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RESEARCH PAPER

Characterization of Al_2O_3 in Fe_3Al-30 vol.% Al_2O_3 Nanocomposite Powder Synthesized by Mechanochemical Process

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ABSTRACT

During the last decade, mechanochemical synthesis, which can provide the nanostructured constituents, has been considered as an alternative technique to the conventional thermite reactions to produce the metallic-ceramic composite. Detection of the reinforcement in such nanocomposite powders has been provided challenges as a result of low volume fraction and high induced lattice strain. In this work, the mechanochemical reaction of a non-stoichiometry Fe_2O_3-Al system (Fe_2O_3+Al+Fe powder mixture) was performed to produce the Fe_3Al-30 vol.% Al_2O_3 nanocomposite. The progress of the reaction was followed by X-ray diffractometry (XRD) and transmission electron microscopy (TEM). XRD analysis of mechanochemically synthesized Fe_3Al-30 vol.% Al_2O_3 nanocomposite showed no evidence of the produced Al_2O_3 phase, whereas TEM analysis revealed the crystalline Al_2O_3 phase. The X-ray absorption by component higher mass absorption coefficient (Fe_3Al matrix) in highly strained nanocomposite leads to a decrease in the diffraction intensity of components with lower mass absorption coefficient and with low volume fraction (Al_2O_3). High-temperature heat treatment lead to crystallite growth as well as lattice strain reducing, which resulted in the capability of detection of Al_2O_3 by XRD analysis.

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INTRODUCTION

Displacement chemical reaction, which is the reaction between precursors through the exchange of the element, has been numerously studied to the synthesis of a ceramic-metallic composite. Most of the investigated displacement reactions have been focused on the reduction of metal-oxides, -chlorides and -sulfides by a more reactive metal such as Al, Zn, and Mg. The products of displacement reaction of a ceramic and reactive metal typically consist of two phases, the newly formed metallic phase (as a result of reduction of the ceramic phase) and the newly formed ceramic phase (as a result of oxide, chloride, or sulfide formation of reactive metal). Displacement reaction between metal oxides and reactive metals can be done in various routes such as molten-reaction, reactive-sintering, self-propagating high-temperature synthesis (SHS), and mechanochemical synthesis. The main advantage of these methods to produce metallic-ceramic composite is the in-situ formation of components as a result of displacement reaction, which will be resulted in the formation of phases in the composite with homogenous relationship [1-7].

During the last decade, mechanochemical synthesis has been considered as an alternative

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technique to reactive-sintering and SHS to produce the metallic-ceramic composite powder because of its advantages such as low temperature requirement as well as capability of the formation of nanostructured constituents [3-6, 8]. Hence, the metallic and ceramic phases will be homogenously distributed and connected to each other in a composite microstructure (as a result of in-situ formation) and produce a nanostructured composite (as a result of high energy mechanical collisions induced by ball milling process).

The sequential fracture and welding of the precursors during high energy collisions in the grinding media is the primary mechanism of mechanochemical reactions, which can be resulted in formation of short-range diffusion paths leading to chemical reactions without kinetic constraint. Moreover, such high energy mechanical collisions during milling can result in the formation of nanostructured products.

Generally, the displacement reactions can be occurred through completely different reaction kinetics, namely sudden or gradual reaction. A self-propagating combustion will be taken place in the sudden reaction mode, in which the reaction enthalpy is high enough. On the other hand, the gradual mechanochemical reaction will be done without any combustion because of low formation enthalpy change of the products, and consequently, the kinetic of reaction cannot be influenced by such a low heat generated during the reaction. The sudden mechanochemical reaction has been experimentally revealed by a quick increase in the temperature of milling media as a result of the heat of combustion. In contrast, the gradual mechanochemical reaction has no sign of temperature changes [2, 4, 7].

