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Spinel-Structured Nanoparticles for Magnetic and Mechanical Applications

Malik Anjelh Baqiya, Ahmad Taufiq, Sunaryono, Khuroti Ayun, Mochamad Zainuri, Suminar Pratapa, Triwikantoro and Darminto

Additional information is available at the end of the chapter

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Abstract

Nanoparticles of Fe$_3$O$_4$ have been successfully synthesized using a simple coprecipitation technique from natural iron sands, employing HNO$_3$ and NH$_4$OH as dispersing and precipitating agents, respectively. The substitution of Fe with Mn to result in Fe$_{3-x}$Mn$_x$O$_4$ (0 ≤ x ≤ 3) was conducted to control the magnetic strength of this nano-sized spinel powder. It is shown that magnetic properties depend not only on the particle size and Mn doping but also on the particles clustering. The applications for magnetic fluids, gels, and coating are extensively described. Meanwhile, the spinel MgAl$_2$O$_4$ nanoparticles have also been prepared by the same simple method from commercial starting materials. This powder was used as a nano-reinforcer of Al-matrix composites. In addition, MgAl$_2$O$_4$ micro-sized powder forming a thick layer was successfully grown by electroless plating on the interface of matrix-filler in Al/SiC composites. The strengthening of mechanical properties with respect to the varying uses of these MgAl$_2$O$_4$ powders is discussed.

Keywords: Fe$_3$O$_4$, MgAl$_2$O$_4$ Powders, Coprecipitation, Magnetic, mechanical properties

1. Introduction

Spinels have the general formula of AB$_2$X$_6$, where X can be oxygen (oxides) or a chalcogen element, such as sulfur (thio-spinels) and selenium (seleno-spinels). A and B in the spinel structures can be divalent, trivalent, or tetravalent cations, such as iron, magnesium,
aluminum (Al), zinc, manganese, chromium, and titanium. The various compounds of spinel family including their chemical and physical properties depend not only on the arrangement of cations and anions in the structures but also on how the spinels are produced. The spinels can be magnetic or non-magnetic compounds depending on the nature of the cations among the A and B sub-lattices. Fe$_3$O$_4$ (FeO.2Fe$_2$O$_3$) is one of the so-called spinel ferrite having magnetic properties, whereas MgAl$_2$O$_4$ is also spinel (should not be confused with the spinel structure described earlier) which is non-magnetic one. This chapter covers some of the physical properties of the spinel compounds in more detail.

2. Magnetite (Fe$_3$O$_4$) nanoparticles

Fe$_3$O$_4$ (magnetite) or the black iron oxide in the form of nanoparticles has huge potential for applications in many fields. However, preparing Fe$_3$O$_4$ particles in small size with high quality is enormously challenging for several reasons. Therefore, the preparation of Fe$_3$O$_4$ nanoparticles in several forms and various sizes with high purity and homogeneity becomes an essential task before applications. The following section provides more details on the preparation and applications of Fe$_3$O$_4$ nanoparticles.

Several synthesis methods to prepare high-purity Fe$_3$O$_4$ nanoparticles in various forms and sizes have been reported in the literature. In general, Fe$_3$O$_4$ nanoparticles have been successfully prepared through sonochemical [1], thermal decomposition [2], ionothermal [3], hydro-thermal [4], micro-emulsion [5], sol-gel [6], modified hydrolysis [7], solvothermal [8], electrospinning [9], coprecipitation [10] methods, and so forth. However, high quality of the particles, such as good particle size distribution with high crystalline, structural and compositional homogeneity, still has become one of the main challenges in preparing Fe$_3$O$_4$ nanoparticles [11].

The improvement of synthesis methods has also been carried out for producing Fe$_3$O$_4$ nanoparticles in order to reduce cost and time of preparation. A simple method to produce Fe$_3$O$_4$ nanoparticles via coprecipitation method has been introduced using a local natural iron sand from Indonesia as a starting material. This coprecipitation method is considered to be the easiest method for preparing Fe$_3$O$_4$ nanoparticles [12] because of its simplicity, efficiency, and inexpensiveness [13]. The use of starting material from commercial product can be substituted by natural iron sand.

