JOURNAL OF MATERIALS SCIENCE **39** (2004) 5403–5405

The kinetic study of the synthesis of magnesium aluminate spinel from mechanochemically treated mixtures of oxide-hydroxide

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The kinetics of solid-state reaction of magnesium aluminate (MA) spinel formation from the mechanically activated mixtures of both Mg and Al oxides and hydroxides was studied in situ by high-temperature X-ray diffraction at elevated temperatures. The degree of conversion α of the MA spinel formation was determined by the Rietveld method. The dependence of the conversion degree of the MA spinel formation on the time of isothermal heating of the particular mixtures was studied. Time dependence α(t) of the crystalline $MgAl_2O_4$ formation at the temperature T was analysed by the equation corresponding to the first order kinetics $\alpha(t) = P1 \cdot [1 - P2 \cdot exp(-k \cdot t)]$, where $P1$, $P2$, and k are the parameters. The rate constants k and the activation energies of the crystalline $MgAl_2O_4$formation for the selected mixtures were calculated by the fitting the kinetic data. Comparison of acquired data shows that the most beneficial results for MA spinel synthesis were obtained from the mechanically activated hydroxide mixture $Mg(OH)_2 + Al(OH)_3$.

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$; MA spinel) is of technological interest, particularly for its refractory properties. It possesses useful physical, chemical, thermal and optical properties at both the room and elevated temperatures. The conventional preparation technique—solid-state synthesis from simple oxide and/or hydroxide mixtures allows to produce powdered spinel at temperatures 1450–1750°C [1]. One of the methods, which enables to decrease the temperature of solid-state synthesis, is the mechanochemical procedure consisting of the milling of a binary component solid mixture [2].

In this paper, the kinetics of solid-state reaction of MA spinel formation from mechanically activated mixtures of both Mg and Al oxides and hydroxides was studied.

2. Experimental

Stoichiometric mixtures of the crystalline powders of Mg and Al oxides and hydroxides (see Table I) were prepared by homogenisation (for 2 h) in a planetary mill Pulverisette 5 (Fritsch, Germany) at a relatively low milling intensity. For the homogenisation of the reactants, the chamber and milling balls made of the agate were used. Mechanically activated samples (see Table II) were prepared from the homogenised mixtures by high-energy milling. The

TABLE I Homogenised mixtures of the precursors for the synthesis of $MgAl_2O_4$ spinel

Sample name	Composition of binary mixture	Stoichiometric ratio
HOM A	$Mg(OH)_2 + Al(OH)_3$	27:73
HOM B	$Mg(OH)_2 + Al_2O$	36:64
HOM C	$MgO + Al_2O_3$	28:72
HOM D	$MgO + Al(OH)_3$	20:80

TABLE II Mechanically activated mixtures of the precursors for the synthesis of $MgAl_2O_4$ spinel

Sample name	Composition of binary mixture
AGOS A	$Mg(OH)_2 + Al(OH)_3$
AGOS B	$Mg(OH)_2 + Al_2O$
AGOS C	$MgO + Al_2O_3$
AGOS D	$MgO + Al(OH)_3$