It is well known that the theoretical adiabatic temperature (T_{ad}) of a displacement reaction can represent the temperature of released heat of such reaction. T_{ad}, which can be calculated based on the heat of reaction as well as melting points and heat capacities of products, can be used as a criterion for determining the modality of the reaction. For the self-propagating combustion reactions, the T_{ad} of a reaction should be higher than 1800 K in a thermally ignited system (SHS synthesis) and higher than 1300 K for a mechanochemical reaction [2-4]. Hence, most of the displacement reaction between metal oxides and reactive metals (according to the Ellingham diagram) can be happen through a sudden self-propagating combustion reaction. Numerous studies on mechanochemical reduction of metal oxides such as CuO, Fe_2O_3, NiO, ZnO, Nb_2O_5, MoO_3, and etc. by Al have been reported, which resulted in formation of Al_2O_3-M (M=Cu, Fe, Ni, Zn, Nb, Mo) nanocomposite powder [1-6]. Such reduction of metal oxides by Al in the stoichiometry ratio of precursors will be happening through a sudden self-propagating combustion reaction, whereas in the non-stoichiometry ratio will be happening in a gradual mode without combustion. It is worth to mention that the non-stoichiometry ratio of metal oxides and Al precursors will be usually selected to adjust the volume fraction of constituents in composite and/or to synthesize new component. The high heat of reaction in the stoichiometry ratio leads to the formation of crystalline constituents during mechanochemical synthesis. On the other hand, in the non-stoichiometry ratio, the combustion will not happen, and the products could be amorphous. The X-ray diffraction (XRD) method is used as a unique and facile method to evaluate the structural changes during mechanochemical synthesis, and this technique has only reported the crystalline and amorphous state of the products. XRD method has a limitation in the detection of low volume fraction constituents in the multi-component materials. Furthermore, X-ray diffraction can be significantly affected by nano-scale crystalline size as well as lattice strain, which are happen in the mechanochemically synthesized nanocomposite powder. Hence, complementary analysis such as electron diffraction using transmission electron microscopy (TEM) is needed for finding the amorphous or crystalline state of products of the mechanochemical synthesis technique.

In this paper, the incapability of XRD for detecting of relatively low volume fraction of Al_2O_3 with the nano-scale crystallite size synthesized by the mechanochemical reaction in a non-stoichiometry Fe_2O_3-Al system (Fe_2O_3+Al+Fe powder mixtures to produce Fe_3Al-30 vol.% Al_2O_3 nanocomposite) was considered.

MATERIALS AND METHODS

The raw materials were Fe_2O_3 (< 5µm, 99.99% purity, Merck), Fe (< 300µm, 99.5% purity), Al (particle size < 100µm, 99.5% purity), and nanosized-Al_2O_3 (n-Al_2O_3, particle size < 100nm, 99.98% purity, Johnson Matthey Co) powders. Two different powder mixtures were selected to

produce the Fe_3Al-30 vol.% Al_2O_3 nanocomposite, namely MC-Fe_3Al-30Al_2O_3 (synthesized by the mechanochemical process of Fe_2O_3+Al+Fe powder mixture) and MA-Fe_3Al-30Al_2O_3 (Synthesized by the mechanical alloying process of n-Al_2O_3+Al+Fe powder mixture). A Spex8000 type ball mill consists of two 75 ml volume hardened steel vials was used for milling of powder mixture under argon atmosphere. The total powder mixture of 7 g without any process control agent was used, and the ball-to-powder weight ratio was selected as 5:1. The powder obtained by the mechanochemical synthesis process was used for further characterization. To study the effect of heat treatment, the milled powder was uniaxially cold pressed at a pressure of 250 MPa and then sintered in vacuum (10^{-2} torr) at 1400 ºC for 1 h.

X-ray diffraction (XRD) analysis was performed to determine the phase transformation during mechanochemical reaction and sintering using a Philips X'PERT diffractometer with Cu K_α radiation (λ=0.15418 nm). Williamson-Hall method [9] was used to analysis of XRD patterns for calculating the crystallite size and average lattice strain of samples. Transmission electron microscope (TEM) observations were performed using a Philips CM200 field emission gun microscope (camera constant (λL) = 0.7521 nm.mm) equipped with energy dispersive spectrometer (EDS). TEM specimens were prepared by deposition of a suspension of powders in ethanol on a carbon-coated copper microgrids.