As for the preparation of Fe$_3$O$_4$ nanoparticles using coprecipitation method, the ratio of ferrous and ferric ions is very crucial affecting the synthesis result. The effects include the particle diameter and magnetic properties. Iida et al. [14] have reported that the valence of the metal salt is an important factor for determining the particle size of the magnetic particles. In their experiments, they have succeeded in obtaining Fe$_3$O$_4$ nanoparticles in the size range of 9–40 nm with various molar contents of ferrous ions in the total amount of the iron ions. Furthermore, Gnanaprakash et al. [15] have also reported that initial pH and temperature of the iron salt solution during coprecipitation process have strong influences for the formation of magnetite nanoparticles. They reported that the average of particle size having initial pH value
of 0.7, 1.5, 3, and 4.7 are 6.7, 7.6, 9.9, and 9.9 nm, respectively. Determination of particle size is very important according to how they will be used for certain applications, namely for magnetic fluids and gels.

In the magnetic nanoparticles’ syntheses, the so-called templating method has been employed to form certain particle shapes and sizes, such as one dimensional (1-D) particles or nanorods. Lian et al. [16] have successfully synthesized nanorods of Fe₃O₄ through the addition of polyethylene glycol (PEG) 1000 as a template with the average particle diameter and length of 80 nm and 2 µm, respectively. Therefore, templating technique has important role on the particle growth of magnetic nanomaterials. The greater value of the PEG’s molecular weight will lead to the higher possibility to obtain nanorods resulted from the synthesis [17]. Furthermore, based on the research of He et al. [18], Fe₃O₄ nanowire has successfully been prepared depending on the volume ratio of PEG and H₂O. They have found that the best formation is achieved with the ratio of 1:3; a higher ratio gives higher viscosity and inhibits the particle formation.

3. Fe₃O₄ spinels for magnetic fluids and gels

Generally, the study of Fe₃O₄ nanoparticles has attracted attention for several disciplines. Physicists investigate the physical properties and propose the theories of the Fe₃O₄ nanoparticles. Chemists focus on the synthesis methods of the Fe₃O₄ nanoparticles. Biologists concentrate on developing Fe₃O₄ nanoparticles in bioapplications. Meanwhile, engineers study Fe₃O₄ nanoparticles with a focus on technological applications. Therefore, there is a great deal of interest in Fe₃O₄ nanoparticles by scientists and engineers, starting from synthesis and characterizations and followed by their many application potentials.

Fe₃O₄ ferrofluids or magnetic fluids are colloidal suspension containing magnetite nanoparticles in single domain, which are dispersed in a liquid carrier. Ferrofluids have unique characteristics because they have both the liquid and magnetic properties. In the ferrofluids, the liquid carriers can be polar or nonpolar medium. In order to prevent agglomerations, the Fe₃O₄ nanoparticles should be layered or covered by an appropriate material as a shell [19]. In the last decades, it has been reported that the Fe₃O₄ ferrofluids can be applied in various fields, that is, optical grating, optical switching [20], thermoelectric conversion [21], quenching media [22], sensor [23], controlling lubricant migration [24], biomedical applications [25], and so forth.

Another application for the magnetite spinel is in ferrogels, namely a hydrogel containing magnetic ferrous particles. The Fe₃O₄-ferrogel can be defined as a polymer (nano)composites with polyvinyl alcohol (PVA) and Fe₃O₄ as the matrix and filler, respectively, cross-linked together with a certain amount of liquid (water). Ferrogels can be physically or chemically cross-linked without any chemical reaction between them. The physical properties of ferrogels depend on the preparation conditions, such as polymer and solvent ratio, particle size, distribution and concentration of the magnetic material. By combining the elastic medium and the magnetic properties from the particles, the elastic behavior of ferrogel can be manipulated
by external magnetic field. This leads to a great opportunity for various advanced applications, namely soft actuators and artificial muscles [26].

In the development of magneto-elastic materials, Li et al. [27] have prepared a polymeric gel in variety of shapes depending on the temperature. Furthermore, Zrínyi et al. [28] have developed a magneto-sensitive gel with Fe$_3$O$_4$ as the magnetic filler. Ramanujan and Lao [26] have successfully produced magnetic gel consisting of PVA and micro-sized Fe$_3$O$_4$ particles for artificial tissues. They have demonstrated an elastic behavior of the gel controlled by an external magnetic field.

4. Spinel MgAl$_2$O$_4$ grown as a thick coating and fillerreinforcer in composites

Compared to the conventional aluminum alloys, aluminum metal matrix composites (Al-MMC) have been used in many kinds of applications (e.g. automobiles) due to their high specific strength and Young’s modulus, improved yield and creep strengths, light weight, and excellent properties of wear resistance. The important parameter for improving their performances lies in the structure and bonding properties between the matrix and fillers. Some materials in any form of particles have been widely used as the particle-matrix interfaces in order to improve the wettability [29], namely MgO, SiC, and Al$_2$O$_3$ in the micro- or nanostructures. It has been noted that the interface, particles size, and its distribution as well as the concentration (volume fraction) play a basic role in the modification of Al-MMC.

