Synthesis and Staging of the Phase Formation for Strontium Ferrites in Thermal and Radiation-Thermal Reactions

U V Ancharova, M A Mikhailenko, B P Tolochko, N Z Lyakhov, M V Korobeinikov, A A Bryazgin, V V Bezuglov, E A Shtarklev, A Yu Vlasov and Z S Vinokurov

1 Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia
2 Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russia
3 Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

E-mail: ancharova@gmail.com

Abstract. The strontium ferrite radiation-thermal synthesis process due to heating by intensive electron beam is described. The radiation-thermal and thermal strontium ferrite synthesis processes kinetics were studied and compared.

1. Introduction

The heating of the reaction mixture by the intensive electron beam greatly changes the chemical synthesis reaction kinetics as compared with the thermal processes. Investigations of the irradiation influence on the high-temperature synthesis kinetics have shown [1-4], that the electron irradiation significantly speeds up the synthesis process at relatively low temperatures for a number of different oxide systems (NaFeO$_2$, BaTiO$_3$, NiFe$_2$O$_4$, LiFe$_5$O$_8$, MnFe$_2$O$_4$, ZnFe$_2$O$_4$ and many others). It was found that the electron beam is a powerful factor in speeding up the solid state reactions, at least when the reaction rate is determined by the diffusion of reactants through the product layer.

This work is devoted to the study and description of radiation-thermal process in the synthesis of ferrite ceramic materials during irradiation by intensive electron beam with energy of 2.4 MeV.

2. Experimental

Reaction mixtures were prepared by a mechanochemical method in a planetary ball mill AGO-2 (acceleration of milling bodies 20 g) of the stoichiometric composition of iron oxide and the strontium carbonate of reagent grade or analytical grade purity.

Investigations of the reaction products and reaction kinetics of the in situ thermal and ex-situ radiation-thermal strontium ferrite synthesis were held by X-ray diffraction method using synchrotron radiation. Measurements were carried out at the 6th beamline "Precision diffractometry" of VEPP-3 storage ring (shared research center SSTRC [5], located in BINP SB RAS). X-ray beam of synchrotron radiation after collimator slits was monochromatized by reflection from Si (200) crystal planes and had the wavelength $\lambda \sim 1\text{Å}$. The shorter wavelength (compared to $\lambda \sim 1.54\text{Å}$ from Si (111) crystal planes more intense reflection) have been chosen for decrease in fluorescence from iron atoms in the reaction mixtures on the one hand. In addition, on another - for increase in the range of
reciprocal space registered vectors by the linear position-sensitive detector OD-3 [6] having a fixed angular range of 30 degrees. The detector was set to an angular range of 20-50 degrees, where the most significant diffraction reflections of the reaction products got.

The thermal synthesis of strontium ferrite had performed in air - by heating in high temperature chamber Anton Paar HTK 2000N, for \textit{in situ} investigations of chemical reaction.

The radiation-thermal synthesis had carried out by irradiation with intensive electron beam. The radiation-thermal treatment performed using accelerator ILU-6, located in Budker Institute of Nuclear Physics SB RAS. The electron energy was set 2.4 MeV, the pulse beam current was 320 mA, the pulse duration was 0.5 ms. Figure 1 shows the reactor with the sample inside installed under the accelerator’s beam extraction device.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{reactor.jpg}
\caption{The reactor placed under the ILU-6 beam window}
\end{figure}
Treated mixtures were placed in a corundum crucible. The surface density of the layer was 0.2 - 0.25 g/sm², thus ensuring uniform electron beam heating inside the samples. Crucibles with reaction mixture or other samples were placed into a heat-insulated reactor having the side walls made of firebrick shown in Figure 2 and covered with a plate made of foam-quartz (density 0.15 g/sm³) having thickness of 0.2 - 0.3 cm. The reactor was under the accelerator beam window as shown in Figure 1.

**Figure 2.** The inner working area of the reactor for radiation-thermal synthesis

The electron beam parameters (electron energy, pulse beam current and pulse repetition frequency) were set by the accelerator control program. The accelerator control program has the option to maintain the treated sample temperature according to the temperature chart set in special accelerator control program window shown in Figure 3. Normally the program varies the pulse repetition rate to maintain the required temperature, next regulation level – pulse beam current variation.

**Figure 3.** The temperature chart (blue line) and process temperature (red line) in the accelerator control program window

Usually the temperature chart for ferrites synthesis consisted of two parts: the linear heating and the temperature maintenance at the plateau. The cooling of reaction mixtures was carried out in a natural way (in some experiments the cooling was retarded due to controlled electron beam heating). The heating rate in all experiments was 100°C/min. The temperature plateau at set temperature of 700-1000°C was achieved in 10 minutes. The average beam current in the heating stage does not exceed 4.5 mA, and was 1.5-2.5 mA at the plateau.
3. Results

In the *in situ* X-Ray diffraction experiments with strontium ferrites thermal synthesis at temperatures of 700, 800 and 900°C it observed, that at the first synthesis stage during the mixtures heating with rate of 100°C/min the defects annealing goes. The X-ray diffraction patterns were analysed by Rietveld method. The observed line broadening caused by the size of coherent scattering regions and microstrains gradually decreases with heating. Then the reaction of the strontium ferrites high-temperature synthesis starts. Its ways differ depending on the synthesis temperature.