RESULTS AND DISCUSSION

Since, high-temperature mechanical properties of Fe_3Al intermetallic compound can be improved by incorporation of hard ceramic particles such as Al_2O_3 into the matrix [10, 11], several studies have been reported to produce Fe_3Al-Al_2O_3 composites such as Fe_3Al-20 vol.% Al_2O_3 composite synthesized by the reactive-sintering process [11]. By mechanochemical process, Fe_3Al-57 vol.% Al_2O_3 nanocomposite powder can be synthesized by a stoichiometry powder mixture ($3Fe_2O_3$+8Al), which was identified as a sudden (combustion) mechanochemical reaction [12]. Since the high fraction of Al_2O_3 in the matrix can significantly affect the properties and performance of Fe_3Al compound, it is usually desirable to incorporate a lower fraction of reinforcements (Al_2O_3) in the matrix (Fe_3Al). To synthesize the Fe_3Al-Al_2O_3 composite with a lower volume percent of Al_2O_3, the elemental Fe was added to the Fe_2O_3+Al powder mixture [13, 14]. The thermodynamics studies based on adiabatic temperature, T_{ad}, revealed [13] that the addition of elemental Fe powder to Fe_2O_3+Al powder mixture change the modality of mechanochemical reaction from sudden (combustion) to gradual mode.

XRD patterns of Fe_2O_3+Al+Fe powder mixture as-received and after different milling times are shown in Fig. 1 (a-f). As can be seen, the peak position of precursors remained unchanged up to 6 h of milling time, but the width of XRD peaks increased as a result of refinement of crystallite size as well as increase in the level of internal strain. The crystallite size and average lattice strain of Fe_2O_3 were calculated to be 54 nm and 0.93%, respectively. The microstructure of powder particles at this stage has consisted of Fe_2O_3 particles embedded in Fe/Al layered structure, which has been revealed previously [13]. Fe_3Al phase began to form after 8 h of ball milling. On further milling, the fraction of Fe_3Al phase gradually increased. As seen in Fig 1(d), the peaks of Fe_3Al rise up beside the Fe peaks, and the peaks could be divided into two shoulders, indicating the formation of a new product. After 20 h of milling time, only three symmetric peaks were observed on the XRD pattern, implying that the formation of Fe_3Al is completed. The Fe_3Al intermetallic compound had a disordered structure with crystallite size and average lattice strain of 40 nm and 1.15%, respectively.

The Bragg peaks of Al_2O_3 are not observed on XRD pattern of final products (Fig. 1). The absence of Al_2O_3 peaks can be due to the amorphous structure of mechanochemically synthesized Al_2O_3 phase, which may be resulted from non-combustion (gradual) reaction mode. On the other hand, low volume fraction as well as the nano-scale crystallite size with high lattice strain of mechanochemically synthesized Al_2O_3 phase in this sample, could also be the reason. Hence, Electron diffraction and EDS analysis were performed using TEM to investigate the elemental analysis and crystallinity of the mechanochemically synthesized Al_2O_3 phase. The bright-field (BF) image of the mechanochemically synthesized Fe_3Al-30 vol.% Al_2O_3 (MC-Fe_3Al-30Al_2O_3) powder particle along with the EDS analysis and corresponding selected area diffraction (SAD) pattern are presented in Fig. 2. EDS analysis indicated some area with a high concentration of aluminum and oxygen elements