A typical way to improve the mechanical properties of Al-MMC is by additional reinforcement or interfacial modification. Recently, the spinel MgAl$_2$O$_4$ has been applied for this purpose. In the last decade, MgAl$_2$O$_4$ has been produced by several methods such as solid-state reaction [30], high-energy ball milling [31], polymerization method [32], pyrolysis [33], sol-gel processes [34, 35], and coprecipitation techniques [36–38]. The shape and size of the spinel particles vary depending on the preparation techniques [39, 40]. This spinel can be prepared in the form of ceramic foams [41, 42], whiskers [43–45], thin films [46, 47], nanoparticles [37, 48, 49], and also layer of particle bonding in composite materials [50]. For the Al/SiC composites, in which Al acts as the matrix and SiC acts as the filler reinforcement, Al$_4$C$_3$ phase can be formed at the interface between matrix and fillers. This phase weakens the mechanical strength of the composite. Up to now, several experimental techniques have been proposed to prevent this problem including adding excessive Si into the matrix and introducing a thin coating layer on the SiC particle surface. The formation of interlayer phase is believed to be a stable interfacial bonding that improves the mechanical properties of the composite. However, the detail of this mechanism remains unclear.

Particulate-reinforced composites with micron-sized filler of various materials are the most commonly used composites in daily life. Particles are typically introduced to enhance the matrix elastic modulus and yield strength. It has been shown that the novel properties of composites are improved by adding nano-scaled particles as the fillers [51]. The key role of mechanical strength in composites is the interface-bonding quality between matrix and filler.
materials. The nano-sized particles have much greater total area compared to particles with larger size at the same volume. The interface interaction can therefore be extended by reducing particle size of fillers down to nanometer scale.

Meanwhile, synthesis of particles in nanometer size of various materials is still an active area of research. Because of their very small size, nanoparticles tend to be aggregate to each other to form larger size particles [52]. As nanometer-scaled filler, the particles have to be kept separate in the matrix. In this context, an effort to maintain nanoparticles as fillers from agglomeration was achieved by the introduction of a surfactant. Tetra-methyl-ammonium-hydroxide (TMAH) could be used as surfactant in the process of filler-matrix-mixing media. Aluminum was chosen as matrix, while MgO and MgAl\(_2\)O\(_4\) were used as nano-fillers. In the case of Al/SiC composites, a thin-layer MgAl\(_2\)O\(_4\) is coated onto the SiC filler to enhance matrix-filler interfacial bonding leading to increased mechanical strength. The SiC fillers were coated by spinel MgAl\(_2\)O\(_4\) by electroless plating, soaking SiC particulate powder in solutions containing Mg and Al ions before heating process to grow spinel phase on the surface.

5. Preparation of Fe\(_3\)O\(_4\) nanoparticles from iron sands

The detail of synthesis method for the preparation of Fe\(_3\)O\(_4\) nanoparticles was described in our previous works [53–57]. The iron sand was extracted by a magnetic separator to obtain dominantly Fe\(_3\)O\(_4\) powders. Using a magnetic stirrer, the hydrochloric acid (HCl) was used to dissolve the Fe\(_3\)O\(_4\) powder to produce FeCl\(_3\) and FeCl\(_2\) solutions at room temperature as written in Eq. (1).

\[
\text{Fe}_3\text{O}_4 + 8\text{HCl} \rightarrow 2\text{FeCl}_3 + \text{FeCl}_2 + 4\text{H}_2\text{O} \quad (1)
\]

The solution of FeCl\(_3\) and FeCl\(_2\) was then reacted by dropping slowly ammonium hydroxide (NH\(_4\)OH) to produce black precipitate at room temperature. The reaction mechanism for producing Fe\(_3\)O\(_4\) particles is described as Eq. (2) [54]

\[
2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} + 4\text{H}_2\text{O} \quad (2)
\]

