

Underwater Explosive Shock Consolidation of Nanocomposite Pr₂Fe₁₄B/ α -Fe Magnetic Powders

Zhi-Qiang Jin,^{1,2} Chris Rockett,¹ J. Ping Liu,² Kazuyuki Hokamoto³ and Naresh N. Thadhani¹

¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

²Department of Physics, University of Texas at Arlington, Arlington, Texas 76019, USA

³Shock Wave and Condensed Matter Research Center, Kumamoto University, Kumamoto 860-8555, Japan

Dynamic consolidation of powders was studied to fabricate exchange-coupled Pr₂Fe₁₄B/ α -Fe nanocomposite bulk magnets, using explosively generated shock waves transmitted through water. The planar shock wave propagating into the powder had a peak pressure calculated to be ~ 12 GPa. Extensive plastic deformation of the powders and solid-state interfacial bonding of the ribbon flakes was obtained during shock compaction, resulting in fabrication of bulk compacts with nearly full density. Retention of nano-scale structure, and in fact further refinement of the grain size, ensured exchange coupling between the hard and soft phases, resulting in magnetic properties better than those of resin-bonded commercially available magnets. Post-shock annealing of the compacts at 750 and 850°C resulted in deterioration of the magnetic properties due to slight grain growth and decoupling of exchange interactions between hard and soft phases. The results illustrate that dynamic shock consolidation employing explosive loading is a viable method for fabricating bulk nanocomposite magnets and the rapid thermal excursions can be controlled to minimize and in fact eliminate the detrimental effects otherwise observed during high temperature sintering and annealing of the powders.

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1. Introduction

The ever-increasing interest in the preparation of high performance permanent magnets has focused attention on exchange-coupled nanocomposites because of their low rare-earth content and potentially high-stored energy density.¹⁻⁶ These magnets usually consist of either ultra-fine soft magnetic grains embedded in hard magnetic phase matrix or hard magnetic grains embedded in soft magnetic phase matrix. The soft magnetic phase has high magnetization, while the hard phase provides larger magnetic anisotropic field. When these hard/soft phases are of nano-scale dimensions, exchange coupling between the phases, significantly improves their magnetic properties due to the alignment of magnetic moment of soft magnetic phase parallel to the average direction of the magnetization of the hard magnetic phase matrix.¹

In order to prepare bulk isotropic nanocomposite magnets, considerable attention has to be given to the generation of high density and the retention of nanostructure during processing. Shock compaction of powders is a dynamic consolidation technique, which provides a viable method for densification of nanocrystalline powders.⁷ This technique makes it possible to consolidate powders to form bulk density compacts, while retaining the nano-scale structure. Shock waves originating from the impact of a projectile or from explosive detonation can create pressures from a few to tens of GPa, resulting in inter-particle bonding in the time duration of microseconds.⁸⁻¹¹ The main attraction of this approach is that fully dense bulk compacts can be fabricated without introducing significant changes in microstructure.¹² Recently, shock consolidation of bulk nanocrystalline magnetic alloys, such as NdFeB,¹³ SmCo,¹⁴ and SmFeN magnets,¹⁵ has been reported. Explosive compaction, with the shock wave transmitted into the powders through a water layer, provides the ability to employ a more dispersed shock

wave of prolonged duration, which in some cases is beneficial for attaining better consolidation by providing an increased time for interparticle bonding.¹⁶ Successful underwater explosive compaction of carbon fiber reinforced Al composites as well as several metallic and ceramic powders has been reported.¹⁷ In the present paper we report on experimental observations regarding the retention of nanostructure and magnetic properties in fully dense nanocomposite Pr₂Fe₁₄B/ α -Fe magnets consolidated using shock waves generated by explosive detonation and transmitted into the powders through a water medium.

