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Original Research Paper

Steady-shear magnetorheological response of fluids containing solution-combustion-synthesized Ni-Zn ferrite powder

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ABSTRACT

Magnetically soft nickel-zinc ferrite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) powder with high saturation magnetization was synthesized by solution combustion route using metal nitrate as precursors and glycine as fuel. The particles were found to have irregular morphology. Three different magnetorheological fluids (MRFs) were prepared by dispersing 10, 20 and 40 wt% of these particles in thin silicone oil. The behaviour of the MRFs was studied under steady shear conditions at different applied magnetic field strengths (B). The yield strength (τ_Y) and viscosity (η) of all the MRFs were found to increase with B and particle fill fraction ϕ, while the response of the MRFs was strongly influenced due to the morphology, microstructure and saturation magnetization of the particles. Owing to the low density of the particles, the observed off-state viscosity is high. However, the excellent thermo-oxidative and chemical stabilities of these magnetic oxide particles than metallic magnetic particles make these MRFs dependable for applications in harsh working environments. In addition, the low cost and feasibility of large scale preparation of these magnetic oxides makes these MRFs further attractive for industrial applications.

1. Introduction

Magnetorheological fluids (MRFs) are smart fluids which have the ability to tune their viscosity reversibly in split-second time, via an externally applied magnetic field. This unique ability makes the MRFs useful for applications involving mechanical shock mitigation and vibration damping, without any permanent failure. The most relevant magnetorheological parameter deciding the efficiency of mechanical impact addressal is the yield strength developed in the MRF on magnetic activation. Conventionally, a high yield strength value can be expected from the MRFs containing metallic magnetic (Fe, Co, Ni or their alloys) particles having high saturation magnetization [1–5]. However, MRFs containing these metallic particles suffer from poor dispersion stability and extremely difficult redispersibility post-sedimentation in carrier fluid as well as chemical instability in ambience/work environments. Although there are methods to circumvent these issues by making use of additives to MRFs [6–12] or coating the particles [13–17], these deteriorate the magnetic properties of particles leading to a decrease in speed of response of the MRF. Moreover, cumbersome synthesis [3,4,18–21] and stringent conditions of preservation of the functional magnetic particles add to the cost of such MRFs, limiting the feasibility of their industrial scale usage.

Hence, in our present work, we investigate the magnetorheological response of MRFs containing an alternate magnetic oxide powder, i.e., Ni-Zn ferrite particles. The interest in choice of Ni-Zn ferrite powder is due to its excellent chemical and thermo-oxidative stabilities and low mass-density (which eliminates the need of additives or coating agents in the MRF). Furthermore, this method of production is highly economical with low (a few minutes) production time, which is industry-friendly. Unlike metallic (such as Fe) particles, the preservation of the Ni-Zn ferrite sample is easy. In addition to the fact that synthesis of Ni-Zn ferrite by solution combustion technique [22,23] needs no sophisticated techniques, it is a reproducible method which uses low-cost precursors. In this study, we have chosen a specific composition, $Ni_{0.5}Zn_{0.5}Fe_2O_4$, due to its best magnetic properties (compared to all other compositions of Ni-Zn ferrites) in terms of saturation magnetization and magnetic softness [24].

Besides their good magnetorheological property, the MRFs containing ferrimagnetic oxide particles also show enhanced dispersion stability against sedimentation due to their low density. There are noteworthy works on magnetorheological fluids based on calcium ferrite nano-crystal clusters [25], manganese ferrite/-

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graphene oxide nanocomposites [26] and highly magnetic zinc ferrite nano-crystal clusters [27].

In the forthcoming sections, we discuss the synthesis procedure of Ni-Zn ferrite powder and their structural, morphological and magnetic properties. This is succeeded by the preparation of MRFs and their magnetorheological characterization under steady-state shear conditions, at different applied magnetic field strengths. The magnetorheological parameters viz. yield strength, ratios of on-state to off-state viscosities of MRFs, their significance and the relationship between these parameters to particle microstructure and magnetic nature are discussed.

2. Materials and methods

2.1 Synthesis of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder and preparation of MRFs

Ni-Zn ferrite powders of different compositions can be synthesized by various methods [28–36], however, the choice of synthesis depends on the required physical and magnetic properties of the product phase. Solution combustion method initially employed by Hwang et al [37] was a two-step process, which involves an initial sol–gel auto-ignition process followed by calcination at an elevated temperature to obtain crystalline ferrite powder with high saturation magnetization (M_S). The process followed in the present synthesis method is a one-step process. In this method, stoichiometric amounts of the precursors (the oxidizer and fuel) were taken. The precursor mixture was magnetically stirred in a borosil container on a hot plate (temperature not exceeding 95 °C) with minimum water content until bubbling, after which the container was transferred to a pre-heated muffle furnace, maintained at ~500 (± 25) °C. The combustion reaction directly occurs at 500 °C. The oxidizers were the metal nitrates and the fuel was glycine. The choice of glycine as fuel was due to the more negative combustion heat (−3.24 kcal g^{-1}) as compared to other fuels such as urea (−2.98 kcal g^{-1}) and citric acid (−2.76 kcal g^{-1})] [38]. In the above synthesis, the total metal nitrate to fuel mass ratio was 3:4.44. This ratio of oxidizer to fuel necessitates no external supply of oxygen [37]. The balanced equation for the reaction to obtain two $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder is given below.

$$\frac{1}{2}Ni(NO_3)_2\cdot 6H_2O + \frac{1}{2}Zn(NO_3)_2\cdot 6H_2O + 2Fe(NO_3)_3\cdot 9H_2O + \frac{40}{9}NH_2CH_2COOH \xrightarrow{\Delta} Ni_{0.5}Zn_{0.5}Fe_2O_4 \times \frac{80}{9} + CO_2 + \frac{100}{9}H_2O + \frac{20}{9}N_2$$

The combustion reaction proceeded with visible flares and the reaction got completed by about 10–15 s after the initiation of reaction. Following this, the furnace was switched off and the foamy product formed was allowed to cool naturally inside the furnace. The fluffy product formed was ground well using agate mortar and pestle before characterization. The obtained $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder was labelled as NZFP.