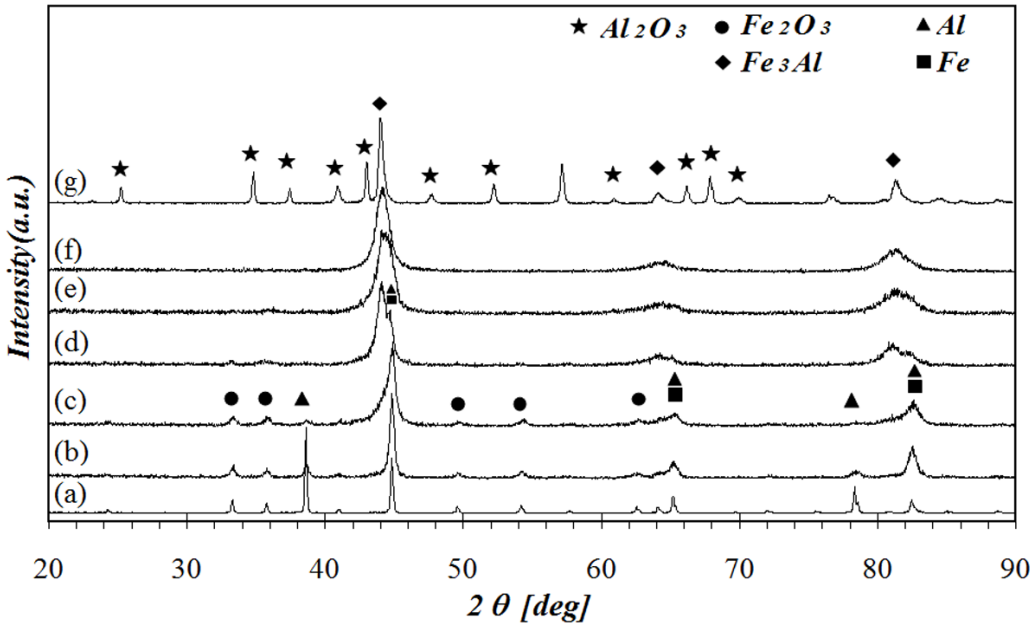

Fig. 1 XRD patterns of Fe_2O_3-Al-Fe powder mixture (a) as-received, (b-f) after 3, 6, 8, 10, and 20 h of milling time, respectively, and (g) after 20 h of milling time followed by sintering at 1400 ºC for 1 h.

corresponding to the Al_2O_3 phase. The spectra of carbon and copper are from carbon-coated copper grid. The corresponding SAD pattern showed no amorphous ring indicating that Al_2O_3 has a crystalline structure. Therefore, it can be concluded that the Al_2O_3 phase can be formed directly during the gradual mechanochemical reaction in the non-stoichiometry powder mixture of Fe_2O_3+Al+Fe and absence of the diffraction peaks of Al_2O_3 can be due to its low volume fraction as well as nanocrystalline nature of synthesized powders.

To investigate the effect of crystallite size as well as lattice strain on the XRD pattern, the Al_2O_3 nanopowder (n-Al_2O_3) was added to the Al+Fe powder mixture, and ball milled to synthesize the mechanically alloyed Fe_3Al-30 vol.% Al_2O_3 (MA-Fe_3Al-30Al_2O_3) nanocomposite powder. XRD

