In Situ Determination of Nd-Fe-B Crystallization Pathways

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Introduction

Microstructural evolution in rapidly solidified rare-earth permanent magnets, primarily $Nd_2Fe_{14}B$ (2-14-1), has been extensively studied, most often as a function of processing and post heat treatment [1]. The most effective microstructural control is achieved by quenching to a nanophased or amorphous alloy and then annealing for short periods of time at elevated temperatures, typically around 1050K. While much can be learned from samples in their post-annealed condition, characterization of the dynamics of the microstructural evolution during devitrification and grain coarsening is often left to indirect means such as thermal analysis or magnetization measurements. In addition, nonstoichiometry and solute additions to 2-14-1 can have profound effects on the as-quenched microstructure and thereby determine the crystallization pathway during annealing [2]. In particular, alloying additions of titanium and carbon are found to enhance glass-forming ability (GFA) in 2-14-1 melts [3]. In order to understand the effect of solute additions on crystallization behavior and to directly measure the crystallization pathways in rapidly solidified Nd-Fe-B-based alloys, we performed a series of high-temperature transmission x-ray diffraction (HTXRD) experiments on Nd-Fe-B-ribbons from room temperature to 1073K by using high-energy synchrotron radiation and a Debeye-Scherrer geometry [4]. Analysis of the HTXRD data obtained from both stoichiometric and Ti/C-modified 2-14-1 provides the data on the relative proportions of the crystalline and amorphous phases as well as changes in the crystalline phase lattice parameters as functions of temperature. HTXRD performed in the transmission geometry with high energies provides a unique probe into the dynamics of the devitrification process of quenched 2-14-1 alloys.

Methods and Materials

Melt-spun 2-14-1 alloys with and without alloying additions of Ti/C (2 and 6 at. %) were prepared from arc-melted high-purity Nd (99.95%), Fe (99.99%), and B (99.5%) elements. They were melt-spun on a Cu wheel in Ar atm at tangential wheel speeds of 40, 25, and 20 m/s. As discussed below, none of the samples were totally amorphous, and all contained a small fraction of nanophased 2-14-1 and α-Fe in addition to the Nd-Fe-B amorphous matrix. The compound TiC was observed in samples with a Ti/C content of 6 at. %. The *in situ* devitrification of the rapidly solidified, 2-14-1-based ribbons was performed at the Midwest Universities Collaborative Access Team (MU-CAT) beamline 6-ID-B at the APS. The data presented in this study were obtained with incident energies of around 40 keV (~0.31 Å). Details on the experiment are presented in Reference 4. By using an area detector, spectra were taken every 20 s during heating from room temperature to 1073K at a rate of 10K/min. Reitveld analysis was carried out by using the General Structure Analysis System (GSAS) program to determine lattice parameters and phase proportions [5].

Results

Phase fraction determination from the Rietveld analysis of the samples in their as-quenched state are provided in Table 1. Samples containing 6 at. % Ti/C had a small number of 10- to 20-μm primary TiC crystals. Since it was shown that these large crystals do not react with the matrix, the phase fractions were normalized to glass + 2-14-1 + α-Fe. In the samples containing 2 at. % Ti/C, crystalline TiC was not observed in the as-quenched state. The high α-Fe content in the sample containing 6 at. % Ti/C melt-spun at 40 m/s was found to be a result of melt pool instability that resulted in regions of poor quench; this was verified by microscopic and magnetic measurements [6]. The Ti/C-modified alloys show a 0.3% decrease in the *c*-axis lattice parameter and a smaller 0.1% increase in the *a*-axis lattice parameter for the 2-14-1 structure when compared with those obtained for a stoichiometric nanocrystalline 2-14-1 sample melt-quenched at 25 m/s and heated to 1073K. The contraction of the *c*-axis for Ti/C-modified alloys, relative to the basal plane of the stoichiometric alloy, is observed over all temperature ranges.

