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Step-by-step powder composite mechanosynthesis for functional nanoceramics

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To study the possibility of Fe₃O₃ mechanochemical reduction by preliminary mechanically alloyed Fe+20%Al compound their powder mixture was subjected to high-energy ball-milling in Ar atmosphere, with the milling time varying between 2 and 12 minutes. The milled samples obtained at various times of milling were characterized by X-ray diffraction and Mössbauer spectroscopy. As a result gradual α-Fe₂O₃ reduction via formation of intermediate Fe-Al-O oxides was observed. The presence of the intermediate Fe₂AlO₄ spinel phases stable over long milling time is stated. Mechanocomposite Fe+20%Al transformation to α-Fe(Al) solid solutions which evolve peculiarly with the milling time, was observed also. The kinetics of α-Fe₂O₃ reduction process was analyzed in comparison with the same processes in the systems: α-Fe₂O₃ + Al and α-Fe₂O₃ + Al + Fe.

1. Introduction

The possibility of taking the advantage of particular properties of the constituent materials to meet specific demands is the most important motivation for the development of composites. In this way we are working on varying the mechanosynthesised composites final structure for different purposes. Recently, we have studied the processes of Al₂O₃/Fe-Al [1], Fe₂O₃/Fe₃O₄/Fe [2] nanocomposites mechanochemical formations. The thermite solid state reduction reaction of α-Fe₂O₃ with metallic reductant (Al, Fe) was realized in those processes. α-Fe₂O₃ was consistently reduced to Fe through intermediate binary and ternary oxides. Reduced Fe subsequent alloying with reductant surplus resulted in Al₂O₃/intermetallic phases composites formation. The metal-reductant surplus in the mixture leads to deceleration of Fe₂O₃ reduction and incapsulated structures formation. Fe as additional reductant caused some shift of the activation barrier of Fe₂O₃ reduction. The ordering-disordering phenomena led to amorphous iron-based magnetic phase formation in grain-boundary regions. This phase is stable for a long milling time and after heating up to 500°C [2]. Its formation creates the additional competitive process to Fe₂O₃ destruction. To study the possibility of Fe₂O₃ mechanochemical reduction, alloyed Fe-Al intermetallic compounds in high energy planetary ball mill activation of pre-milled Fe+20%Al mixture with Fe₂O₃ have been performed.

2. Experimental

Ball milling of 8 g Fe powder with 2 g of Al powder was performed in AGO-2 planetary ball mill for 20 minutes in a vial sealed under Ar. Then 3 g of α-Fe₂O₃ powder was added into 5 g of pre-milled Fe-Al mixture and again subjected to 2, 6 and 12 minute ball milling. Vial volume was 250 cm³. Balls diameter and mass were 5 mm and 200 g respectively. The speed of drums rotation was ~1000 rpm.
The $^{57}$Fe Mössbauer spectra (MS) were recorded at room temperature with $^{57}$Co(Rh). X-ray diffraction (XRD) of as-milled and annealed powder samples was performed at Rigaku DX/Max diffractometer with Cu Kα radiation.

3. Results and discussion

X-ray diffraction image of Fe+20%Al powder mixture milled for 20 min is shown in Fig1 (a). The broadened peaks with maxima at the angles of FeAl may correspond not only to disordered (or even amorphous) FeAl phase and its solid solution but also to structural reflections of FeAl$_2$ and Fe$_2$Al$_5$ intermetallics also. The presence of well resolved narrow Al peaks on the diffraction pattern indicate unreacted Al.