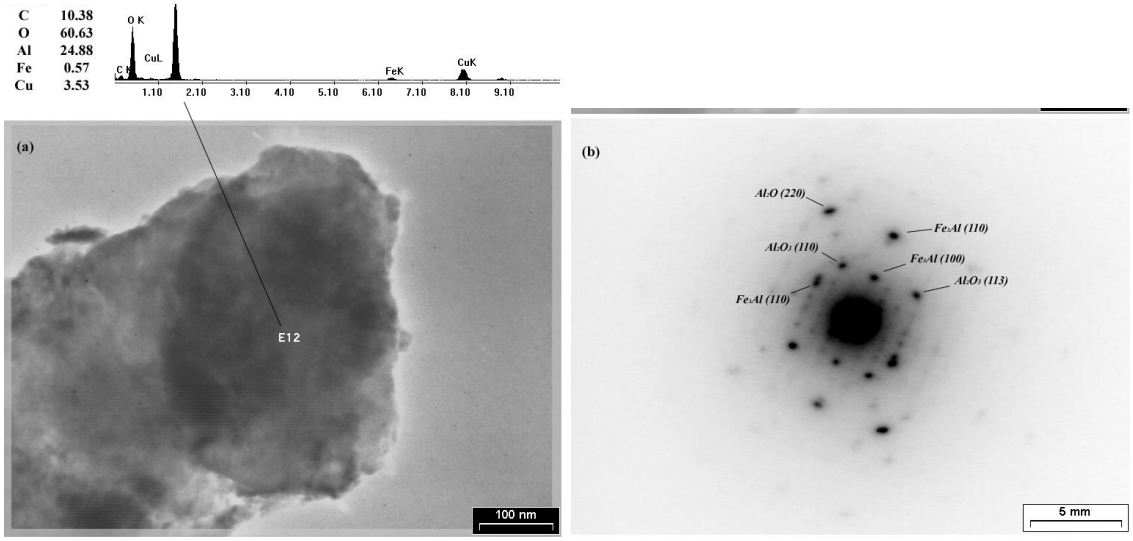

Fig. 2 (a) TEM bright field micrograph of Fe_2O_3-Al-Fe powder mixture (Fe_3Al-30 vol.% Al_2O_3 nanocomposite) after 20 h of milling time along with EDS analysis and (b) corresponding SAD pattern.

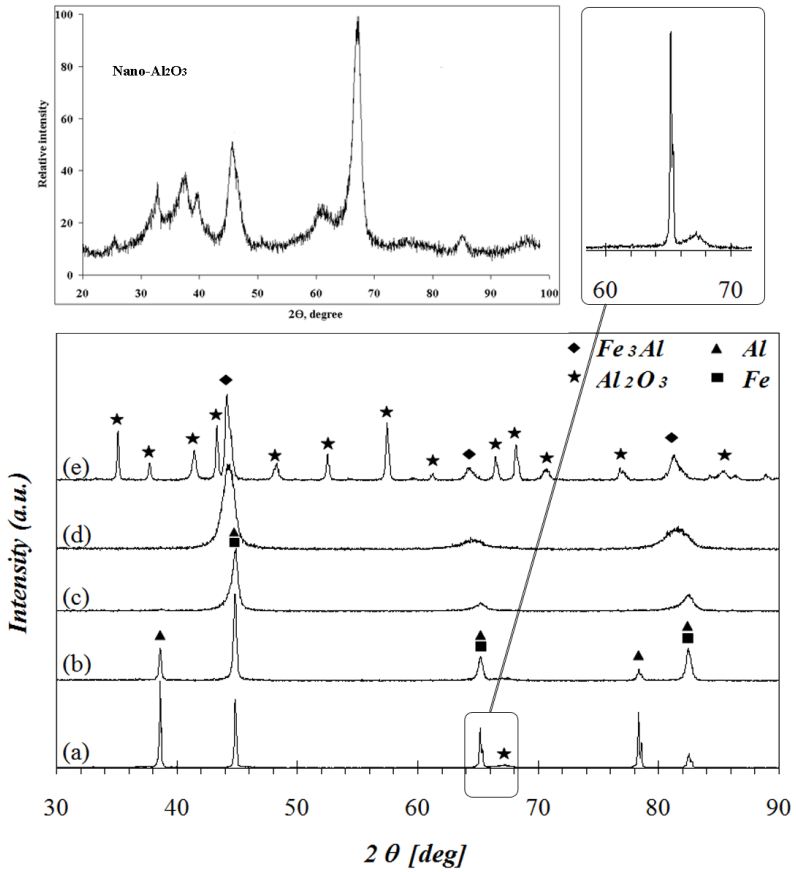

Fig. 3 XRD patterns of nano-Al_2O_3+Fe+Al powder mixture (a) as-received, (b-d) after 1, 8, and 20 h of milling time, respectively, and (e) after 20 h of milling time followed by sintering at 1400 ºC for 1 h.

patterns of n-Al_2O_3+Al+Fe powder mixture as-received and after different milling times are shown in Fig. 3. As seen, only one weak peak related to the Al_2O_3 phase are observed on the XRD pattern of the as-received sample. The XRD pattern of n-Al_2O_3 is given in the inset of Fig. 3 showing the crystalline structure of the n-Al_2O_3 phase with the highest intensity at 2θ = 67.4. The crystallite size of the n-Al_2O_3 powder was calculated by Scherrer formula to be about 10 nm. After 1 h of ball milling, the XRD peak of n-Al_2O_3 virtually vanished because of the broadening effect. After 20 h of milling time, the peaks related to the Fe_3Al phase could be identified (Fig. 3 (d)). The crystallite size and average lattice strain of Fe_3Al in MA-Fe_3Al-30Al_2O_3 after 20 h milling time calculated from XRD pattern are 25 nm and 1.21%, respectively.

