that the rate of atomic defect generation during deformation is proportional to the deformation rate. Assuming that the rate of deformation scales with milling intensity \(q\), we write \(dc/dt = k_m q\), where \(k_m\) is a constant. Substituting this expression into Eq. (2) yields

\[
c_f^{ss} = \frac{1}{k_v} \sqrt{\frac{k_m q}{k_2}} \tag{3}
\]

According to the theory of defect evolution in irradiated alloys, the sink strength \(k_e\) is related to the instantaneous crystal size \(D\) as \(k_e^2 = k_3 D^{-n}\), where \(k_3\) is a constant and \(n\) is a positive number which depends on the morphology and distribution of sinks [27,29,30]. If the amorphous/crystal interfaces are the active sinks and the crystallites are equiaxed, \(k_e^2 = k_3 D^{-2}\) [28]. Inserting this expression into Eq. (3) yields

\[
c_f^{ss} = \frac{D^2}{k_3} \sqrt{\frac{k_m q}{k_2}} \tag{4}
\]

The defect enhanced diffusion coefficient \(D_{DED}\) can be written in terms of the steady-state atomic defect concentration \(c_f^{ss}\) as [28]:

\[
D_{DED} = D_0 c_f^{ss} = D_0 \frac{D^2}{k_3} \sqrt{\frac{k_m q}{k_2}} \tag{5}
\]

where \(D_0\) is a constant. The rate of crystal growth can now be expressed as [28,29]:

\[
\frac{dD}{dt} = k_0 D_{DED} \tag{6}
\]

where \(k_0\) is proportionality constant. Combining Eqs. (5) and (6), we can now write

\[
\frac{dD}{dt} = \frac{k_0 D_0 D^2}{Dk_3} \sqrt{\frac{k_m q}{k_2}} = k_0 D_0 \frac{D}{k_3} \sqrt{\frac{k_m q}{k_2}}
\]

or

\[
\frac{dD}{dt} = k_q D \tag{7}
\]

where \(k_q\) is a crystal growth parameter:

\[
k_q = k_0 \frac{D_0}{k_3} \sqrt{\frac{k_m q}{k_2}} \tag{8}
\]

3.2. Rate of crystal attrition

We make an analogy between the shrinkage of embryos during crystallization and impact-induced crystal attrition during milling to develop an expression for the rate of crystal size reduction. We assume that impact forces during milling can force Fe atoms to jump across the crystal–amorphous matrix interface, resulting in a reduction in crystal size. Classical nucleation theory [31] assumes that the rate of shrinkage of a cluster is proportional to its interfacial area \(\pi D^2\), where \(D\) is the cluster size. Analogously, the attrition rate of a crystal during milling-induced crystallization should also be proportional to the area of the crystal–amorphous interface, \(\pi D^2\). Moreover, as the shrinkage rate of embryos in classical nucleation theory depends on thermal activation, we assume that the attrition rate of the crystals depends on the intensity of the mechanical milling \(q\). This assumption is consistent with Martin [22], who suggested that the ballistic jump frequency should depend on milling intensity in the same way that the diffusional jump frequency depends on temperature. Thus, we make the following ansatz for milling-induced crystal attrition:

\[
\frac{dD}{dt} = -k_a q D^2 \tag{9}
\]

where \(k_a\) is constant with respect to \(q\) and \(t\). We define a crystal attrition parameter \(k_a\) as

\[
k_a = k_a q \tag{10}
\]

Thus, the crystal attrition rate can be expressed as

\[
\frac{dD}{dt} = -k_a D^2 \tag{11}
\]

3.3. Rate of crystal size evolution

Combining the expressions for the rates of crystal growth (Eq. (7)) and attrition (Eq. (11)), the overall crystal size evolution is

\[
\frac{dD}{dt} = k_q D - k_a D^2 \tag{12}
\]

In Eq. (12) we have related the rate of crystal growth, crystal attrition and the steady-state crystal size to the milling intensity \(q\) (recall that \(k_a\) is proportional to \(q\) and \(k_q\) to \(q^{1/2}\)). The first and second terms in Eq. (12) represent crystal growth and attrition, respectively. Eq. (12) can be solved for the time-dependent crystal size \(D\) as:
\[ D(t) = \frac{(k_x/k_a)}{1 + \left(\frac{(k_x/k_a)}{D_a} - 1\right) \exp(-k_x t)} \] (13)

We compare the experimental measurements of crystal size vs. time at various milling speeds to our model. The predicted crystal sizes (Eq. (13)) are shown together with the experimental data in Fig. 6. In making this comparison, we fitted the unknown constants, \(D_1\), \(k_x\) and \(k_a\) to the experimental data to obtain the best fit. The values of \(k_x\) and \(k_a\), determined in this manner, are shown in Table 1. The theoretical results and the experimental data are in very good agreement (see Fig. 6). Since the crystal size evolution rate is zero at steady-state, we determine the steady-state crystal size \(D_{ss}\) by setting Eq. (12) to zero:

\[ D_{ss} = \frac{k_x}{k_a} \] (14)

The same result can be found from Eq. (13) by going to the infinite-time limit.