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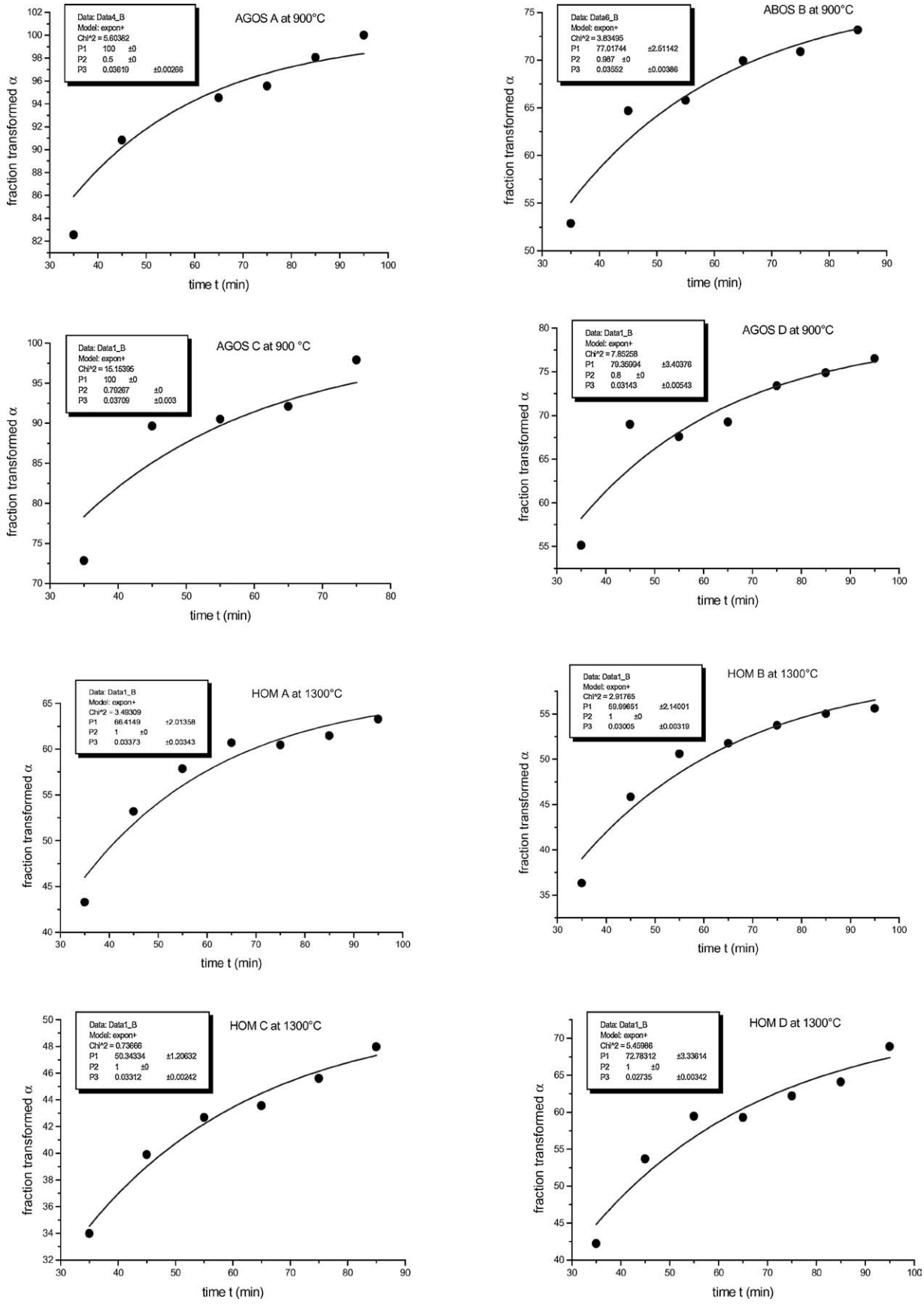

Figure 1 The dependence of the degree of conversion of the formation of $MgAl_2O_4$ spinel on the time of isothermal treatment for mixtures AGOS and HOM.

high-energy milling process was carried out in a planetary ball mill AGO 5 (Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia). In this case, grinding chamber and balls made of stainless steel were used. The mechanical activation took 4 h.

The kinetic study of the synthesis of MA spinel from the mechanically treated mixtures was carried out using diffractometer Siemens D500 (Germany) equipped with a high-temperature camera. According to the previous work [3, 4], the temperatures 1300 and 1400°C were used for the kinetic study of the synthesis of MA spinel from the homogenised precursors, and 800 and 900°C for the study of the formation of MA spinel from the mechanically activated samples. The degree of conversion (α) of the formation of the spinel was determined from the measured diffraction peaks intensities by Rietveld method.

3. Results and discussion

Time dependence $\alpha(t)$ of the formation of crystalline $MgAl_2O_4$ from both homogenised and mechanically activated mixtures at the temperature T was analysed by the equation corresponding to the first order kinetics: $\alpha(t) = P1 \cdot [1 - P2 \cdot \exp(-P3 \cdot t)]$, where $P1$, $P2$ and $P3$ are the parameters.