2. Experimental

Melt-spun Pr₂Fe₁₄B based nanocomposite ribbons with 20 mass% α -Fe, having average grain size below 20 nm, were used as the starting material. Explosive shock compaction was performed at Kumamoto University in Japan. The ribbon flakes were first pulverized to 10–200 μ m powders and then pressed into a powder container prior to shock compaction. Aluminum powder was also placed at the bottom of the nanocomposite magnetic powder, to act as a shock absorber and attenuate the pressure wave. A stainless steel cover plate was placed on the top of the powder bed, on which a water container of 5 mm column height was placed. Water acts as a shock-transmitting medium and pressure modulator. An explosive container was then placed on the top of the assembly to create a planar shock wave, which was transmitted through the water container prior to compressing the powder. The explosive produced by Asahi-Kasei Corp was SEP whose density and detonation velocity were 7 km/s and 1300 kg/m³, respectively. With this geometry, described in more detail elsewhere,¹⁷ the pressure acting on the powder can be controlled by varying the height of the water column. In the present work, the shock pressure transmitted through the water and into the powder layer was calculated to be

around 12 GPa.

The density of the recovered sample was determined using the Archimedeian method. Vicker's hardness measurements were performed using the Leco DM-400F microhardness tester. The starting material and recovered specimen were characterized by X-ray diffraction (XRD) analysis using Cu K_{α} radiation ($\lambda = 0.154$ nm), scanning electron microscope (SEM), and transmission electron microscope (TEM). The magnetic properties were measured using a superconducting quantum interference device magnetometer with a maximum applied field of 5.6 MA/m (70 kOe). Effective demagnetization factors of 1.4 were considered by approximating the samples as a prolate spheroid with typical aspect ratio of 2.

3. Results and Discussion

Following shock compaction, the consolidated specimens were recovered in the form of 30 mm diameter by 5 mm thickness discs. The compact had a high density, up to 98% of theoretical mass density (TMD), as measured using Archimedeian method, which is comparable to that (97–98%TMD) of sintered magnets¹⁸⁾ and superior to the densities ($\sim 80\%$ TMD) of commercially available resin bonded magnets. Microhardness measurements yielded Vicker's hardness values in the range of 9–12 GPa, which is greater than that of starting material (~ 8 GPa), indicating evidence of work hardening and strong interparticle bonding.

Figure 1 shows low and high magnification SEM images of the recovered bulk nanocomposite magnets with fracture surface parallel [Figs. 1(a) and 1(c)] and perpendicular [Figs. 1(b) and 1(d)] to the shock propagation direction. Successful bonding with strong cohesion between the powders and elimination of voids are apparent. It can be

seen from Fig. 1(a) that the thickness of flake-shaped particles is around 25–30 μm , which is smaller than that (40 μm) of starting material. An average ductility of 30% is responsible for deformation and filling of interstitial voids during shock-consolidation. Because the powders are in form of flat flakes, they have a tendency for alignment during initial uniaxial pressing, with the flat surfaces perpendicular to the pressing direction. These flakes appear to retain their alignment even after shock compaction. Extensive plastic deformation and solid-state interfacial bonding are induced because of the passage of the shock wave through the water medium and into the powder. Figures 1(b) and (d) shows evidence of extensive plastic deformation of the powder flakes in the process of void collapse and densification to full density. Microcracks believed to have been formed by interaction of tensile release waves, were observed in the compacts and found to be almost perpendicular to the shock wave propagation direction.

X-ray diffraction (XRD) patterns of the starting powder material and the explosively consolidated sample are shown in Figs. 2(a) and (b), respectively, revealing the nanocomposite structure consisting of the hard magnetic $\text{Pr}_2\text{Fe}_{14}\text{B}$ and soft magnetic $\alpha\text{-Fe}$ phases. The difference in the two traces is the observation of an increased width of diffraction peaks in the explosively compacted sample, indicating a reduction of the grain size during shock compaction. XRD traces shown in Figs. 2(c) and (d), also reveal that subsequent (post-shock) heat treatment of the compacts at 750 and 850°C for 3 minutes causes narrowing of the diffraction patterns and a slight increase in grain size. The average grain size calculated using X-ray diffraction peak broadening analysis¹⁹⁾ are, 25, 19 and 28 nm, for starting material, as-consolidated sample and the two annealed samples, respectively.