In order to synthesize Mn\(_x\)Fe\(_{3-x}\)O\(_4\) nanoparticles discussed later and investigate its magnetic properties, the variation of Mn concentration from MnCl\(_2\) solution was also prepared to form Mn\(_x\)Fe\(_{3-x}\)O\(_4\) (0 < \(x\) ≤ 1). The dissolved MnCl\(_2\) solution was mixed using a magnetic stirrer followed by a drop-wise addition of NH\(_4\)OH to obtain the precipitate of Fe\(_3\)O\(_4\) and Mn\(_x\)Fe\(_{3-x}\)O\(_4\). The magnetic moment of Mn\(^{2+}\) ion is 25% higher than that of Fe\(^{3+}\) ion. Therefore, introducing Mn\(^{2+}\) into Fe\(_3\)O\(_4\) to form Mn\(_x\)Fe\(_{3-x}\)O\(_4\) structure will theoretically enhance the magnetization of Fe\(_3\)O\(_4\) [58]. A washing process of the precipitate was then carried out for several times using distilled water until achieving normal pH condition. Finally, the Fe\(_3\)O\(_4\) powders were prepared by drying process at 100°C for 1 h. For the preparation of Fe\(_3\)O\(_4\) magnetic fluid, tetra-methyl-
ammonium-hydroxide (TMAH), as the stabilizing layers of the particles, was added in the precipitate. In the present investigation, Fe$_3$O$_4$ ferrogels were also synthesized using freezing-thawing method as described in Refs. [57, 59].

To study the crystal structure, the particle size and its distribution as well as form and structural factor, and the magnetic properties of the sample, the Fe$_3$O$_4$ powders were then characterized by means of X-ray diffractometry (XRD), small-angle neutron scattering (SANS) spectrometer and superconducting quantum interference device (SQUID) magnetometer, respectively. The XRD measurements were carried out in the 2θ range from 20° to 70° using Cu-Ka radiation. A 36-m SANS spectrometer was used to investigate the primary and secondary particles as well as the fractal structure of Fe$_3$O$_4$ nanoparticles. The detailed SANS measurements have been given elsewhere [54, 60]. The two-lognormal analysis was also performed to investigate the clustering effect of the magnetic fluid and hydrogel [55, 57].

6. Preparation of spinel MgAl$_2$O$_4$ as filler reinforcers

Magnesium oxide (MgO) and magnesium-aluminum oxide (MgAl$_2$O$_4$) as fillers were synthesized by employing coprecipitation process. Mg (Aldrich, 99.9%) and Al (Aldrich, 99.9%) were dissolved in HCl (12.63 molar) with stoichiometric molar fraction. The NH$_4$OH (6.5 molar) was used as precipitating agent to produce Mg(OH)$_2$ and MgAl$_2$O$_4$ after filtering, washing process with distilled water for several times, and finally drying at 100°C. The resulting powders were then heated at 500°C for 1 h to convert them into MgO and MgAl$_2$O$_4$ phases. The powders were checked with XRD and transmission electron microscope (TEM) to explore the phase purity, crystallite size, particle shape, and size.

The MgO and MgAl$_2$O$_4$ powders were mixed with TMAH as surfactant to form a colloid system, consisting of individual MgO or MgAl$_2$O$_4$ particles which were homogeneously dispersed. To fabricate composites, Al powders as matrix were added into the colloid system and followed by thorough stirring and grinding to achieve homogeneity. The mixed powders were dried at 100°C for 3 h and then pressed into pellets having a diameter of 1 cm. During pelletization, the powders were compacted using a force of 1.5 kN applied for 15 min in an isostatic die with zinc stearate on the inner disc. Before sintering process at 500°C for 1 h, pellets were pre-sintered at, respectively, 200 and 400°C for 20 min each. All heat treatments were conducted in a furnace with a controlled atmosphere of low vacuum (∼10$^{-3}$ atm).

The samples produced consist of Al/MgO and Al/MgAl$_2$O$_4$ composites with various volume fractions (% vol) of fillers covering 10, 20, and 30%. We have also prepared the corresponding samples fabricated without TMAH for comparison. To study the effects of surfactant addition during the process on the fabricated composites, measurements of densities, porosity, elastic modulus by compressive test, and microhardness (Vicker’s hardness number, VHN) of the samples were carried out.

Furthermore, to prepare the Al/SiC composites, the aluminum (PA) powders and particles of SiC ceramics (220 mesh) were employed as starting materials. The SiC reinforcement particles
were cleaned by ultrasonic cleaner in alcohol (90%), and then dried in oven at 100°C. The SiC particles were then soaked in an electrolyte media of 40 ml HNO\textsubscript{3} containing Al and Mg ions as the part of the electroless-plating mechanism. The process of metal oxide coating was done using a magnetic stirrer at 125°C. The oxidation of SiC particles to grow the MgAl\textsubscript{2}O\textsubscript{4} layer was performed in a furnace at 200°C for 1 h, and continued at 400°C for another 1 h. The electrolyte media for electroless plating can be controllably adjusted to grow various metal oxides on the SiC surface, such as MgO, CuO, Al\textsubscript{2}O\textsubscript{3}, and so forth, besides MgAl\textsubscript{2}O\textsubscript{4}. The metal oxide-coated SiC particles were mixed with Al powders in n-butanol (wet mixing) using magnetic stirrer at 100°C, having SiC volume fraction (%vol) of 10, 20, and 30%. The heating process of the green pellets was carried out in a vacuum (10\textsuperscript{-3} Torr, rotary pump) by applying a pre-sintering at 200°C for 20 min and followed by sintering at 600°C for 1 h.