Refinement of crystallite size as well as increasing the lattice strain leads to the increase in the width of XRD peaks remarkably, while reduces their intensity [15]. These results indicate that the Al_2O_3 phase produced by mechanochemical reaction route (MC-Fe_3Al-30Al_2O_3) tends to show no peaks on the XRD experiment. The nanocrystalline structure of MC-Fe_3Al-30Al_2O_3 was also confirmed by TEM observations. Fig. 4 shows BF image, dark-field (DF) image, and SAD pattern from MS Fe_3Al-30Al_2O_3 nanocomposite powder prepared after 20 h milling time. The corresponding SAD pattern exhibits the Debye-Scherrer rings which is the characteristic of a fine crystalline structure. The DF image suggests a crystallite size of < 50 nm which accords well with 40 nm estimated using the XRD pattern by Williamson-Hall approach.

The absence of Al_2O_3 peaks in the XRD pattern of Cu-Al_2O_3 nanocomposite powder (prepared by mechanochemical reaction of CuO+Al+Cu powder mixture) was also reported by Hwang and Lee [16] as well as Thanh et. al. [17]. In addition, similar results also reported in Al(Zn)/Al_2O_3

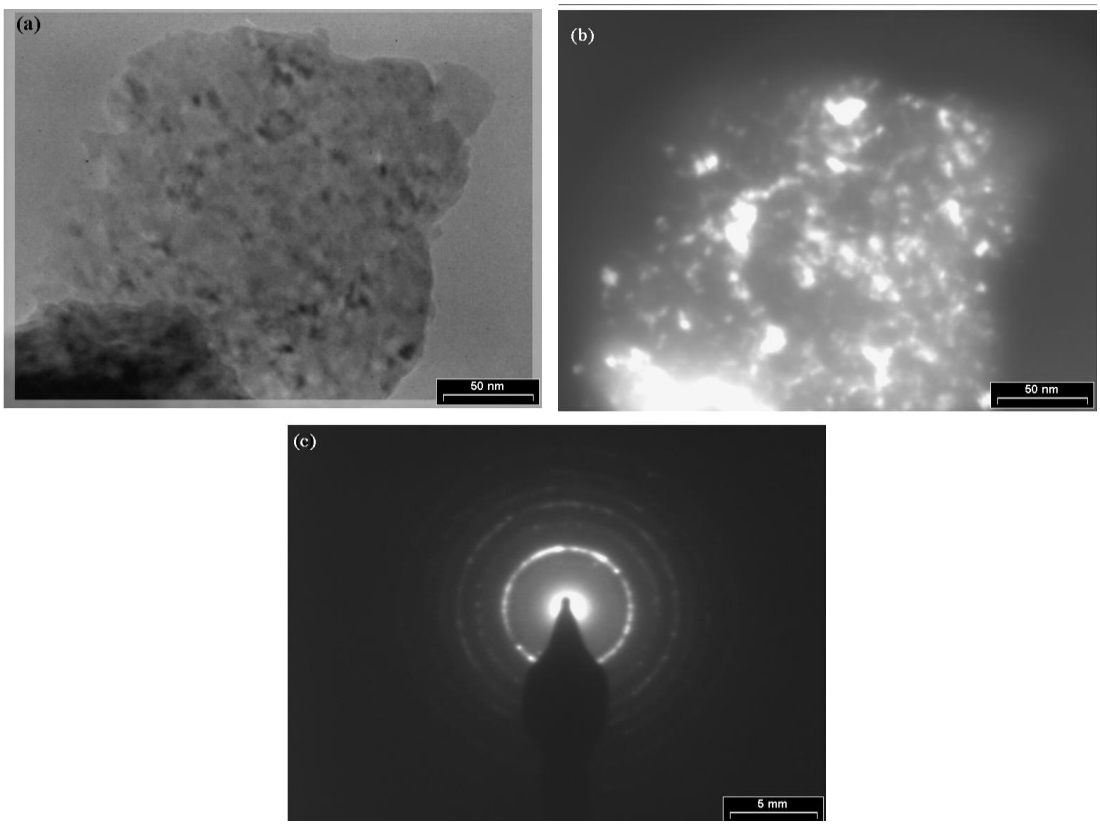

Fig. 4 TEM micrograph of Fe_2O_3-Al-Fe powder mixture (Fe_3Al-30 vol.% Al_2O_3 nanocomposite) after 20 h of milling time, (a) Bright field image, (b) Dark field image, and (c) SAD pattern.

nanocomposite [18].

Moreover, the low peak intensity of Al_2O_3 can also be attributed to the X-ray absorption by the Fe_3Al matrix as well as the lower volume fraction of Al_2O_3. Leonard and Koch [19] proposed that the intensity of diffraction peaks has a relation with the mass absorption of the materials in mechanically milled powder consisted of two or more phases. In this study, the Al_2O_3 peaks can be suppressed by Fe_3Al-matrix because of the relatively higher absorption coefficient of Fe_3Al (269.2 cm^2/gm [15]) in comparison to that of Al_2O_3 (31.7 cm^2/gm [15]).

