



EVOLUTION OF $\text{Fe-Al}_2\text{O}_3$ NANOCOMPOSITE THROUGH BALL MILLING

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ABSTRACT

Direct ball milling of Al_2O_3 was carried out separately which led to contamination of WC from the vial. So, reactive milling was tried out for synthesis of nanocomposite of $\text{Fe-Al}_2\text{O}_3$. Source of iron oxide used was i.e. Fe_2O_3 and Al as reductant. Effect of reductant (%Al) was studied and it was confirmed that 20% excess Al is required for the completion of the reaction. More than optimum amount of reductant led to the formation of iron aluminides (FeAl and Fe_3Al), whereas lesser amount led to the formation of FeAl_2O_4 . The thermal treatments were also carried out and no phase change was observed. Reactive Milling was also carried out in dry condition and it was observed that after few minutes of milling reaction had got completed.

Keywords: Nanocomposite, Reactive Milling, Ball milling, Dry Milling

1. INTRODUCTION

There has been a growing interest in development of new materials that provide giant effects, since the discovery of giant magnetoresistance (GMR) in the granular alloys [1]. Among them the observation of GMR in tunnel-type nanostructures, e.g., granular materials in insulating matrix [2], polycrystalline material with insulating grain boundaries [3], and in mesoscopic multitunnel junctions [4] has opened new perspectives. On the other hand enhanced coercivity and high permeability with high electrical resistivity have also been reported in granular nanocomposites. Particularly interesting properties are expected when the particle size is in the single domain range but it is strongly influenced by interparticle interaction. Applications favor non-interacting single domain particles having uniform size and shape and have high magnetization. Metallic particles of Fe or Co, isolated electrically and magnetically by a non-magnetic component, nonmetallic component satisfy these requirements ex. $\text{Fe-Al}_2\text{O}_3$ system.

One of the methods adopted for producing the nanocomposites is mechanical alloying (MA). McCormick and Schaffer used Reactive Milling to produce a wide variety of solid-solid chemical reactions [5]. Reactive milling means to reduce metal oxide (MO) by a more reactive metal(R) to obtain metal (M) and oxide (RO). The advantage in this process is that one can produce metal or compound at room temperature. Normally these reactions are thermodynamically feasible at room temperature but are restricted by kinetics. Reactive milling or MA provides a way to increase the kinetics of the reaction. Although earlier workers have reported the synthesis of $\text{Fe-Al}_2\text{O}_3$ by milling, a detailed investigation of phase formation has not been studied yet. In the present article we report synthesis of $\text{Fe-Al}_2\text{O}_3$ nanocomposite by reactive milling and limitation of direct ball milling.

2.0 EXPERIMENTAL PROCEDURE

Ball milling was carried out in Frisch P5 planetary mill at 300rpm. The duration of ball milling was up to 25hrs with WC vial and balls, the size of the ball being 10mm. The process-controlling agent used was Toulene. The ball to powder ratio was varied from 10:1 to 25:1.

The characterization was carried out using XRD (PHILIPS PW 1792) diffractometer. The target material was Co (having wavelength $\lambda = 1.789 \text{ \AA}$), with Ni as filter. Thermal treatments were also carried out under H_2 atm at three different temperatures i.e. 673K, 873K and 1073K for 1hr.

3.0 RESULTS AND DISCUSSION

3.1 Direct Ball milling of $\gamma\text{-Al}_2\text{O}_3$ in WC vial

One of the ways of producing Nanocomposite of Fe- Al_2O_3 can be direct ball milling of Fe and Al_2O_3 . Milling of Al_2O_3 was carried out in WC vial for 20h with 10:1 BPR. Fig.1 shows the XRD. It is observed that after 10h of milling the intensity of the reactant phase has reduced and some new peaks are forming, the product peak gets broadened and intensified with increased milling time. The broadening of peak signifying that the grains size is in nano range. It is found that some peaks are of $\alpha\text{-Al}_2\text{O}_3$ and while others are of WC (contamination from the vial). On giving the thermal treatment to the milled samples, the peaks get sharper and narrower owing to increase in grain size but there is no change in phase formed.

Direct milling leads to contamination during milling as Al_2O_3 is ceramic and is very hard in nature. While milling, WC wears away and contaminates the sample, which is not desirable. Another observation is transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ during milling. It is known that $\alpha\text{-Al}_2\text{O}_3$ is more stable form of Al_2O_3 and is formed at high temperature. So, by mechanical milling transformation has taken place from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ at room temperature. Mechanical milling introduces a lot of defects and thus increases free energy and leading transformation to $\alpha\text{-Al}_2\text{O}_3$.