7. Results and discussion

7.1. Fe\textsubscript{3}O\textsubscript{4} nanoparticles: magnetic properties and applications

The XRD pattern of Fe\textsubscript{3}O\textsubscript{4} nano-powders is shown in Figure 1. All peaks in the pattern show a single phase of spinel structure corresponding to the crystal structure of Fe\textsubscript{3}O\textsubscript{4} with PDF No. 19-0629 without any impurity. Based on the Rietveld analysis, the sample has lattice parameter \(a = b = c\) of approximately 8.377 Å.

![Figure 1. The XRD pattern of Fe\textsubscript{3}O\textsubscript{4} nano-powders (using Cu-K\textalpha radiation).](image)

The SANS pattern of the Fe\textsubscript{3}O\textsubscript{4} nano-powders is presented in Figure 2. The SANS data were analyzed using a lognormal spherical model as a form factor \(P(R)\) and mass fractal model as a structure factor \(S(q)\), following Eqs. (3) and (4), respectively,
with $R_0$ and $\sigma$ representing the radius of the distribution and standard deviation, respectively [61],

$$S(q) = 1 + \frac{DF(D-1)}{(qR)^D[1+1/(q^2\xi^2)^{D-1}/2]^2} \sin[(D-1)\tan^{-1}(q\xi)] \tag{4}$$

where $q$, $\Gamma$, $D$, and $\xi$ represent the scattering vector, gamma function, fractal dimension, and cut-off distance, respectively [62]. The SANS curve was fitted globally using two lognormal spherical model as form factor combining with mass fractal model as structure factor regarding Eq. (5) [54]

$$I(q) \simeq \int_0^\infty N_1(R_1) F_N^2(q,R_1) dR_1 + \int_0^\infty N_2(R_2) F_N^2(q,R_2) dR_2 S(q,\xi,D,R_2) \tag{5}$$

Here, $I$ is the density, $N$ is the number density of particles, $R_1$ is the primary particle, $R_2$ is the secondary particles or clusters, and $F$ is the scattering amplitude.
Based on the analysis using lognormal and mass fractal models, the Fe$_3$O$_4$ nano-powders have hierarchical nanostructure with the primary particles of 3.8 nm as a building block constructing secondary particles as clusters of 9.3 nm. The clusters of Fe$_3$O$_4$ nanoparticles have a fractal structure in three-dimension with fractal dimension of 2.9. The SANS data analysis of magnetic nanoparticles coincides with the image produced by high-resolution transmission electron microscopy (HRTEM) as shown in the previous work [54]. The details of the analysis of SANS data of the Fe$_3$O$_4$ nanoparticles were presented in the previous work [54].

The magnetic properties of the Fe$_3$O$_4$ nanoparticles as well as M versus H variations and zero-field-cooling (ZFC) curves are presented in Figures 3 and 4. The M versus H curve of the Fe$_3$O$_4$ nanoparticles was collected at room temperature by sweeping the magnetic field from -5 to 5 T. The Fe$_3$O$_4$ nanoparticles have saturated magnetization of 37.1 emu/g. Regarding Figure 3, it is clear that the M-H curve of sample has S-shape with nearly zero coercivity field, indicating the superparamagnetic behavior at room temperature. This result is consistent with the recent paper by Abboud et al. [63] where the magnetization was almost zero in the absence of external magnetic field. The superparamagnetic phenomenon in the magnetic nanoparticles has also been observed in the Fe$_3$O$_4$@SiO$_2$ core-shell composites [64], the dispersed Fe$_3$O$_4$ in the polymer matrix [65], and Fe$_3$O$_4$-LiMo$_3$Se$_3$ [66]. Moreover, the zero-field-cooling (ZFC) measurement was also carried out to investigate the superparamagnetic phenomenon of the sample as shown in Figure 4. Based on the results in Figure 4, it is evident that the sample has a maximum peak of magnetic blocking temperature, $T_B$, at 243 K. Theoretically, $T_B$ depends on the particle size and shape so the increase of nanoparticle's volume will increase the $T_B$ value [67].
Dutta et al. [68] have reported that Fe$_3$O$_4$ nanoparticles with the particles size ranging from 4 to 12 nm have blocking temperature lower than 100 K, which is not similar to the result of this work. The difference of these results can be explained in a sense of the presence of clusters or aggregations phenomena in the present work. In Ref. [68], the samples were constructed with primary particles in relatively homogeneous samples without any clusters or aggregations. On the other hand, the sample in this work consists of hierarchical nanostructures of primary particles forming secondary particles or clusters with fractal dimension in three-dimensions. Despite the particles size and anisotropy constant, the clusters of magnetic nanoparticles give an effect on the blocking temperature. Theoretically, at magnetic-blocking temperature, the thermal energy of particles is comparable with the anisotropy energy barrier. In bulk, the Fe$_3$O$_4$ is ferrimagnetic generated by net magnetic moments at tetrahedral and octahedral sites. The effect of clusters on magnetic properties was also documented by other researchers [69, 70].