To investigate the effect of crystallite growth as well as lattice strain reducing on their X-ray diffraction, the consolidation (cold pressing and sintering at 1400 ºC for 1 h) of the MC- and MA-Fe_3Al-30Al_2O_3 nanocomposite powders synthesized after 20 h of ball milling time were performed. XRD patterns of sintered MC-Fe_3Al-30Al_2O_3 and MA-Fe_3Al-30Al_2O_3 samples are shown in Fig. 1(g) and Fig. 3(e), respectively. As seen, the sintering had no effect on peak position of Fe_3Al phase but led to the development of the Al_2O_3 peaks on XRD patterns. As expected, the intensity of the XRD peaks increased while their width decreased. The crystallite size and average lattice strain of the Fe_3Al and Al_2O_3 phases for sintered samples are calculated to be 115 nm, 0.59% and 69 nm, 0.19%, respectively for the MC-Fe_3Al-30Al_2O_3, and 86 nm, 0.69% and 66 nm, 0.18%, respectively for the MA-Fe_3Al-30Al_2O_3. These observations show that the X-ray absorption by component with higher mass absorption coefficient may be occurred in highly strained nanocrystalline powder and stress releasing and crystallite growth resulted from heat treatment cause to remove this effect.

CONCLUSION

The mechanochemical reaction of non-stoichiometry Fe_2O_3-Al system (Fe_2O_3+Al+Fe powder mixture) was performed to produce Fe_3Al-30 vol.% Al_2O_3 nanocomposite. The results showed that XRD analysis could not be able to detect the mechanochemically synthesized Al_2O_3 phase, whereas TEM analysis showed the crystalline Al_2O_3 Phase. XRD pattern of Fe_3Al-30

vol.% Al_2O_3 nanocomposite prepared by ball milling of the nano-Al_2O_3+Al+Fe powder mixture was also showed no peaks of the Al_2O_3 phase. The X-ray absorption by component higher mass absorption coefficient (Fe_3Al matrix) in highly strained nanocomposite lead to decrease in the diffraction intensity of component with lower mass absorption coefficient and with low volume fraction (Al_2O_3). High-temperature heat treatment of both samples led to crystallite growth as well as lattice strain reducing resulted in capability of detection of the Al_2O_3 by XRD analysis. Since the XRD analysis is the common characterization method of composite materials, these results can be a significant reference work showing the inability of XRD analysis to detect the in-situ formed reinforcement phases in mechanochemically synthesized nanocomposite powder.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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