While Fig. 6 shows a good match between experimental crystal size evolution data and our model, it does not explain why the steady-state crystal size changes with milling speed in the way that it does. To understand this, we need to determine how the crystal growth parameter \(k_g\) and the crystal attrition parameter \(k_a\) vary with milling speed (Eq. (14)). Milling intensity \(\eta\) is defined as the rate of momentum transfer per unit mass of powder particles during mechanical milling and can be expressed as [18,32,33]:

\[ \eta = \frac{M_p V_r f}{M_p} \] (15)

where \(V_r\) is the linear velocity of the vial, \(M_p\) is the mass of the milling balls, \(M_p\) is the mass of the powders and \(f\) is the impact frequency. The impact frequency and linear velocity of the vial can be written in terms of the rotational speeds of the frame \(\omega_p\) and vial \(\omega_v\) as \(f = k(\omega_p - \omega_v)\) and \(V_r = k_v(\omega_p - \omega_v) R_v\), respectively. \(k\) and \(k_v\) are constants and \(R_v\) is the radius of the frame. Substituting these expressions in Eq. (15) yields an expression for the milling intensity:

\[ \eta = \frac{M_p k_v R_v k(\omega_p - \omega_v)^2}{M_p} \] (16)

In the Pulverisette-5 ball mill, \(\omega_p\) and \(\omega_v\) are related by \(\omega_v = -1.25\omega_p\) [18] and the ratio of the mass of the ball to the mass of the powder is \(M_b/M_p = 20\). Hence, for our experimental system

\[ \eta = 101.25k_v k_b R_b \omega_p^2 \] (17)

<table>
<thead>
<tr>
<th>(\eta) (nm(^3) min(^{-1}))</th>
<th>150 rpm</th>
<th>200 rpm</th>
<th>250 rpm</th>
<th>300 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_x) (min(^{-1}))</td>
<td>0.012</td>
<td>0.022</td>
<td>0.034</td>
<td>0.049</td>
</tr>
<tr>
<td>(k_a) (nm(^3) min(^{-1}))</td>
<td>0.142</td>
<td>0.231</td>
<td>0.309</td>
<td>0.387</td>
</tr>
</tbody>
</table>

Table 1

Variation of \(k_x\) and \(k_a\) obtained by fitting the theoretical expressions to the experimental data of crystal size as a function of milling time for Nd\(_{10}\)Fe\(_{85}\)B\(_5\) ribbons (see Fig. 6).

Substituting this expression for the milling intensity \(\eta\) into Eqs. (8) and (10), we find:

\[ k_x = k_0 \frac{D_0}{k_s} \left[ \frac{101.25k_v k_b R_b}{k_2} \omega_p \right] \] (18)

and

\[ k_a = [101.25k_v k_b R_b] \omega_p^2 \] (19)

Eqs. (18) and (19) suggest that the rate of increase of the crystal attrition parameter \(dk_a/d\omega_p\) is greater than \(dk_g/d\omega_p\) for all milling speeds \(\omega_p\). To compare this prediction with the experimental data, we used the values of \(k_x\) and \(k_a\) determined from the fitting to the experimental data (see Fig. 6 and Table 1) and plotted these parameters with respect to milling speed \(\omega_p\) (Fig. 7). We observed that the experimentally observed dependence of \(k_x\) and \(k_a\) in Fig. 7 is consistent with the theoretical model: \(k_x \propto \omega_p\) (Eq. (18)) and \(k_a \propto \omega_p^2\) (Eq. (19)).

Since \(D_{ss} \propto \frac{k}{k_a} \) (Eq. (14)) and \(k_g\) and \(k_a\) are proportional to \(\omega_p\) and \(\omega_p^2\), respectively; \(D_{ss}\) should be proportional to \(1/\omega_p\). We plotted \(D_{ss}\) vs. \(1/\omega_p\) to compare our experimental data with our prediction (Fig. 8). The experimental data could be fit to a straight line with a positive slope, consistent with the model. The data point for the lowest milling speed, i.e. 150 rpm, deviates slightly from the linear fit.

At low milling speeds powder particles tend to stick to the ball surfaces and the milling container. When material gets stuck to the milling media surfaces, ball-to-powder ratio (BPR) increases artificially (the stuck powder particles do not participate in the milling). This artificial increase in the ball-to-powder ratio and the fact that much less powder is available for milling, lead to an increased impact frequency and hence milling intensity. Thus, when cold welding is significant, powder particles experience a higher milling intensity than the milling intensity they experience when cold welding is minimal and hence the correlation between \(D_{ss}\) vs. \(1/\omega_p\) deviates slightly from a straight line when mechanical milling is performed at low milling speeds, e.g. 150 rpm.

4. Conclusions

Amorphous Nd\(_{10}\)Fe\(_{85}\)B\(_5\) ribbons were synthesized by melt spinning and these ribbons were subsequently subjected to mechanical milling. This mechanical work leads to deformation-induced nucleation and growth of \(\alpha\)-Fe nanocrystals in the amorphous matrix. The crystal growth kinetics and the evolution of grain size were investigated by Rietveld refinement XRD analysis. A new kinetic model was proposed to explain the experimental findings. The main conclusions of this study are as follows:

- Milling speed significantly affects steady-state crystal size. Increasing milling speed resulted in decreased steady-state crystal \(\alpha\)-Fe nanocrystals size.
The kinetic model predicted steady-state crystal size represents a balance between two competing atomistic processes: defect-enhanced diffusional atomic jumps (leading to crystal growth) and impact-induced ballistic atomic jumps (leading to crystal attrition).

According to the model, the rates of crystal attrition and crystal growth were a strong function of milling speed. With increasing milling speed, the increase in the rate of crystal attrition was predicted to be quadratic and greater than the linear increase in the rate of crystal growth. The model also predicted a linear decrease in steady-state crystal size with respect to increasing milling speed. These predictions are consistent with the experimental results.

The kinetic model developed in this work is applicable to crystallization in a variety of systems which are driven far from equilibrium by external processes such as mechanical milling and irradiation.

References