3.2 Reactive Milling of $\text{Fe}_2\text{O}_3\text{-Al}$

Earlier work was carried out by Caer et al [6] on $\text{Fe}_2\text{O}_3\text{-Al}$ system. They had used different sources of Fe_2O_3 for their study. They were able to synthesize Fe- Al_2O_3 using stoichiometric amount of Al instead of excess. The milling was carried out in planetary mill using Stainless steel vial under Ar atmosphere for 1h and 3h with ball to powder ratio of 40:1. They also showed that some amount of Al goes in Fe. Effects of heat treatment and reductant were not studied.

The milling experiments were carried out with varying amount of reductant and as a case study 20% excess Al has been discussed in detail. Fig.2 shows the XRD patterns for 20% excess Al- Fe_2O_3 at different milling times with 25:1 BPR. The 0h sample XRD peaks can be seen from fig.2. Within 4h of milling the intensity of the most intense peak of Al significantly decreases and a shoulder develops on the (200) peak of Al. It is important to note that Fe(110) peak overlaps with the Al(200) peak and that the most intense peak of $\alpha\text{-Al}_2\text{O}_3$ appears usually very close to that of Fe(110) on the lower angle side. Hence, it is very difficult to identify the early stages of reaction between Al and Fe_2O_3 leading to the formation of Fe by XRD and can be seen from fig.2. However, the decrease in the intensity of Al peak and the development of a shoulder on the lower angle side of the Al(200) peak clearly demonstrates that the reaction between Al and Fe_2O_3 occurs within 4h, leading to the formation of nanocrystalline Fe and Al_2O_3 . Continued milling further reduces the Al(111) peak, while broad peak near the Al(200) position intensifies, suggesting the increase in the volume fraction of nanocrystalline Fe in the

mixture. The intensity of Al(111) peak becomes small after 25h of milling and also Fe_2O_3 peaks almost vanishes suggesting that the reaction has gone to completion after 25h of milling. It is also important to note that Al_2O_3 peaks are not observed during milling of Al and Fe_2O_3 , excepting for a shoulder on the left side of Fe(110), which corresponds to the most intense peak of $\alpha\text{-Al}_2\text{O}_3$. Similar XRD curves were generated for stoichiometric, 10% excess Al and 30% excess Al after milling. Fig.3 shows a comparative XRD after 25h of milling with use of different amount of reductant. While the stoichiometric and 10% excess Al samples showed some residual Fe_2O_3 after 25 hours of milling, the samples with 30% excess Al showed complete disappearance of the reactants suggesting that 20% or 30% excess Al is necessary for the completion of the reaction. The crystallite size of Fe formed by the reactive milling was calculated to be 10nm in all the above mentioned cases. Fig.2 shows the XRD pattern after annealing at 673K, and 1073K for 1h. It is clear that after annealing at 673K the most intense peak of Fe(110) coming out of the broad overlapped peak. After, annealing at 1073K, all the three most intense peak of Fe can be seen along with Al_2O_3 peaks. In case of stoichiometric and 10% excess Al samples, all the three most intense peaks of Fe can be seen along with FeAl_2O_4 phase, leading to formation of Fe- FeAl_2O_4 nanocomposite as can be seen from fig.4. Interestingly, 20% and 30% excess Al samples do not show the formation of FeAl_2O_4 . Annealing at higher temperature (1073K), has led to the formation of FeAl intermetallic in case of 30% excess Al sample as is evident from Fig.4. From the formation of FeAl, it is clear that some unreacted Al remains in the nanocrystalline state, which on annealing at high temperature reacts with the Fe to yield FeAl. Interestingly, high temperature form of Al_2O_3 is formed ($\alpha\text{-Al}_2\text{O}_3$) on annealing at 1073K for 30%Ex. Al, while in other cases (20%Ex. Al), low temperature form ($\gamma\text{-Al}_2\text{O}_3$) has been observed to form. From these systematic studies we suggest that 20% excess Al as ideal amount of reductant required for the complete reduction of Fe_2O_3 .