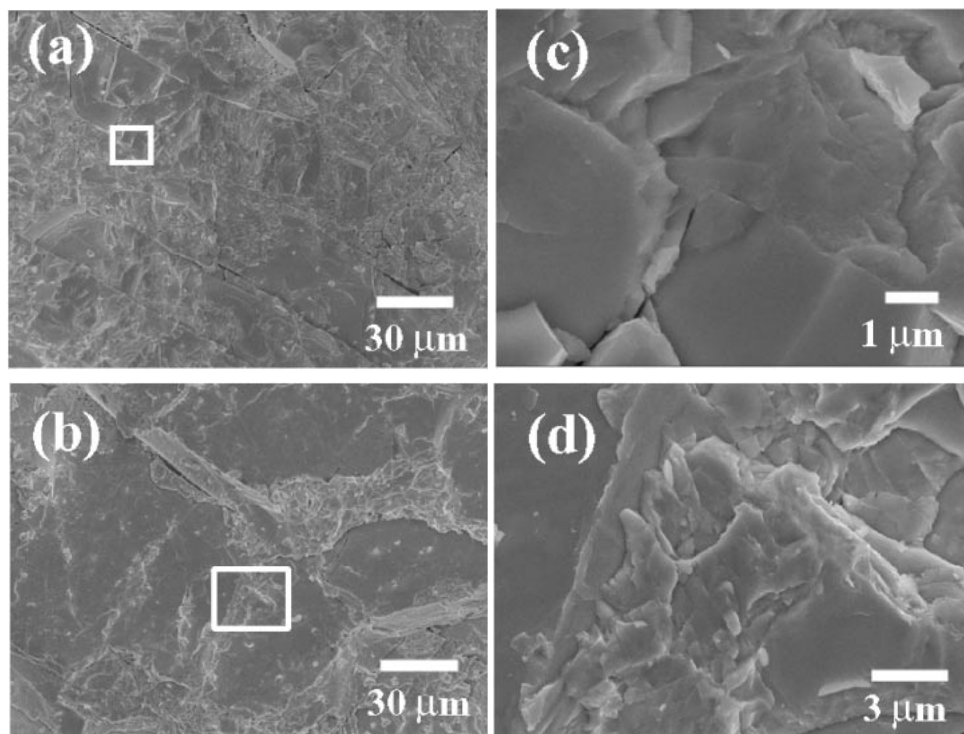


Fig. 1 SEM images of the recovered bulk nanocomposite magnets with fracture surface (a) parallel and (b) perpendicular to the shock propagation direction. (c) and (d) are high magnification images of framed regions shown in (a) and (b), respectively.

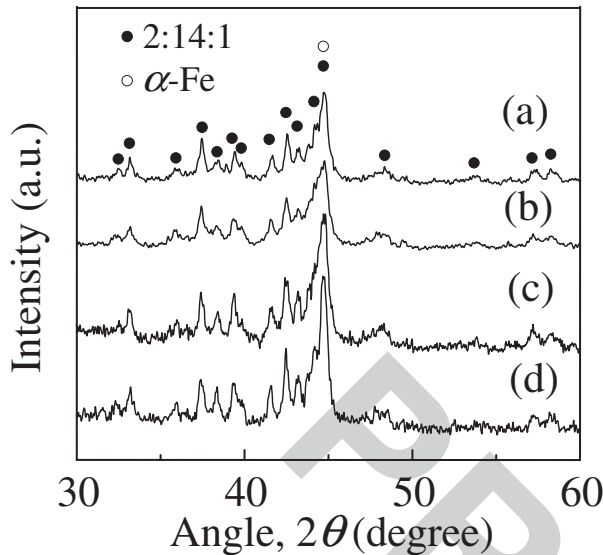


Fig. 2 X-ray diffraction patterns of starting material (a), as-consolidated sample (b), and post-shock annealed samples with thermal treatment for 3 minutes at 750°C (c) and 850°C (d).

