Unusual Thermal Expansion of Rapidly Solidified $Nd_2Fe_{14}B$

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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, primarily as a function of processing and post-heat treatment.[1] The most effective microstructural control is achieved by quenching a nanophased or amorphous alloy and then annealing for short periods of times at elevated temperatures, typically around 800°C. While much can be learned from post-heat treatment analysis, investigation of the dynamics of the microstructural evolution is left to indirect means, such as thermal analysis or magnetization measurements. In addition, the effect of nonstoichiometry and solute additions can have a profound effect on the as-quenched microstructure, which in turn will affect the crystallization pathway during annealing. In order to understand the effect of solute additions on the crystallization behavior and to directly measure the crystallization pathways, we performed a series of high-temperature x-ray diffraction (HTXRD) experiments on rapidly solidified Nd-Fe-B alloys from room temperature to 800°C using high-energy synchrotron radiation and a Debeye-Scherrer geometry.[2] The proportion of crystallization to amorphous phase fraction and changes in lattice parameters were determined for both stoichiometric and TiC added to 2-14-1. The effect of solute additions on changes in cell parameters was clearly noted. It was demonstrated that HTXRD using transmission geometry and high energies provides a unique probe into a dynamic crystallization process.

Methods and Materials

(1) Melt-Spun Alloys. Alloys of 2-14-1 with and without TiC (2 and 6 at. %) were prepared by arc melting high-purity Nd (99.95%), Fe (99.99%), and B (99.5 %) under Ar. The tangential wheel speed was varied to vary the quench rate. The addition of TiC was shown to improve the glass formability of 2-14-1. As will be discussed below, none of the samples was totally amorphous, and all contained a small fraction of nanophased 2-14-1 and Fe. TiC was observed in samples with Ti and C content over 2 at. %.

(2) HTXRD. The *in situ* crystallization of the rapidly solidified ribbons was performed at the 6-ID-B beamline. The data presented in this study were obtained with incident energies around 40 keV. The exact wavelength for each run was determined using NISTSi standard (640b). The melt-spun ribbons were ground into powder in an inert atmosphere, loaded into 2 mm ID thin-walled amorphous silica tubes. Prior to sealing, the tubes were evacuated to a pressure < 10^{-2} mbar and then backfilled with Ar. The detector was a 200 x 250 mm Fuji image plate with pixel dimensions of 100 x 100 µm.

Results and Discussion

Each spectrum was fit using GSAS. The amorphous background was modeled using a 14-term polynomial expansion, while the crystalline phases identified were 2-14-1, Fe, and TiC, if added. As-quenched samples showed predominately glass (up to 90 wt. %), 8 to 9 wt. % 2-14-1, and remainder Fe and TiC, if added above 2%. From room temperature to ~100°C, there was a slight expansion of the unit cell volume for 2-14-1. From 100 to 400°C the volume dropped rapidly, primarily due to contraction in the basal plane (Fig. 1). From 400°C up to the crystallization temperature, the thermal expansion is linear with a positive slope. There is a second inflection in the thermal expansion during crystallization. Unlike at 400°C, the c-axis undergoes the more dramatic change, but only for the TiC-containing compounds. This is indicative of ejection of Ti/C from the as-quenched crystal structure, while the negative thermal expansion below 400°C is a result of spontaneous magnetostriction.[3] More detailed analysis of the atomic position are ongoing to better assess the changes in crystal chemistry with temperature.

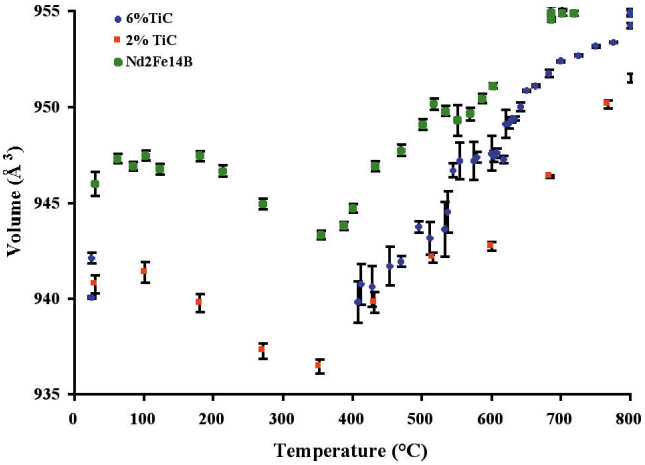

FIG. 1. Changes in the unit cell volume for the $Nd_2Fe_{14}B$ structure ($P4_2/mnm$) as a function of alloy composition and temperature.

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