MRFs were prepared by dispersing 10, 20 and 40 wt% (weight fractions ϕ = 0.1, 0.2 and 0.4) of the NZFP particles in silicone oil without any additives. The kinematic viscosity of silicone oil is ~140 cSt with a specific density of (ρ) 0.96 g/cc. The MRFs were labelled as NZFP-10, NZFP-20, NZFP-40, respectively. The MRF samples were homogenized by mechanical mixing and ultrasonication for ~15 min before magnetorheological characterizations.

2.2 Characterization of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ powder and MRFs

The NZFP sample was characterized by X-ray diffraction (XRD) using a ***PANalytical X'Pert Pro*** diffractometer (λ = 1.540 Å). The phase purity ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) was confirmed by performing Rietveld refinement [39] of XRD pattern using ***FullProf*** [40] and relevant structural information were obtained. The structural and magnetic properties of sample were characterized by ^{57}Fe Mössbauer spectroscopy at RT in transmission mode. The Mössbauer spectra were least square fit using the computer program ***NORMOS*** [41,42]. The morphological characterization of sample was carried out by scanning electron microscopy (SEM). The magnetic property of sample was characterized using ***PPMS 14 T Quantum Design*** magnetometer at RT.

Steady state shear response of all MRF samples (NZFP-10, NZFP-20 and NZFP-40) were carried out using ***Physica MCR 301*** (***Anton Paar***) rheometer, augmented with magnetorheological cell (MRD 70/1T). The magnetorheometer was operated in parallel plate geometry with a shear plate of diameter ~20 mm. The direction of magnetic field was normal to the shear plane, with maximum field strength of 1.2 T. Using water circulation, the temperature of MRF was maintained at RT (28 ± 1 °C).

Before each test, the MRF sample was homogenized by shearing at a rate of 100 s^{-1} for ~5 min. The sample height was confined to 0.3 mm during the entire experiment. The detailed method of magnetorheological characterization is provided elsewhere [43]. The applied field strengths (B) were 0.0, 86.5, 181.5, 365.2, 956.3 and 1200 mT. The corresponding shear stress (τ) and viscosity (η) values were recorded simultaneously, as a function of shear rate ($\dot{\gamma}$), for each B. The maximum applied shear rate was limited to 1000 s^{-1} to avoid expulsion of the MRF at higher shear rates.

3. Results and discussion

The XRD pattern (Fig. 1(a)) confirmed the formation of pure phase spinel (***Fd$\bar{3}$m***) structured $Ni_{0.5}Zn_{0.5}Fe_2O_4$. The Miller indices corresponding to the Bragg reflections of the XRD pattern are shown in Fig. 1(a). The Rietveld refinement of cation occupancy confirmed the stoichiometric phase. The lattice parameter (a) and crystallite size (L) determined by applying Scherrer formula (for (*3 1 1*) Bragg peak of NZFP) are 8.4399 Å and 34.2 nm, respectively. The X-ray density of NZFP sample was ~5.2 g/cc.

The Mössbauer spectrum of NZFP sample (Fig. 1(b)) shows two magnetically split sextets with different isomer shift (δ) values (Table 1), which correspond to the presence of Fe atoms at the tetrahedral (Th) and the octahedral (Oh) sites. Other spectral parameters such as magnetic hyperfine field (B_{hf}) and subspectral area ratios and line width (Γ) are listed in Table 1, which confirm the phase pure $Ni_{0.5}Zn_{0.5}Fe_2O_4$ sample. The ratio of subspectral areas (Th/Oh) confirmed the stoichiometry of the sample.

The scanning electron micrograph for NZFP sample (Fig. 1(c)) shows irregular shaped, network structured powder particles with approximate particle size of ~100–1000 nm. The foamy network structure is formed due to the evolution of gases during the combustion process and during drying/shrinkage of the slurry post combustion. Evolution of higher amount of gases makes the structure porous [44–50]. However, at the synthesis temperature (~500 °C), the coalescence of finer particles is difficult to achieve, especially in ferrites. Furthermore, in solution combustion method, it is very difficult to control the size/shape of the particles, rather the crystallite size can be tuned using different solvents, fuel to oxidizer ratios and temperatures of the reaction [22]. The higher synthesis temperature (~500 °C) facilitates in improving the magnetic properties (increased saturation magnetization) [37].

The M-H loop of NZFP sample (Fig. 1(d)) shows soft magnetic nature of the samples with high M_S value (~62.4 emu/g), narrow hysteresis loop (low $H_C \approx 40.4$ Oe and $M_R \approx 3.7$ emu/g) along with high value of mass susceptibility ($\chi_m \approx 86.8$ emu/g kOe).

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