Fig. 1 shows the dependence of the degree of conversion on the time of isothermal treatment at 1300 and 900°C for homogenized mixtures (HOM) and mechanically activated mixtures (AGOS), respectively.

The rate constant ($P3$) obtained by fitting the kinetic data was used for the calculation of activation energy of the crystalline $MgAl_2O_4$ formation in selected mechanically activated mixtures (AGOS A, AGOS B). Table III shows the rate constant $P3$ (further k) depending on the temperature T of the isothermal heating for the samples AGOS A and AGOS B.

Activation energy E of the crystalline $MgAl_2O_4$ formation at the heating of milled mixtures was calculated from the Arrhenius expression:

$$k = A \cdot \exp(-E/RT) \qquad (1)$$

where A is the frequency factor and R is the gas constant ($R = 8.31441$ J/mol·K). An Arrhenius plot $\ln k = f(1000/T)$ for both mixtures is displayed in Fig. 2. The activation energy of the formation of crystalline MA spinel was calculated by the expression:

$$S = -E/1000 \cdot R \Rightarrow E = -1000 \cdot S \cdot R \text{ [J/mol]}, \quad (2)$$

where S is the slope of the $\ln k = f(1000/T)$ dependence.

TABLE III Rate constants of the formation of MA spinel from the mechanically activated mixtures of precursors AGOS A and AGOS B (see Table II for explanation)

Temperature T (K)	AGOS A Rate constant k(1/min)	AGOS B Rate constant k(1/min)
1073	0.02926	0.01057
1173	0.03619	0.03552

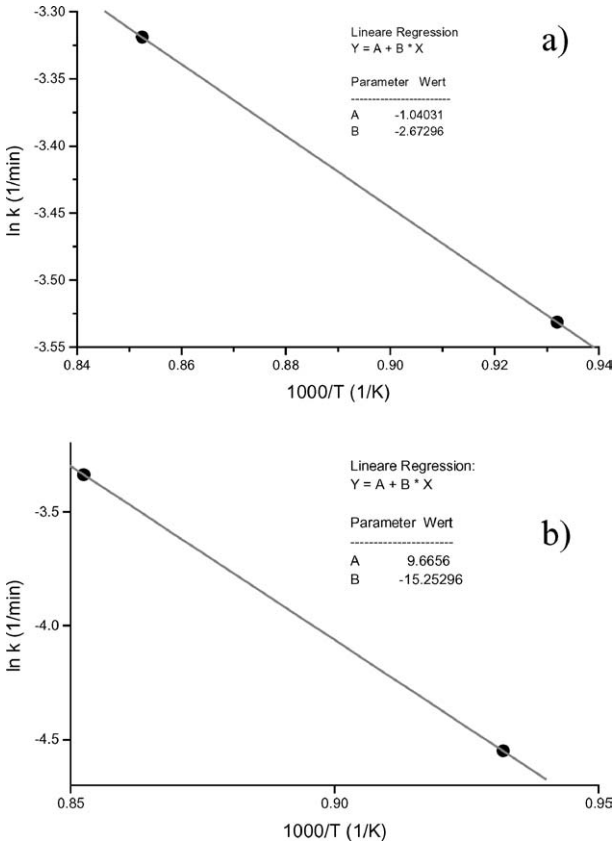

Figure 2 Arrhenius plot $\ln k$ vs. $1000/T$ for AGOS A (a) and AGOS B (b).

Activation energy of the crystalline MA spinel formation at the heating of the mixture AGOS A and AGOS B is 22 kJ/mol and 127 kJ/mol, respectively. From the comparison of recrystallization process leading to the crystalline MA spinel formation of the two mechanically activated samples it is evident that the activation energy of the formation of crystalline MA spinel from AGOS A mixture is 6-times lower than that from the AGOS B mixture. This result is in line with previous observations [2, 4] and can be practically used for effective synthesis of MA spinel.

Acknowledgements

The authors thank the Slovak Grant Agency VEGA for the financial support of the project 1/0350/03.

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Received 11 September 2003
and accepted 27 February 2004