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14. ABSTRACT
Current research at the US Army Research Laboratory (ARL) has been focused on understanding the underlying physics of external fields on materials synthesis and processing, also known as Energy Coupled to Matter. This technical note will describe a combination of synthesis processes by which a new composite material will be produced for future work in thermomagnetic processing at ARL. This novel process will be used to fabricate ceramic parts with tailored physical properties to enable new applications that benefit the Army. Potential applications could include new devices or equipment that enhance the performance of Soldier and vehicle protection systems.

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Contents

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1. Introduction

Recent work in materials processing and manufacturing research has been focused on using nontraditional parameters to influence the properties of the final parts. This includes the application of high-strength magnetic fields on materials during synthesis, processing, and/or densification. In the case of ceramics, there is significant work being completed on the forming process of alumina under a magnetic field.[1–6] Most recently by Sakka et al.,[5,6] researchers were able to develop a highly textured microstructure from both slip casting and gel casting under a magnetic field. The bodies maintained a relatively high degree of texture after sintering despite particle rearrangement during the sintering process.

Oak Ridge National Laboratory has conducted research on the application of high-strength magnetic fields during high-temperature processing for alloy formation. It has been shown through computer simulations that the addition of an approximately 9-T external magnetic field can influence phase development in steel alloys.[7–9] Furthermore, additional studies have demonstrated texture development in weakly magnetic metals during sintering under an applied magnetic field.[1–3,9] Current research within the US Army Research Laboratory has been focused on Energy Coupled to Matter for exploring fundamental physics during processing in external fields to obtain novel materials with tailored properties. One future goal is the development of a core-shell structures in which the magnetic core is responsive under an applied magnetic field and the nonresponsive portion of the shell is the majority phase. A process will be described for producing magnetic magnetite (Fe_3O_4) nanoparticles with a thick shell of alumina to be used during thermomagnetic processing. The process will be inspired by similar procedures described in the literature.[10]

2. Synthesis Method

Clean laboratory glassware was required to avoid impurities in the end product. Deionized (DI) water (H_2O) was degassed using house nitrogen (N), allowing for the N to bubble through about 100 mL of H_2O for 10 min before starting synthesis.

A 2:1 ratio of iron Fe^{3+} ions to Fe^{2+} ions from Fe (III) sulfate and Fe (II) chloride was required for the synthesis process. Fe_3O_4 is a ferrite that has both cation valences in the oxide, as demonstrated in the following chemical reaction:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- = Fe_3O_4 + 4H_2O. \quad (1)$$

To acquire the correct ratio, it was necessary to know the exact amount of H_2O hydrating the sulfate and the chloride. These data were obtained from thermogravimetric analysis up to a temperature of at least 1,000 °C to enable the formation of iron oxide. The results were used to back-calculate the exact stoichiometry of the precursor materials.

Once the DI H_2O was degassed, it was poured into a sample reaction vessel with the precursor materials. This was an exothermic reaction completed in a fume hood, adding the H_2O slowly. While the mixture was boiling and cooling down, a solution of sodium hydroxide (NaOH) was prepared in DI H_2O and degassed with house N (as described earlier) for a minimum of 60 min. Once the NaOH solution was finished degassing, an Fe/H_2O mixture was slowly added to the NaOH solution while continuing to bubble house N through the system. Keeping oxygen (O) out of the system was necessary to prevent premature oxidation of the Fe cations. After this step, the Fe_3O_4 particles precipitated out of solution, leaving behind H_2O, NaCl, and Na_2SO_4.

Next, the solution was heated at approximately 85 °C and stirred while continuing to bubble N through the suspension. After 3 h, the heat was turned off, allowing the solution to cool while keeping the N bubbling. Once the suspension was cooled, it could be filtered. While filtering, the mother suspension continued to bubble N. The Fe_3O_4 was washed twice in DI H_2O and once in isopropyl alcohol (IPA). Following the IPA rinse, the Fe_3O_4 was heated in a beaker up to 100 °C with N blowing on it so the IPA could evaporate. Once the IPA was evaporated, drying was continued in an oven. The surface area was measured (by N absorption in BET [Brunauer-Emmet-Teller]) on the resulting Fe_3O_4 nanoparticles and found to be 133 m^2/g.

An in situ nanoprecipitation process was used to coat the Fe_3O_4 particles with alumina.[11] Prior to precipitation, 2 solutions were prepared, including an acidic solution (solution A) and a basic solution (solution B). The acidic solution consisted of aluminum (Al) nitrate, magnesium (Mg) nitrate, and rare earth (RE) nitrate in stoichiometric amounts to acquire a composition of $RE_{0.002}Al_{1.998}O_3$ with 250 ppm of magnesium oxide. Adding Mg to alumina had the dual purpose of creating structural distortion to assist in dissolving the erbium into the Al octahedral site and behaving as a grain growth inhibitor. DI H_2O was added to the mixed nitrates to acquire a 7.5-M solution of $Al(NO_3)_3$ (RE and Mg nitrates were not included in the calculation). The basic solution consisted of 11% by weight ammonium bicarbonate and 3% by weight ammonium hydroxide in DI H_2O. Both solutions were stirred until all crystals were dissolved, adding heat when necessary.

Once solutions A and B were prepared, a third solution, referred to as the buffer, was mixed to host the reactions. The amount of buffer solution (2% by weight ammonium bicarbonate in DI H_2O) was dependent on the batch size. The pH of the buffer was adjusted to approximately 7 by adding a small amount of nitric acid. To coat the Fe_3O_4 particles, approximately 1.5-wt% Fe_3O_4 (based on the calculated mass of alumina) was added to the buffer solution and allowed to stir vigorously, keeping the particles suspended. Finally, solutions A and B were added drop-wise to the buffer/Fe_3O_4 suspension such that the pH remained at approximately 7 during the entire precipitation step. When solution A was exhausted, the resulting suspension was allowed to age while stirring vigorously overnight.

The following day, the suspension was filtered from the NaCl solution. The resulting powder was washed twice with DI H_2O and once with IPA. After washing, the powder was placed into an oven to dry. The dry powder was gently crushed and calcined at 1,300 °C for 30 min in air. The final surface area of the calcined composite powder was 7.28 m^2/g, which was a significant change from the as-synthesized Fe_3O_4 nanoparticles. It is possible that this was the result of the coating of alumina on the surface reducing the total surface area.

3. Conclusion and Future Work

Fe_3O_4 nanoparticles have been synthesized with high surface area using a mixture of Fe valence cations to precipitate the particles from solution. The particles were confirmed to be magnetite by X-ray diffraction, consistent with the observation of particles sticking to magnetic stir bars. The resulting nanoparticles were coated with alumina by nanoprecipitation onto the particle surface and calcined. The surface area was shown to decrease, likely due to either alumina coating or grain growth of the powders during calcination.

Future work will involve additional characterization of the alumina/Fe_3O_4 composite powder, including detailed X-ray diffraction with a molybdenum X-ray source to limit florescence from the Fe in the sample. Microscopy will be conducted to determine if the core/shell structure was obtained, and transmission electron microscopy may be used to observe the bonding between the Fe_3O_4 core and the alumina shell. Once the characterization has been completed, work will begin on the magnetic field processing of this new composite material.

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List of Symbols, Abbreviations, and Acronyms

Al	aluminum
DI	deionized
Fe_3O_4	magnetite
H_2O	water
IPA	isopropyl alcohol
Mg	magnesium
N	nitrogen
NaOH	sodium hydroxide
O	oxygen
RE	rare earth

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