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Magnetic aspects of the ferromagnetic "bulk metallic glass" alloy system Nd–Fe–Al

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Abstract

Detailed structural and magnetic characterization was carried out on nominally amorphous melt-spun ribbon based on the composition $Nd_{60}Fe_{30-x}Al_{10+x}$ to pursue the origins of its anomalously large coercivity values. The combined structural and magnetic analyses point to the existence of antiferromagnetic motes within the melt-spun ribbon. The average diameter of these motes is 1.2 ± 0.5 nm and their crystal structure is related to the $Nd_6Fe_{13-x}Al_{1+x}$, δ-phase structure, which under equilibrium conditions is the primary solidification phase near the $Nd_{60}Fe_{30}Al_{10}$ composition. These motes are hypothesized to strongly couple to the ferromagnetic matrix phase in an "exchange-bias"-type manner and confer extremely high values of coercivity at low temperature. The composition dependence of the δ-phase Néel temperature is reflected in the composition dependence of the onset of large values of coercivity in the melt spun ribbons. The results obtained from melt-spun ribbons are compared to those obtained from a 10 gm drop-cast ingot 6 mm diameter of the same nominal composition and are found to be internally consistent. Delineation of the solidification pathway in the vicinity of the composition $RE_{60}Fe_{30}Al_{10}$ provides a sound physical explanation of the variety of microstructures and associated variety of magnetic behavior found in cast and melt-spun forms of this material.

Keywords: Bulk metallic glass; Ferromagnet; Ac susceptibility; Phase diagram; Coecivity

1. Introduction

Since their first synthesis in 1951 [1], amorphous metallic materials have generated great interest from scientists and engineers alike due to the unique electronic and mechanical properties arising from a lack of long-range crystallographic

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order. It is possible to utilize rapid solidification techniques such as melt-spinning and splat-cooling to obtain the amorphous state in selected metallic compositions, but only with the most extreme quenching conditions, typically exceeding 10^6 K/s. Therefore, the announcement [2] that certain metallic alloys can be vitrified into a completely amorphous state from the liquid at modest cooling rates of 10 K/s or slower was met with extreme interest in the materials science community and has since stimulated a large body of work on the so-called ''Bulk Amorphous'' alloys [3] or bulk metallic glasses (BMG). BMG alloys may be cast into rods up to 2 cm or more in diameter and have intriguing technological potential by virtue of their ability to be formed by injection molding and net-shape forming [4]. Prior to 1993 there were no BMG alloys developed that exhibited ferromagnetism at room temperature; in 1995 Inoue and co-workers first published results on ferromagnetic BMG alloys that contained a very large number of elements with typical compositions of Fe–(Al, Ga)–(P,C,B,Si) [4] and Co–Cr–(Al,Ga)–(P,B,Si) [5]. In 1996 Inoue and co-workers [6] announced the development of BMG rods (1–12 mm diameter) of composition $RE_{60}Fe_{30}Al_{10}$ (RE = Nd or Pr) with appreciable coercivities at room temperature. These and related alloys modified by Co [7] and Ce and Si [8] have since generated considerable interest of both applied and fundamental nature because the magnitude of this reported coercivity, up to 0.4 T at room temperature, is an apparent contradiction to the conventional understanding of the relationship between nanostructure and coercivity in amorphous materials. Both a very large anisotropy field and a very strong domain wall pinning mechanism are required to account for the observed coercivity which exceeds 10 T at temperatures below 10 K. While the random anisotropy model [9] may account for the anisotropy field, the nature of the pinning sites in an amorphous material is unclear. Among other explanations, previous authors have speculated that the RE–Fe–Al BMGs possess short-range order which confers coercivity [10]. Other researchers [11,12] have postulated the idea that ferromagnetic single-domain clusters are responsible for the large coercivity. To clarify the origin of the coercivity in the reported BMG alloys $R_{60}Fe_{30}Al_{10}$ (R = Nd or Pr) as well as to assess their promise as novel permanent magnets, a thorough structural and magnetic study of nominally amorphous melt-spun samples of composition $Nd_{60}Fe_{30-x}Al_{10+x}$ ($-2 \leqslant x \leqslant 6.5$) was undertaken. As it is expected that the solidification route, microstructure, and composition of melt-spun ribbons of this alloy are more homogeneous than those of their bulk analogues, study was concentrated on the ribbon form of the BMG composition $Nd_{60}Fe_{30-x}Al_{10+x}$. A variety of diverse probes, including synchrotron X-ray diffraction (XRD) and advanced transmission electron microscopy (TEM), were used to characterize the amorphous material in its as-solidified state as well as during in situ devitrification and to clarify the relationship between the microstructure and the coercivity. The magnetization behavior was determined using vibrating sample magnetometry (VSM), and DC and AC SQUID magnetometry and the data were analyzed in the frameworks of superparamagnetism and the Casimir-du Pré models, as appropriate.

As reported in part by the present authors elsewhere [13,14], it is demonstrated that solidification of $Nd_{60}Fe_{30}Al_{10}$ from the melt does not result in an entirely amorphous material; rather, highly stable nanoscopic aluminide and/or silicide phases, or motes, are found in the nominally amorphous melt-spun alloys of $Nd_{60}Fe_{30}Al_{10}$. Not only do these motes affect the short-range order of the system and provide heterogeneous nucleation sites for crystallization, they also determine the coercivity of the alloy. The coercivity of the resultant largely amorphous materials is hypothesized to arise from magnetic exchange coupling between the ferromagnetic clusters and the antiferromagnetic motes, which results in a very strong interaction analogous to that of ''exchange-bias'' coupling [15]. Furthermore, the counterintuitive empirical observation [12,16] that cast rods of the purported BMG compositions possess an amorphous interior and a nanocrystalline exterior may be explained on the basis of the expected solidification behavior in the pertinent region of the Nd–Fe–Al ternary phase diagram. This explanation provides a scientific underpinning to the