Research article

Optimizing glass formation in ferromagnetic alloys through chemical fluxing

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We identify a reduction reaction of boron oxide by Si during melt fluxing of the Fe-Co-Si-B-P system, which results in an unexpected and significant B enrichment and Si depletion in the alloy. Taking this reaction into account, an optimized Fe-Co-Si-B-P alloy free from oxide inclusions and demonstrating a global peak in glass forming ability is formed. Following a 22-h high temperature fluxing of the melt, alloy with composition $Fe_{57.5}Co_{20.2}Si_{10.2}B_{2.1}P_{10}$ transforms to $Fe_{57}Co_{19.2}Si_{6.8}B_{7.4}P_{9.6}$, and its critical rod diameter increases from 1 mm to 5 mm. The alloy also demonstrates excellent soft ferromagnetic performance characterized by a magnetic saturation of 1.53 T.

Ferromagnetic metallic glasses have been of interest since their discovery in 1967 [1], due to their low coercivities and high magnetic permeabilities, arising from atomic homogeneity at length scales comparable to the magnetic correlation length [2]. These soft magnetic properties have led to their widespread use in automotive magnetics, magnetic sensors, power supplies, and power transformers [3]. Currently, commercially available ferromagnetic metallic glasses are produced via the rapid quench process of melt spinning, producing cooling rates ranging between 10^4–10^6 K/s. The necessity of such high cooling rates limits the thickness of the quenched glassy part to micrometer-thick ribbons. To improve the glass forming ability (GFA), and increase the critical process thickness of those early ferromagnetic glass formers, nonferrous metals such as Ga, Cr, Nb, Mo and Zr have been added to great effect [4–9]. While beneficial to the GFA, this increase in glass stability comes at the expense of magnetic saturation, as these non-ferrous

metals reduce the magnetic moment per atom of the alloy. Another means of improving GFA is melt fluxing, which has been widely used to purify metal/metalloid glass formers. Specifically, boron oxide fluxing has been known to improve the glass forming ability of metallic glasses since 1984 [10]. Boron oxide fluxing has been reported to also improve the thermal [11], mechanical [12], and magnetic [4] properties of metallic glasses by removing oxide particles from the melt [13,14]. This technique has also been applied to ferromagnetic glass formers with good success [4,5].

Oxide particles are generally entrained in the melt as inclusions. Such oxides are generally high melting point compounds that are chemically stable at melt processing temperatures typical for metallic glass-forming alloys. They act as heterogeneous nucleation sites, catalyzing crystallization of the melt upon cooling, and thus limiting the GFA [13]. In the presence of boron oxide flux, the oxide inclusions are purged from the melt. The exact purging mechanism is not well understood, but is thought to be driven by either a chemical reduction mechanism where the inclusion oxide reduces boron oxide to form a higher order oxide, or an equilibrium dissolution mechanism arising from an equilibrium solubility of the inclusion oxide in boron oxide.

In this study we found that in addition to oxide purification, boron oxide fluxing of a metallic glass bearing Si gives rise to a chemical reaction by which the alloy becomes enriched in B and depleted in Si. Here, we thoroughly studied a ferromagnetic-based glass bearing Si and B and lacking non-ferrous metals. We exploit this reduction reaction to implement a unique optimization approach by which the alloy is purified from oxide inclusions, while also undergoing a large, but predictable shift in composition. With this approach, an optimum composition

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may be identified, which in its purified (i.e. post-fluxed) form would demonstrate a global maximum in glass forming ability.

Metallic glass ingots were prepared by induction melting mixtures of the appropriate amounts of iron (99.953), cobalt (99.953), boron (99.53), silicon (99.99993), platinum (99.993), palladium (99.9953), and phosphorous (99.9993) in sealed quartz tubes under an Ar atmospheres [15]. The ingots were fluxed with dehydrated boron oxide in a vertical tube furnace at 1350 °C over various fluxing durations. The molten alloy is then injected into a quartz tube, having a 0.5 mm thick wall, using an argon back-pressure where it is subsequently water quenched. This fluxing process occurred using small (5 mm) spheres of material surrounded by flux, in order to obtain a large surface area to volume ratio, and thus, speed up the kinetics of the reaction.