*Table 1. Quantitative phase constitution of the as-quenched melt-spun Nd-Fe-**B** with various Ti/C contents and quenching wheel speeds.*

TiC (wt%)	Wheel speed (m/s)	Glass (wt%)	2-14-1 (wt%)	α-Fe (wt%)
6	40	75.9	17.3	5.2
6	20	93.5	4.7	1.4
2	25	75.9	24.0	<0.5
0	25	71.3	28.0	0.7

While further work is necessary to determine the site of Ti substitution within the 2-14-1, the initial lattice contraction with increasing temperature and the observed depression of the Curie temperature T_c are consistent with Ti (ionic size = 2.00 Å) substituting for Nd (2.64 Å) rather than Fe (1.72 Å) [7].

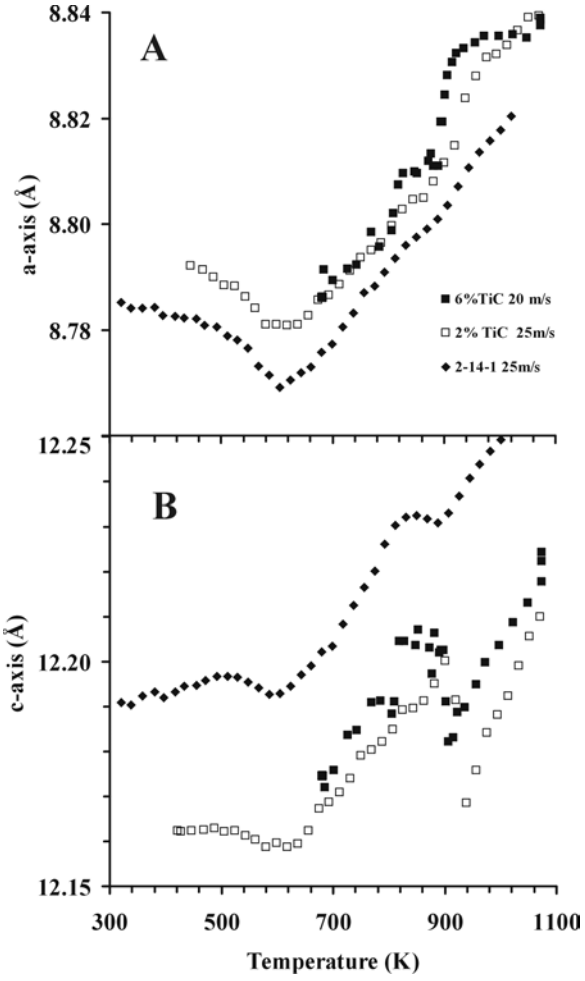

FIG. 1. Changes in the a-axis and c-axis lattice parameters for the crystalline portion of the melt-spun ribbon.

Upon *in situ* heating, the HTXRD measurements indicate that the proportion of glassy material to crystalline material did not alter appreciably with increasing temperature up to the crystallization temperatures T_x, which were 885K and 880K for the 6 and 2 wt% Ti/C-added samples, respectively, and 840K for the stoichiometric alloy [8]. Comparing the ratio of the 2-14-1 (410) or α-Fe (110) peak intensity over all scans for a given sample to the peak intensity for each scan provides a measure of the crystalline to amorphous phase fraction, since the scattering volume remains constant (Fig. 2). The gradual increase in the normalized intensity noted in Fig. 2 for temperatures greater than T_x is due to grain coarsening. The more gradual transition observed in the stoichiometric composition may be due to the slower diffusion kinetics as a result of the lower T_x.

In all samples, there are two distinct transitions observed in the trends of the lattice parameters with increasing temperature. The first transition is found near the T_c for the 2-14-1 phase, where the lattice undergoes spontaneous magnetostriction because of the reduction in magnetic exchange interaction in the Fe sublattice [9]. This phenomenon has been confirmed by the Fe-Fe bond length changes that occur near T_c [10]. For temperatures above T_c, the lattice expands with increasing temperature up to the T_x, as expected from the normal phonon contribution [9]. The second transition is found near T_x. Up to the 2-14-1 T_x, the lattice parameters were determined from the very small amount of 2-14-1 that formed during the quench. The effect of solute atoms on the 2-14-1 lattice is dramatically manifested as a sharp increase in the *a*-axis and an even larger decrease in the *c*-axis of the 2-14-1 phase at T_x. One explanation for this behavior is the metastable retention and subsequent expulsion of the alloying additions Ti and C from the 2-14-1 lattice at T_x. Since the stoichiometric alloy exhibits a contraction at T_x, transient compressive stresses during devitrification may also play a role.

