Journal of Industrial and Engineering Chemistry xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Impact of corrosion process of carbonyl iron particles on magnetorheological behavior of their suspensions

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ARTICLE INFO

Article history:
Received 20 March 2018
Received in revised form 16 May 2018
Accepted 1 June 2018
Available online xxx

Keywords:
Carbonyl iron
Thermal oxidation
Magnetorheology
Magnetic particles
Chemical oxidation

ABSTRACT

The study investigates an influence of carbonyl iron (CI) particles' corrosion on magnetorheological performance of their silicone-oil suspensions. Carbonyl iron particles were oxidized thermally at 500 °C in the air or chemically in 0.05 HCl solution and the as-treated particles were subsequently used as a dispersed phase in magnetorheological suspensions. Corrosive layer on surface of oxidized particles was investigated using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Obtained rheological data was treated with Robertson–Stiff (R–S) model to determine yield stress values and in order to find the yield stress values of prepared magnetorheological (MR) suspensions at saturation level a mathematical model was used. The suspensions based on oxidized particles showed lower values of the yield stress, which was significantly manifested at higher magnetic field intensities due to lower saturation magnetization of the particles.

Introduction

Carbonyl iron is an iron-based powder material, which is widely used in an everyday life. One of the applications where CI is used due to its favorable magnetic properties are MR suspensions, which are systems whose rheological properties can be reversibly changed by a magnetic field [1–3]. They are generally composed of a non-magnetic liquid phase in which magnetic particles are randomly dispersed. Such suspensions behave as Newtonian or pseudoplastic fluids; however, in the presence of an external magnetic field they start to act as viscoplastic solid due to creation of chain-like structures from magnetic particles along a direction of the applied magnetic field [4–7]. This transition and the stiffness of internal distribution of the particles within MR suspensions enables to control the viscosity of the systems, which is successfully utilized in many industrial applications [8–14].

From the long-term application point of view, the sedimentation [15] and chemical and thermo-oxidative stability of the MR suspensions are very challenging [16]. The CI particles are the main part of the MR devices and in long term period their ability to maintain their properties is of high importance. Carbonyl iron (generally iron) tends to undergo corrosion processes leading to oxidation of Fe to Fe^{2+} and Fe^{3+} [17] connected with formation of iron oxides in various forms (FeO, Fe_2O_3, Fe_3O_4) on its surface depending on the conditions. For example when iron is exposed to hydrochloric acid it forms ferrous chloride that further reacts to form solid Fe_2O_3. The oxidation of CI particles generally leads to a loose of their magnetic properties since iron oxides possess significantly lower saturation magnetization, M_S, than CI particles [3], and thus, this lowers the mechanical performance of MR devices. The failure of MR suspensions due to underwent oxidation process can be represented by few phenomena: (i) increase in field-off friction and leakage, (ii) decrease in MR effect due to lowering magnetic performance of particle, and (iii) increase in the field-off viscosity [18]. Ulicny et al. [19] investigated the durability of a MR clutch and it has been found that after 540 h of durability test CI particles used in the MR clutch as a dispersed phase exhibited significant oxidation leading to lowering of torque capacity. An oxide layer was found on the surface of CI particles formed mainly by magnetite. It was further stated that the temperature in the gap area, in which the MR suspension is filled, can reach as high as 250 °C [19]. Moreover, oxidized particles can easily led to undesirable increase of field-off viscosity [20]. When the MR suspensions are exposed to high stresses, the brittle layer of iron oxides can be easily delaminated and thus significantly affect

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https://doi.org/10.1016/j.jiec.2018.06.002
1226-086X/

the rheology of MR suspensions [21,22]. Abe et al. found that the level of oxidation of particles depends on the kind of the dispersive liquid and also found out the formation of a stabilized oxidation film on the surface of the particles. The change of the surface of the particles from the very smooth to very roughed was also observed [23]. Furthermore, a liquid medium in which the magnetic particles are suspended can undergo a decrease in molecular weight in a long-term service [24].

There are efforts to protect CI particles from oxidation using polymeric shell coatings [25–28], silica coating of CI particles increasing their thermal and chemical oxidation stability [29,30], and recently inorganic films based on rare earth elements were successfully introduced on surface of CI particles providing increased chemical and thermal oxidation [31]. However, the impact of oxidation of CI particles on their MR performance has not been quantitatively evaluated yet. The polymeric or inorganic shell on their surface enhances thermal as well as chemical stability of CI particles, nevertheless, the oxidation is not fully inhibited and the coating process also significantly increases the price of MR devices.

This study deals with an impact of thermal and chemical oxidative processes of CI particles on MR performance of their silicone-oil suspensions. Two batches of oxidized CI particles were prepared, the first one through a thermal treatment at 500 °C in the air and the second one by chemical oxidation of CI particles in 0.05 M HCl solution. The oxidation of the particles was evaluated using XPS, XRD and scanning electron microscopy (SEM). A silicone-oil suspension based on non-oxidized CI particles was used as a reference MR suspension.