The strontium ferrites synthesis processes were studied at the same temperatures in different ways – the thermal (T) was studied *in situ* and radiation-thermal (RT) was studied *ex situ* ways.

The exposure durations have been chosen from 10 to 70 minutes for the RT processes reaction rate characterization. The conversion level value to the final product (strontium ferrite) over a characteristic time of 30 minutes was selected as a quantitative indicator (Table 1).

**Table 1. Strontium ferrites synthesis over a characteristic time of 30 minutes.**

| Method               | Temperature, °C | Phases, % | Initial | SrO | SrFe₂₃O₁₉ | Sr₃Fe₂O₇ | Sr₄Fe₃O₁₀ | SrFeO₃ |
|----------------------|-----------------|-----------|---------|-----|-----------|-----------|-----------|--------|
|                      |                 |           | SrCO₃  | Fe₂O₃ | SrO       | SrFe₁₂O₁₉ | Sr₃Fe₂O₇ | Sr₄Fe₃O₁₀ | SrFeO₃ |
| Thermal              | 700             | 57        | 32      | 0   | 0         | 0         | 0         | 11      |
|                      | 800             | 44        | 30      | 0   | 0         | 0         | 0         | 26      |
|                      | 900             | 4         | 12      | 24  | 10        | 17        | 0         | 33      |
| Radiation-thermal    | 700             | 66        | 26      | 0   | 0         | 0         | 0         | 8       |
|                      | 800             | 55        | 18      | 0   | 0         | 0         | 0         | 27      |
|                      | 850             | 34        | 2       | 0   | 15        | 0         | 13        | 36      |
|                      | 900             | 21        | 1       | 0   | 13        | 0         | 18        | 47      |
|                      | 950             | 7         | 0       | 0   | 12        | 0         | 22        | 59      |
|                      | 1000            | 0         | 0       | 0   | 13        | 20        | 0         | 67      |

The trend of the time decrease decrease increase-decrease no increase increase increase increase

At temperatures below 850°C there are no significant differences between reaction rates and ways depending on synthesis method – thermal or radiation-thermal. The reaction goes without the intermediate phases’ formation: strontium carbonate directly reacted with iron oxide. Thus the irradiation with intensive electron beam does not speeds up the reaction of strontium carbonate phase with iron oxide, despite the well-known effect [1-4] of reactants diffusion speeding up due to irradiation by intensive electron beam. So, in this case, the reaction rate is not limited by mutual diffusion of the reactants. Apparently, the limiting factor at temperatures below the decomposition of carbonate is the carbon dioxide elimination from the system.
However, at temperatures above 850°C there is a number of differences in chemical reactions for the thermal and radiation-thermal strontium ferrite synthesis.

In situ diffraction experiments during the thermal heating of the reaction mixture showed that at 900°C an intensive decomposition of strontium carbonate \( \text{SrCO}_3 \rightarrow \text{SrO} + \text{CO}_2 \) goes over the time scales smaller than strontium ferrite formation rate. Just for \(~10\) minutes the strontium carbonate concentration reduced in \(~20\) times, while the strontium oxide concentration sharply increased from zero, reaching its maximum value. Thus the high temperature synthesis of strontium ferrite without irradiation at this temperature goes mainly by the iron oxide interaction directly with strontium oxide, which is the product of carbonate decomposition. However, there are small concentrations of the other intermediate phases in the reaction product in addition to the reactants, final product and strontium oxide. They are hexa-strontium ferrite \( \text{SrFe}_{12}\text{O}_{19} \) and Ruddlesden-Popper phase (RP2) \( \text{Sr}_3\text{Fe}_2\text{O}_7 \).

Ex situ phase analysis of high-temperature radiation-thermal synthesis reaction products showed that the radiation-thermal heating of the reaction mixture does not cause the carbonate decomposition over the temperature range up to 1000°C, that is confirmed by experimental radiation-thermal treatment of the pure strontium carbonate. This phenomenon will be discussed in more details in our later works.

Because the strontium carbonate enters directly to the chemical reaction without stage of decomposition to the oxide, a set of intermediate phases in the reaction differs in case of radiation-thermal synthesis: instead of phase RP2 (\( \text{Sr}_3\text{Fe}_2\text{O}_7 \)), phase RP3 (\( \text{Sr}_4\text{Fe}_3\text{O}_{10} \)) was formed. Despite the fact that the reaction goes by a different mechanism then in the thermal process, the reaction product phase (strontium ferrite) concentration grows faster in the radiation-thermal process.

4. Conclusions

The strontium ferrite synthesis speeding up was observed at temperatures above 850°C due to radiation-thermal treatment. In the temperature range up to 1000°C the strontium carbonate decomposition was not observed in the radiation-thermal process (unlike in the thermal process). This effect confirms that the chemical reactions kinetics in radiation-thermal and thermal synthesis of strontium ferrite differ thus forming the different sets of the intermediate phases.

5. Acknowledgments

This work was carried out on the equipment belonging to the shared research center "SSTRC" that is supported by the Ministry Education and Science of Russian Federation.

This work was supported by the Russian Foundation for Basic Research (RFBR) (Grant 12-03-01109-a).

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