In the magnetic nanoparticles, there is the so-called blocking temperature or the energy barrier that can be obtained from ZFC and field-cooling (FC) magnetization curves. With increasing temperature, a curve peak should appear in the ZFC measurement. This peak temperature can be considered as the average $T_B$ in the magnetic material. On the other hand, the increase of magnetic field should decrease the barrier energy, and results in a shift of the blocking temperature to lower temperatures. A typical of nanocrystalline Fe$_3$O$_4$ has shown superparamagnetic behavior (Figure 3). The superparamagnetism is related to the random fluctuation of the magnetization of a single domain when the thermal energy overcomes the anisotropy energy barrier. Below the $T_B$, the magnetization of each domain of nanoparticles is oriented parallel to a certain crystallographic direction or the easy axis with minimum energy. Consequently, the magnetization is blocked in the nanoparticles. Above $T_B$, the thermal energy can
overcome the anisotropy energy (barrier energy) and the magnetization starts fluctuating and the magnetic susceptibility follows modified Curie-law behavior at higher temperatures [71].

The effect of Mn\(^{2+}\) substitution on the magnetic properties of Mn\(_x\)Fe\(_{3-x}\)O\(_4\) nanoparticles has been intensively studied recently [54, 72]. It has been found that the lattice parameters and crystal volume of the Mn\(_x\)Fe\(_{3-x}\)O\(_4\) increase with the increase of Mn content. This is due to the fact that the ionic radius of Fe\(^{2+}\) is smaller than that of Mn\(^{2+}\) substituted in the spinel structure. Fe\(_3\)O\(_4\) without any substitution has a cubic spinel structure, where the Fe\(^{2+}\) and Fe\(^{3+}\) ions occupy the tetrahedral (A) and octahedral (B) sites represented by (Fe\(^{3+}\))\(_A\)(Fe\(^{3+}\)Fe\(^{2+}\))\(_B\)O\(_{2-}\). The Fe\(_3\)O\(_4\) is one example of the cubic inverse spinels, in which there is a mixed valence of Fe ions on the octahedral sublattice. In the Mn\(_x\)Fe\(_{3-x}\)O\(_4\), the cationic distribution can be written as follows [54]:

\[
\left(\begin{array}{c}
\left(\text{Mn}^{2+}\text{Fe}^{3+}\right) \text{A} \\
\left(\text{Fe}^{2+}\text{Fe}^{3+}\right) \text{B}
\end{array}\right)
\]

The Mn\(^{2+}\) ions occupy the A sites of the spinel structure. A further analysis of the SANS data of the Mn\(_x\)Fe\(_{3-x}\)O\(_4\) nanoparticles from \(x = 0\) to 1 using the lognormal function has found that the particle size of the Mn\(_x\)Fe\(_{3-x}\)O\(_4\) depends on the Mn content. In this study, the increase of Mn content results in the smaller size of the nanoparticles. Moreover, the nanoparticles of Mn\(_x\)Fe\(_{3-x}\)O\(_4\) tend to become larger aggregates or clusters. The Mn content, particle size, and particle clustering are important factors influencing the magnetic properties of nanomaterials.

Taufiq et al. [55] have successfully synthesized Fe\(_3\)O\(_4\) magnetic fluid with a chain-like spinel structure using coprecipitation method. These results show that the Fe\(_3\)O\(_4\) ferrofluid has a primary particle size of about 7.6 nm and the size of fractal aggregates of about 45 nm constructing the chain-like structure. Even though there were chain aggregates, a homogeneous particle distribution with low polydispersity value of about 0.4 was found, which is lower than that in the former paper [55]. It is reported that both nanoparticles of Fe\(_3\)O\(_4\) and Mn\(_x\)Fe\(_{3-x}\)O\(_4\) (\(x\) up to 1) exhibit superparamagnetic behavior and their saturation magnetization decreases with increasing Mn content [54, 72].