3.3 Dry Milling

It is known that the reduction of Fe_2O_3 by Al is highly exothermic reaction. So the reaction can take place in two ways depending on the milling condition,

- a) Reaction may involve a very small volume during each collision resulting in gradual reaction. As metal and oxides are immiscible, a nanocomposite is formed.
- b) The impact of milling balls may initiate a self-supporting combustive process.

Combustion results in partial melting and loss of nanometer scale microstructure.

Earlier all the milling was carried out under wet conditions using toluene but in this $\text{Fe}_2\text{O}_3\text{-Al}$ (stoic.) was dry milled using WC vial and ball with 10:1 BPR. It was found that the reaction got completed within few minutes with a combustion reaction taking place and reaction getting completed. Fig.5 gives the XRD before dry milling and after dry milling for $\text{Fe}_2\text{O}_3\text{-Al}$ (Stoic.).

4.0 CONCLUSION

Direct Ball Milling of Al_2O_3 leads to contamination from the vial and so use of Reactive Milling for synthesis of Fe- Al_2O_3 nanocomposite. Reactive milling of Fe_2O_3 using Al as reductant has successfully led to the formation of Fe- Al_2O_3 nanocomposite. 20% Excess amount of reductant is required for the completion of reaction, excess leads to the formation of iron aluminides and lesser amount leads to reduction of FeAl_2O_4 . Fe- Al_2O_3 has also been formed by dry milling in both the cases i.e. Fe_2O_3 with Al as reductant in stoichiometric amount.

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FIGURES

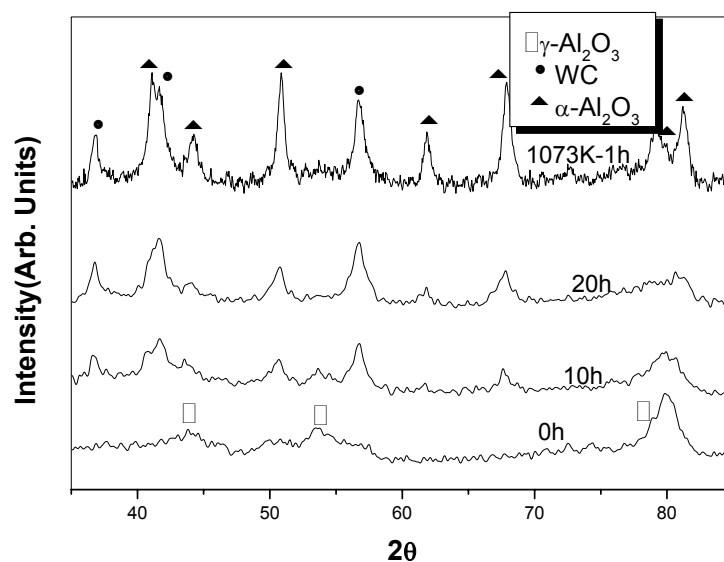
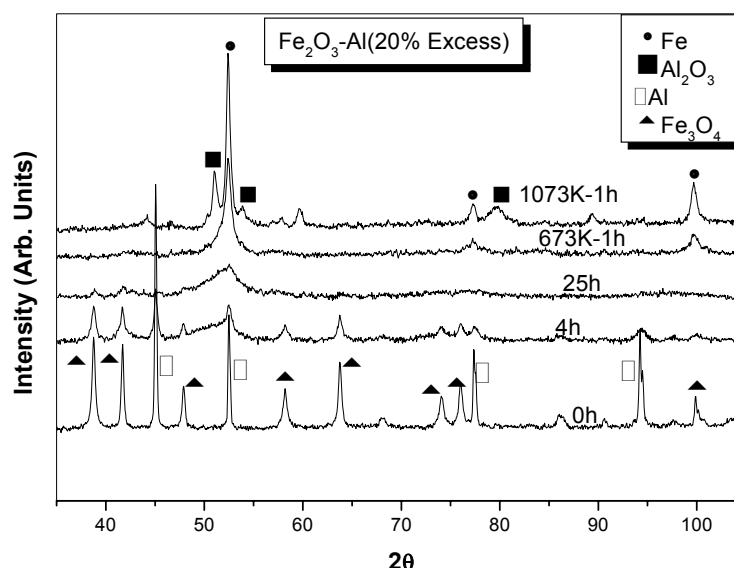
Figure1: Shows XRD for Al_2O_3 milled in WC vial and after thermal treatment