The alloy compositions were evaluated by secondary ion mass spectroscopy (SIMS), using oxygen ions to excite the surface and unfluxed specimens as reference [16]. The amorphicity of the quenched rods was evaluated using x-ray diffraction (XRD) with Cu-Kα radiation. Differential scanning calorimetry (DSC), at a heating rate of 20 K/min, was used to determine the Curie temperature (T_c), glass transition temperature (T_g), crystallization temperature (T_x), solidus temperature (T_s), and liquidus temperature (T_l). DSC was also used as a secondary means of identifying changes in composition by monitoring shifts in T_l. The Curie temperature was also evaluated using thermogravimetric analysis [17].

For magnetic testing, 5 mm rods were stress annealed at 60 K below T_g for 45 min to relax quenched-in stresses induced by the rapid cooling process [4]. Disks sectioned from the rod were electric-discharge-machined into toroids having outer diameters of 5.14 mm, inner diameters of 3.69 mm, and heights of 0.88 mm. The toroids were wrapped with a 30-AWG insulated copper wire producing 40 primary turns and 20 secondary turns. The magnetic properties were characterized using a Walker AMH-200k-S Hysteresisgraph at 50 Hz frequency and 25 kA/m magnetic flux.

In this work, we investigate the effects of boron oxide fluxing on the Fe-Co-Si-B-P system. Selection of this system is motivated by an expectation that the lack of non-ferrous transition metals (such as Mo, Cr, Nb, etc.) would yield a high saturation magnetization as non-magnetic transition metals tend to limit the saturation magnetization of bulk ferromagnetic glasses (typically around 1.1 T) [8]. Indeed, Li et al [18] have demonstrated that a specific composition within this alloy system, $Fe_{68.4}Co_{7.6}Si_9B_{10}P_5$, is a bulk glass former with critical rod diameter of 3 mm and exhibits a saturation magnetization of 1.5 T. The objective of this work was to implement a careful compositional optimization

process, combined with a melt purification process that would allow us to maximize the critical rod diameter of the ferromagnetic alloy while retaining a high saturation magnetization.

Here, we implemented a "biased random walk" algorithm relying on a "steepest ascent approach", similar to that proposed by Na et al [19], to evaluate glass forming ability cusps in composition space. We performed this for fluxed and unfluxed alloys along the composition direction associated with variation of B at the expense of Si. The unfluxed alloys follow the composition formula $Fe_{57}Co_{19.2}Si_{(14.2 - x)}B_xP_{9.6}$, while the fluxed alloys follow $Fe_{57.5}Co_{20.2}Si_{(12.3 - x)}B_xP_{10}$ (note that these composition formulas represent the as-weighed compositions prior to fluxing the alloys).

In Fig. 1, we plot the critical rod diameter versus the atomic concentration of B for unfluxed and fluxed alloys (fluxing time of 110 s). As seen in Fig. 1, the peak in the fluxed alloys is greater than that for the unfluxed alloys by about a factor of 2. But interestingly, the GFA peak in the fluxed and unfluxed alloys appears at very different B/Si concentrations. Specifically, the peak in the unfluxed alloys appears at B and Si concentrations of 6.3 at.% and 7.9 at.% respectively, while that in the fluxed alloys occurs at B and Si concentrations of 2.1 at.% and 10.2 at.% respectively. As such, the optimum alloy in the unfluxed series is $Fe_{57}Co_{19.2}Si_{7.9}B_{6.3}P_{9.6}$ demonstrating a critical rod diameter of 2.5 mm while that in the fluxed series is $Fe_{57.5}Co_{20.2}Si_{10.2}B_{2.1}P_{10}$ and demonstrates a critical rod diameter of 5 mm. Interestingly, the critical rod diameters of fluxed $Fe_{57}Co_{19.2}Si_{7.9}B_{6.3}P_{9.6}$ and unfluxed $Fe_{57.5}Co_{20.2}Si_{10.2}B_{2.1}P_{10}$ are about 1 mm or less (not shown in Fig. 1).