The effect of shock compaction on grain size retention and in fact further refinement was evidenced in detail using TEM observations (Fig. 3). It reveals a very fine microstructure with average grain size of around 15 nm in the explosively consolidated material (Fig. 3(a)), compared to the 25 nm average grain size of the initial powder (Fig. 3(b)). The retention of ultra-fine grain size is due to the minimization of otherwise detrimental effects of heating associated with the dynamic compaction process, and the further refinement is due to intense grain fragmentation resulting from controlled shock-wave consolidation of powder. Grain fragmentation is an important attribute of the shock compaction process and has also been observed in past work on shock compaction of nanocomposites magnetic powders using the gas gun²⁰⁾ as well as during explosive compaction of oxide superconductors.¹⁰⁾

It is well established that shock compression of powders can often lead to bulk temperature increases due to the annihilation of a large volume fraction of voids. Recently, Ryazanov *et al.* calculated the effective temperature rise in some metals during shock wave propagation,²¹⁾ and found that the temperature in the shock wave front in Fe can reach the melting temperature. However, temperature rise during shock compression can be controlled by pre-pressing the powders to high green density, so that detrimental effects on grain size can be minimized since the heating and cooling during shock compaction occurs in time scales of microseconds. Hence, nano-scale structure of the hard and soft magnetic phases can be retained, as illustrated by results of the present work, and exchange coupled nanocomposite magnets with superior properties can be produced.

Figure 4 shows smooth hysteresis loops for the explosively compacted bulk two-phase nanocomposite powder compact and annealed samples, demonstrating the existence of exchange coupling. From the hysteresis loops, the values of remanence M_r at zero applied magnetic field and intrinsic coercivity H_c (the field required to reduce the magnetization

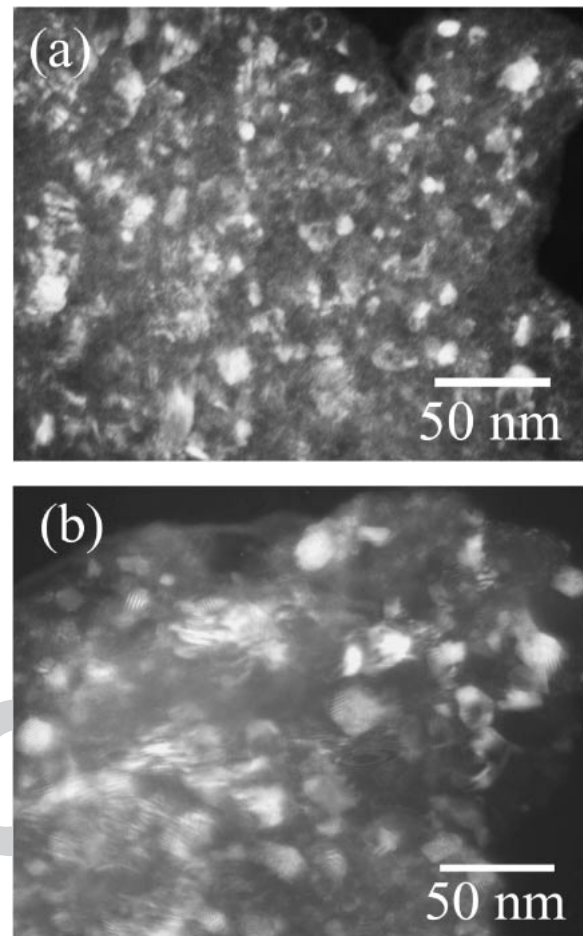


Fig. 3 TEM images of (a) as-consolidated sample and (b) starting materials.