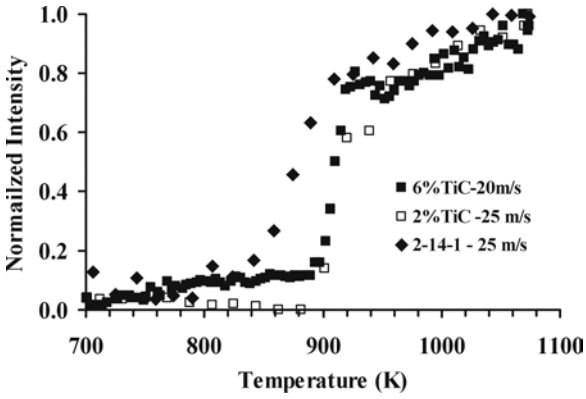

FIG. 2. A plot of the ratio of the most intense peak for each spectrum to the maximum of all the spectra for each sample provides a quantitative measure of the T_s and a qualitative measure of the evolving phase fractions.

Discussion

While there is a wide range in 2-14-1:α-F in the as-quenched alloys, the HTXRD data provide direct evidence that the Ti/C alloying additions to Nd-Fe-B alter the rapid solidification pathway and suppress the formation of properitectic α-Fe in favor of 2-14-1 [8]. This conclusion is supported by a comparison between the

small proportion of α-Fe that forms upon quenching and the relatively large increase in the α-Fe proportion that forms above T_x (Fig. 3). This increase in α-Fe is transient because, after 30 min. at 1123K, the phase fraction of α-Fe is reduced to 2.5 wt%. These data indicate that nucleation and growth of the small proportion of quenched-in clusters of Fe compete with the 2-14-1 phase in both the quenched glass and during solid-state devitrification.

We have demonstrated that time-resolved HTXRD provides a unique insight into the phase selection process in nominally amorphous melt-spun Nd-Fe-B alloys. The role of alloy additions of Ti/C to control formation of properitectic α-Fe is demonstrated. The metastability of the solute(s) into the $Nd_2Fe_{14}B$ phase is shown. Additional work on extracting a precise measurement of the Fe-Fe distances during the magnetostriction is ongoing.

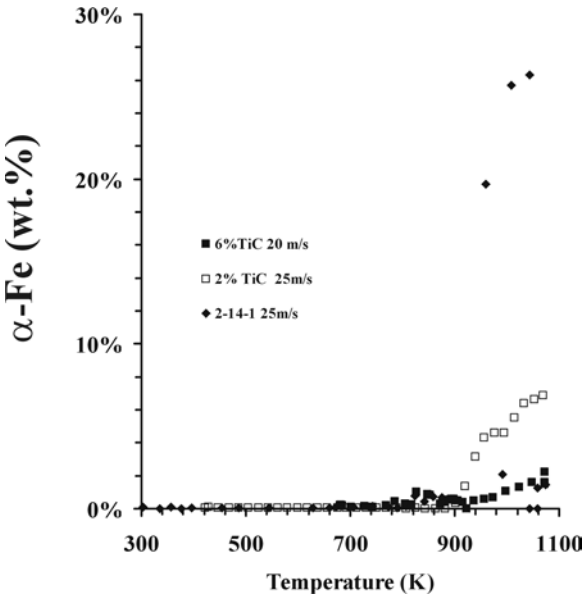

FIG. 3. Plot of the fitted phase fraction of α-Fe. The large fraction of α-Fe for the stoichiometric alloys was confirmed in multiple runs.

Acknowledgments

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