In the research of magnetic hydrogels, Fe\(_3\)O\(_4\) ferrogels have been investigated by Sunaryono et al. [57]. It has been reported that the magneto-elastic properties of the ferrogels were strongly affected by the preparation technique, the ratio of the magnetic particle and the polymer, and magnetic particle content as well as the particle clustering and distribution. It has also been shown that the magneto-elasticity of the ferrogel tends to decrease with the increasing Fe\(_3\)O\(_4\) content from 2.5 to 15% [56, 57]. Further analysis of the SAXS data using the two-lognormal distribution function showed that Fe\(_3\)O\(_4\) in the hydrogel has primary particles of about 3 nm with an average particle distance of about 18 nm. Higher Fe\(_3\)O\(_4\) concentration in the hydrogel leads to the increase of Fe\(_3\)O\(_4\) cluster size. Due to the surface effect, it influences the magnetization value of the ferrogel. Consequently, the saturation magnetization drops with decreasing particle size and the cluster of Fe\(_3\)O\(_4\) nanoparticles in the hydrogel. It has been confirmed that Fe\(_3\)O\(_4\) ferrogel exhibits a superparamagnetic behavior at room temperature which is a crucial parameter for biomedical applications.
7.2. Improved mechanical properties of aluminum matrix composites with surfactant-coated MgAl₂O₄ nanofillers and MgAl₂O₄-coated SiC particulates

Figure 5 presents the XRD spectra (using Cu-Kα radiation, λ = 1.54 angstrom) of MgO and MgAl₂O₄ particles as results of coprecipitation process. The powders seem to be single phase as can be seen from the spectra, where no other additional diffraction peak is observed, except those associated with Miller indexes belonging to the MgO (periclase phase) and MgAl₂O₄ (spinel phase) as specified in Figure 5. Besides, the diffraction peaks are much broadened, featuring that the crystal is in nanometer size. If we take the full-width at half maximum (FWHM) of diffraction peaks, by using Scherrer formula [73] and taking the apparatus-broadening correction into account, we arrive at crystallite sizes of 17.5 ± 2.3 and 6.3 ± 0.7 nm for MgO and MgAl₂O₄ powders, respectively.

![Figure 5. XRD spectra of MgO and MgAl₂O₄.](image1)

![Figure 6. TEM images of (a) MgO and (b) MgAl₂O₄.](image2)
It is interesting to correlate the above crystallite size to the particle size of powders from TEM images depicted in Figure 6. The particle size for both powders, MgO in Figure 6a and MgAl₂O₄ in Figure 6b, is seen to be between 50 and less than 100 nm, confirming that the powders can be classified as nanoparticles. The shape of particles is observed to be varied from spherical, square, square with rounded edge, to semi-rod. Comparing the crystal and the particle sizes, one can consider that both MgO and MgAl₂O₄ powders contain secondary particles, where each particle is constituted by several crystals or grains.

Figure 7. Porosity of sintered Al/MgO and Al/MgAl₂O₄ composites with fillers specified.

Figure 8. Elastic moduli of sintered Al/MgO and Al/MgAl₂O₄ composites with fillers specified.

To discuss further, the physical properties of composites, the density of pellets in the green state (after compaction) and after sintering significantly increases with increasing volume fraction of fillers and the use of surfactant (coated fillers by surfactant). The enhanced density
has led to the lowering porosity in the pellets. By applying the formula to define porosity [52]: 
\[ \rho = 1 - \frac{\rho_s}{\rho_t} \]
where \( \rho_s \) and \( \rho_t \) stand for, respectively, sintered and theoretical densities, the porosity of samples is exhibited in Figure 7. The increase of pellet densification has directly affected the mechanical properties, as reflected by the results of compressive tests (yielding elastic modulus) and hardness (VHN) measurements (see Figures 8 and 9).

![Figure 9. Micro-hardness of sintered Al/MgO and Al/MgAl\(_2\)O\(_4\) composites with fillers specified.](image)

It is worth noting that the role of surfactant is to enhance the physical and therefore mechanical properties of these Al/MgO and Al/MgAl\(_2\)O\(_4\) nanocomposites. The TMAH as a mixing media of matrix and filler is an ionic molecule which will attach on the surface of nanoparticles. A metal-oxide nanoparticle is usually deficient of oxygen ion [74], hence its surface is positively charged. The negatively charged end of TMAH molecule is therefore attracted by metal-oxide surface, while the opposite end is dangled. It may further create the situation where one may consider that MgO or MgAl\(_2\)O\(_4\) nanoparticle is “coated” by TMAH. This in turn avoids nanoparticles from aggregation to each other in the matrix. So, the filler is still in nanometer scale to maintain its larger surface area, especially compared to the agglomerated fillers having the same volume fraction in the composites fabricated without TMAH. The larger filler surface will lead to stronger interface bonding between matrix and filler.