Mössbauer (Fig. 2a) analysis of pre-milled Fe+20%Al presented in bar diagram shows that after 20 min of milling interaction between Fe and Al leads to the formation of highly disordered composite consisted of FeAl, Fe$_2$Al$_5$ and FeAl$_2$ intermetallic phases and disordered Fe(Al) solid solution. We observed isomer shifts and quadrupole splittings change to some extent, increased linewidths of subspectra and even additional subspectra appearance in the case of FeAl phase. As was observed [4] FeAl disordering leads to the magnetically split component being resolved in addition to the non-magnetic singlet. Thus, after 20 minutes of high energy ball milling of Fe+20%Al we obtain intermetallic phase composite.
The XRD pattern (Fig. 1b) and Mössbauer spectrum (Fig. 2b) of simple mixture: Fe$_2$O$_3$ and pre-activated Fe-Al composite correspond to mixed components contributions in the ratio 1:2. The percent of intermetallics component is about 60% that indicate metallic component prevalence.

As is seen from XRD pictures (Fig. 1 c,d,e) the subsequent milling of this mixture results in phase transformations arising from the Fe$_2$O$_3$ and Fe-Al composite interaction. Fe$_2$O$_3$ destruction after 2 min. is reflected in its intensity decrease and structure peaks widening is observed. The main wide composite intermetallic peak becomes narrow. Al peaks disappeared fully. According to Mössbauer data (Fig. 2c) the mixture after 2 min contains Fe$_2$O$_3$, Fe$_3$O$_4$, Fe and 42 % of a disordered intermetallics mixture. Milling for 6 min (Fig. 1 d; Fig. 2) reveals Fe$_2$O$_3$ peaks disappearance on XRD pattern and wide Fe$_3$O$_4$ maxima rise. Mössbauer data confirm that the mixture is composed of Fe$_2$O$_3$, Fe$_3$O$_4$ and disordered intermetallics mixture. It is interesting that at this time of milling traces of ternary compound FeAl$_2$O$_4$ were detected. Finally, after 12 min. (Fig. 1 e) the XRD pattern consists of only wide and asymmetric maxima which reflect the bcc $\alpha$-Fe(Al) solid solution formation. Mössbauer spectrum (Fig. 2) analysis reveal not only $\alpha$-Fe(Al) formation but also disordered intermetallics and ternary oxide. Generally, analyzing Mössbauer data of different milling time gradually Al rich intermetallic phases decrease in accordance with hematite reduction and bcc $\alpha$-Fe(Al) solid solution formation.

**Figure 2.** Mössbauer spectra and phase diagrams of pre-milled Fe+20%Al (a), pre-milled Fe+20%Al simply mixed with Fe$_2$O$_3$(b), mechanoactivated during 2(c), 6(d) and 12(e) minutes.
formation is clearly detected. It should be noted that no oxide phases of aluminum were detected on XRD pattern which is assumed due to possible X-ray amorphous modification of it. Evaluation of aluminum concentration in a-Fe(Al) solid solution was performed by analysis of hyperfine fields distribution of the corresponding Mössbauer spectrum component (Fig. 2 (e)) and reveals the value 7 at%.

Figure 3. The % fraction of Fe$_2$O$_3$ depending on milling time $t$ in (a) the system under study, (b) in comparison with analogous systems $\alpha$-Fe$_2$O$_3$ + Al and (c) $\alpha$-Fe$_2$O$_3$ + Al + Fe.

Fig. 3 demonstrates the kinetics of Fe$_2$O$_3$ destruction in different powder mixture with equal surplus of metal reductant component subjected to high energy ball milling. Amorphous phase formation in the presence of iron compounds leads to the slowing down the oxide reduction process.

4. Conclusions
Mössbauer spectroscopy and X-ray diffraction study of subsequent interaction of $\alpha$-Fe$_2$O$_3$ with pre-mechanoactivated Fe+20%Al composite powder mixture reveal gradual $\alpha$-Fe$_2$O$_3$ reduction via formation of iron binary and ternary oxides up to Fe. On the other hand Fe-Al mechanocomposite transformations lead to disordered $\alpha$-Fe(Al) solid solution and Fe-based amorphous phase formation. Complete amorphous phase formation on the iron surface decreases its reductant ability and slows down the process of $\alpha$-Fe$_2$O$_3$ reduction in comparison with the analogous systems.

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