Experimental part

Sample preparation

Pure CI particles (grade ES; BASF, Germany) were used as a precursor and also as a reference material. The CI particles were further thermally or chemically oxidized, thus, two new samples were prepared using extreme conditions in order to evaluate a high level of the oxidation.

Thermal oxidation

Pure CI particles were treated in a furnace at 500 °C in the air. They were put to the furnace in a ceramic mortar at a room temperature and the heating rate was 10 °C/min. After reaching the final temperature, the furnace was switched off and the particles were left to cool down to room temperature. The particles were then stored in closed ampules in a desiccator. The gain weight of the particles through thermal oxidation process was about 30.6% due to formation of iron oxides, which fits well with the study presented by Mrlik et al. [16]. These particles are further labeled as CI ES-500.

Chemical oxidation

Pure CI particles were treated in a solution of 0.05 M HCl. This concentration was taken according to the literature, where 0.05 M HCl is often used for the investigation of the chemical stability of modified CI particles with a polymeric shell [25,27,32]. Briefly, CI particles were immersed in 0.05 M HCl overnight and the system was gently (50 rpm) mixed using an external mixer. The acidic solution was then left to evaporate at 60 °C and the particles were further dried at 70 °C in a vacuum oven for 24 h. The gain weight of the particles through chemical oxidation was 9.0%. The particles are further labeled as CI ES-HCl.

Particles characterization: XRD, XPS, SEM, magnetization measurements

The crystalline phase structures of prepared materials were identified using X-ray diffractometer MiniFlex 600 (RIGAKU, Japan) equipped with Co X-ray source ($\lambda = 1.79$ Å) in the diffraction angle range 5–90° 2θ. Operation voltage and current being 40 kV and 15 mA, respectively. X-ray photoelectron spectroscopy measurements were performed using a TFA XPS device from Physical Electronics. The base pressure in the XPS analysis chamber was approximately 6×10^{-8} Pa. The samples were excited by X-rays over a 400 μm^2 spot area with monochromatic Al $K\alpha_{1,2}$ radiation at 1486.6 eV. Photoelectrons were detected with a hemispherical analyser positioned at an angle of 45° with respect to the normal to the sample surface. Survey-scan spectra were acquired at a pass energy of 187.85 eV and with 0.4 eV energy step, whereas for Fe 2p, individual high-resolution spectra were taken at a pass energy of 58 eV and with a 0.125 eV energy step. All the spectra were referenced to the main C 1s peak of the carbon atoms, which was assigned a value of 284.8 eV. The spectra were analysed using MultiPak v8.1c software (Ulvac-Phi Inc., Kanagawa, Japan, 2006) from Physical Electronics, which was supplied with the spectrometer. Morphology and size of the particles were investigated using SEM analysis (FEI, NanoSEM450, USA). Magnetization curves of particles were measured by a vibrational sample magnetometer (VSM; Model 7404, Lake Shore, USA) in the magnetic field range of ± 760 kA m^{-1} at a room temperature. The weight of the used samples was between 120–150 mg.

Preparation of MR suspensions

Three MR suspensions were prepared by mixing of the prepared samples with silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic, viscosity $\eta_c = 194$ mPa s). The concentration of the particles in the prepared MR suspensions was always adapted to contain 40 wt% of pure CI. Thus, in the case of MR suspensions based on CI ES, the concentration of the particles was 40 wt%, and in the case of oxidized samples the concentration of the particles was 40 wt% of the pure CI + oxidized mass. Thus, the concentrations of MR suspensions based on CI ES-500 or CI ES-HCl were approximately 46.5 wt% and 42 wt%, respectively.

Magnetorheological measurements

Rheological measurements of the prepared MR suspensions were performed at the shear rates 0.01–100 s^{-1} using a rotational rheometer (MCR 502 Anton Paar, Austria) with an external magnetic cell and a plate-plate geometry with a gap of 300 μm. The MR measurements were carried out in the presence of an external magnetic field of intensity, H, 173–438 kA/m. Before each measurement, the prepared MR suspensions were intensively mixed for about 5 min and in the case of measurement in the presence of an external magnetic field, the magnetic field was applied for 1 min before the measurement in order to provide time enough for the particles to create stable chain-like structures. The measurements were carried out 3 times with a fresh sample for each MR suspension. Oscillatory tests were performed in order to determine viscoelastic behavior of suspensions. Frequency sweep test with fixed strain from linear viscoelastic region ($\gamma = 0.03\%$ obtained from amplitude sweep test) within 0.1–1 Hz was carried out at $H = 438$ kA/m. The magnetic field was applied for 1 min before the measurement in order to provide time enough for the particles to create stable chain-like structures.

Please cite this article in press as: T. Plachy, et al., Impact of corrosion process of carbonyl iron particles on magnetorheological behavior of their suspensions, J. Ind. Eng. Chem. (2018), https://doi.org/10.1016/j.jiec.2018.06.002