The next attractive point to address is that the surfactant-coated MgO filler has led to considerably enhanced elastic modulus (~60%) and microhardness (~40%) of the Al-matrix nanocomposites (Figures 8 and 9). The periclase phase of MgO has simpler crystal structure than the spinel MgAl\(_2\)O\(_4\) one [75, 76]. The former phase is transformed from Mg(OH)\(_2\) at 500°C, whereas the latter one is already stable from 100°C as a result of coprecipitation process. Besides particles consolidation during the sintering at 500°C, the MgO filler will be possibly able to react further in a limited amount with Al matrix to form spinel phase on the matrix-filler interface, creating a strong bonding. Such kind of process, except consolidation, may not occur in the Al/MgAl\(_2\)O\(_4\) composite, because of stable MgAl\(_2\)O\(_4\).
Going to further study on Al/SiC composites, it can be seen in Figure 10 that a very clear distinction exists between SiC particles without coating and with coated metal oxides on the surface based on the modulus elasticity. The entire filler volume fraction (%vol) of SiC in Al-SiC composites using coatings has higher value than that without coating. The experimental results show that the modulus of elasticity of the composites using metal-oxide coating approaches the theoretical prediction [77], estimating a limit of lower and upper bounds. Based on the stress analysis, the composite having filler without metal oxide coating, for all low-volume fraction of reinforcement, the modulus value lies in the outside of the upper and lower bounds, which indicates weak interaction between matrix and filler. This is much different from composites with filler using metal oxides, where for the entire volume fraction of reinforcement, the elastic modulus lies inside the region of the upper and lower bounds, implying that the compactibility between matrix and filler, and reinforcements are therefore going well. One can see in Figure 10 that coating with MgAl$_2$O$_4$ onto the SiC surface has produced the superior Al/SiC composites among the prepared samples, followed by Al$_2$O$_3$ and MgO. The three metal oxides coating materials mentioned seem to be compatible in facilitating and therefore enhancing interfacial bonding between Al matrix and SiC filler in the composites.

8. Conclusions

1. Fe$_3$O$_4$ and the Mn$_x$Fe$_{3-x}$O$_4$ (0 < $x$ ≤ 1) nanoparticles have been successfully prepared by coprecipitation method utilizing a local natural source (viz. natural iron sand) as the main raw material.

2. The structures of Fe$_3$O$_4$ and Mn$_x$Fe$_{3-x}$O$_4$ (0 < $x$ ≤ 1) nanoparticles, magnetic fluid, and magnetic hydrogel have intensively been studied by XRD, TEM, SANS, and SAXS data. These studies show that the magnetic materials have inverse spinel structure with a primary particle size of around 3–4 nm.
3. The magnetic properties have also been investigated by observing the hysteresis (M-H) behavior. It is found that Fe$_3$O$_4$ and Mn$_x$Fe$_{3-x}$O$_4$ ($0 < x < 1$) nanoparticles exhibit superparamagnetic behavior at room temperature which depends on the particle size, doping content, and particle clustering.

4. The physical and mechanical properties of Al/MgO and Al/MgAl$_2$O$_4$ nanocomposites have been enhanced by the introduction of TMAH as surfactant during the mixing process of matrix and filler. The surfactant-coated MgO seems to be a more efficient filler compared to the surfactant-coated MgAl$_2$O$_4$ for the lower content (<30%). The experiment results show that the elastic modulus of the samples with volume fraction of fillers up to 30% was enhanced by more than 60% and 40%, respectively, for Al/MgO and Al/MgAl$_2$O$_4$. The use of other kind of surfactant needs to be explored to further enhance the mechanical properties.

5. A layer of the spinel MgAl$_2$O$_4$ micro-sized grown on the surface of SiC filler has induced the enhancement of mechanical properties of the Al/SiC composites.

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Author details

Malik Anjelh Baqiya$^1$, Ahmad Taufiq$^2$, Sunaryono$^2$, Khuroti Ayun$^1$, Mochamad Zainuri$^1$, Suminar Pratapa$^1$, Triwikantoro$^1$ and Darminto$^{1*}$

$^*$Address all correspondence to: darminto@physics.its.ac.id

1 Advanced Materials Research Group, Department of Physics, Sepuluh Nopember Institute of Technology (ITS), Surabaya, Indonesia
2 Department of Physics, State University of Malang (UM), Malang, Indonesia

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