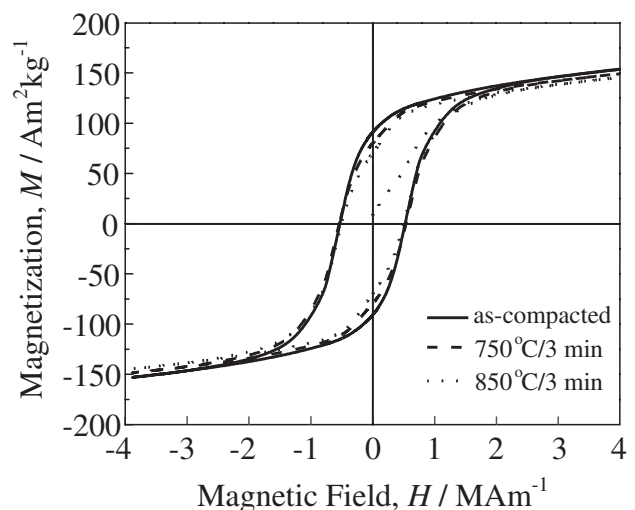


Fig. 4 Hysteresis loops of as-consolidated sample illustrating the magnetic response of the shock consolidated compact and the effect of post-shock annealing on the response.

to zero) can be obtained. The saturation magnetization M_s was extracted from the hysteresis loop measurements by plotting the curve of M versus $1/H^2$ and extrapolating the curve to infinite H . Although the samples consist of magnetically hard and soft phases, smooth single-phase like

hysteresis loop with a remanence ratio (*i.e.*, squareness factor $M_r/M_s \sim 0.6$) over 50% are observed in the explosively consolidated compacts, indicating effective exchange coupling between hard magnetic $\text{Pr}_2\text{Fe}_{14}\text{B}$ and soft magnetic α -Fe phases. The magnitude of squareness factor is one of extrinsic magnetic properties, and is very sensitive to local structural properties,^{22,23)} such as defects, grain size, and strain, and it also relates to the effects of grain alignment and exchange interaction. The squareness is lower compared to those values (0.68~0.82) of sintered anisotropic magnets,¹⁸⁾ which is due to the isotropic characteristic of nanocomposites and the existence of magnetically soft phases that result in the reversal of nucleation fields at low magnetic field. The magnetic properties include, coercivity H_c of 522 kA/m (6.56 kOe), remanence M_r of 95 Am²/kg (emu/g), and maximum energy product $(BH)_{\max}$ of 111 kJ/m³ (14 MGOe) were obtained in shock-compacted sample. The value $(BH)_{\max}$ is superior to that of commercially available isotropic NdFeB bonded magnets (~ 80 kJ/m³ (~ 10 MGOe)).²⁴⁾ The higher $(BH)_{\max}$ is related not only to the exchange coupling in the nanocomposite with fine grain size but also to the high density in the shock consolidated bulk magnet. After heat treatment, a reduction of remanence M_r and squareness factor of the hysteresis loops (dashed curves in Fig. 4) results in a slight deterioration of $(BH)_{\max}$. The deterioration is directly associated with some grain growth and decoupling of exchange interaction between hard and soft phases. The coercivity of the sample was found to increase slightly to 535 kA/m (6.72 kOe) upon annealing at 750°C due to the increase of anisotropic field associated with the grain growth.²⁵⁾ Higher annealing temperature results in the decrease of H_c down to 500 kA/m (6.28 kOe) for 850°C. These heat treatment results indicate that magnetic parameters are very sensitive to the variation of grain size. The overall results also illustrate that explosive shock consolidation of nanostructured powders can be used to fabricate bulk magnets, while retaining and even refining the starting nano-scale structure and grain size and consequently resulting in improved magnetic properties.

4. Summary

Explosive shock compaction employing propagation of shock waves transmitted into powders through a water layer can be successfully used to produce fully dense bulk nanocomposite magnets without grain growth. The high density obtained is attributed to the strong solid-state bonding and retention of laminar morphology through the control of shock loading conditions. The retention of nanostructure and grain size refinement are responsible for optimal magnetic properties. The magnetic properties of explosively compacted samples are superior to those of resin-bonded magnets, showing that explosive compaction can be adopted as a potential technique for development of bulk nanocomposite magnets.

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