Figure 2: XRD after milling and thermal treatment

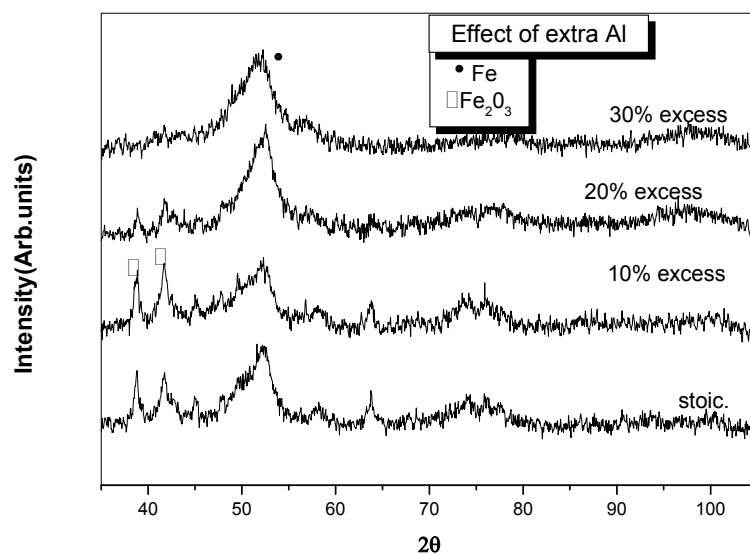


Figure3: Comparative XRD for different amount of reductant after milling

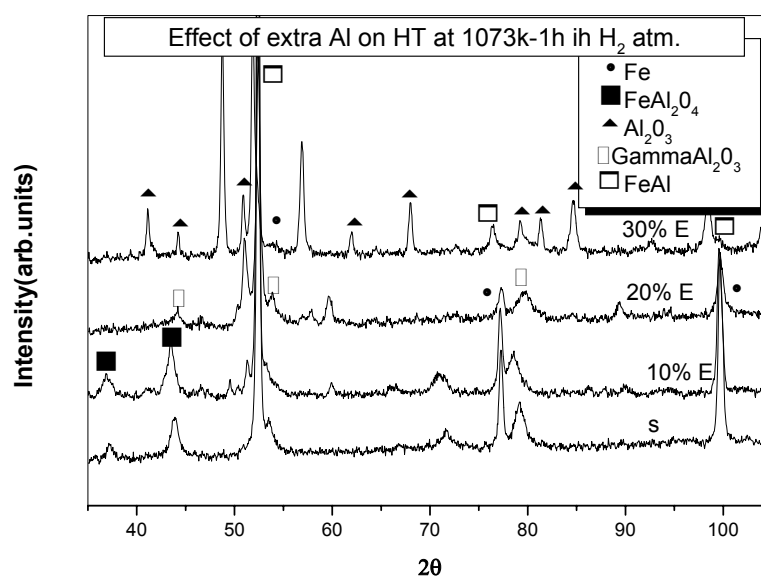


Figure 4: Comparative XRD for different amount of reductant after thermal treatment

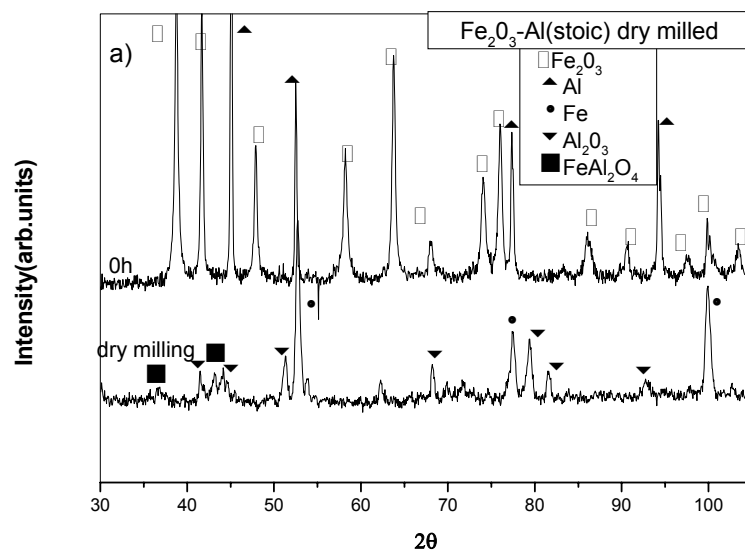


Figure 5: XRD for dry milling