Through a very systematic compositional mapping, Na et al. demonstrated that unique cusps in GFA with each compositional coordinate where one element (or a group of elements) is substituted by another [19]. Here, we verified that the corresponding peaks for the fluxed and unfluxed alloys are indeed unique (i.e. the critical rod diameter is found to be essentially zero in unfluxed alloys at B and Si concentrations of 2.1 at.% and 10.2 at.%, and in fluxed alloys at B and Si concentrations of 6.3 at.% and 7.9 at.%). Here we find that this unusual compositional shift in the GFA peak between fluxed and unfluxed alloys is attributed entirely to a chemical reaction occurring during fluxing, which contributes to significant shift in the alloy composition. Specifically, we find that the composition of the optimum alloy in the fluxed alloy series is not only purified, but is also shifted to a composition that is roughly the composition of the optimum alloy in the unfluxed alloy series. That is, following fluxing, the two alloys at the GFA peaks in Fig. 1 appear to have roughly the same composition.

Using SIMS, the post-fluxed composition of the optimum alloy in the fluxed series, $Fe_{57.5}Co_{20.2}Si_{10.2}B_{2.1}P_{10}$, was evaluated to be
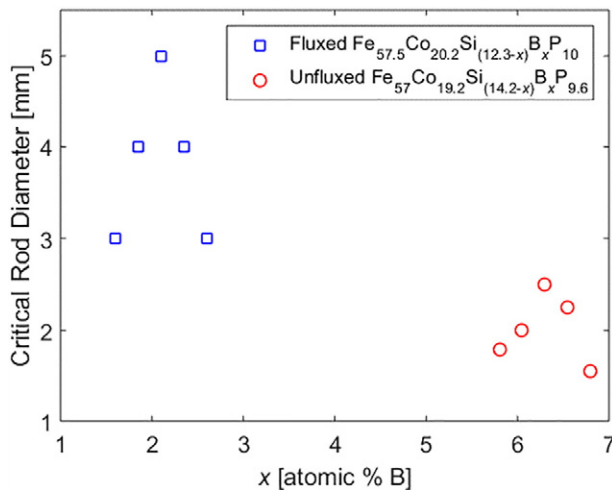

Fig. 1. Dependence of the critical rod diameter of Fe-Co-SI-B-P alloys on the atomic concentration of B in the fluxed and unfluxed alloy with Si being substituted by B in the alloy. The unfluxed alloys follow $Fe_{57}Co_{19.2}Si_{(14.2 - x)}B_xP_{9.6}$, while the fluxed alloys follow $Fe_{57.5}Co_{20.2}Si_{(12.3 - x)}B_xP_{10}$.
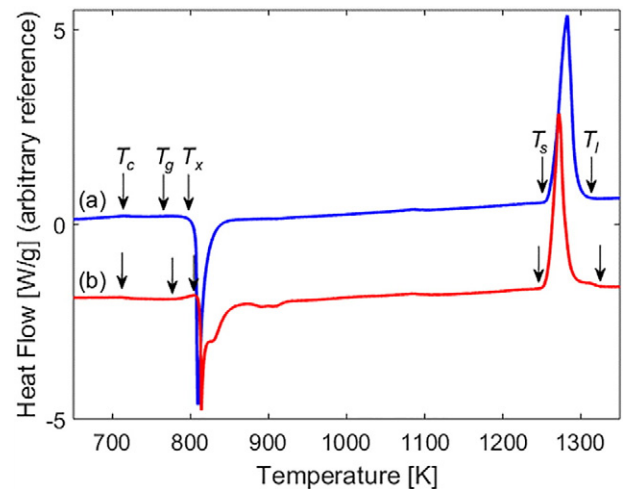

Fig. 2. Calorimetry scans at 20 K/min of: (a) the alloy having the peak GFA in the fluxed series, $Fe_{57.5}Co_{20.2}Si_{10.2}B_{2.1}P_{10}$, and (b) the alloy having the peak in the unfluxed series, $Fe_{57}Co_{19.2}Si_{6.8}B_{7.4}P_{9.6}$. The T_c, T_g, T_x, T_s, and T_l are indicated by arrows.