Mechanocomposites SiO_2/Al for SHS preparation of composites Si/Al_2O_3

Tatiana F. Grigoryeva[1], Tatiana L. Talako[2], Marat R. Sharafutdinov[1], Yuri D. Kaminskiy[1], Irina A. Vorsina[1], Antonina P. Barinova[1], Klaus D. Becker[3], Vladimir Šepelák[3,4], Nikolai Z. Lyakhov[1]

[1] Institute of Solid State Chemistry and Mechanochemistry
Siberian Branch of Russian Academy of Sciences, 630128, Novosibirsk, Russia

[2] Institute of Powder Metallurgy of National Academy of Sciences, 220071, Minsk, Belarus

[3] Institute of Physical and Theoretical Chemistry, Braunschweig University of Technology, D-38106, Braunschweig, Germany

[4] Institute of Geotechnics, Slovak Academy of Sciences, 04353, Košice, Slovakia

1 Introduction

Self-propagating high-temperature synthesis (SHS) is one of the most promising ceramic powder preparation techniques because it has various advantages such as low energy requirement, higher purity of the products and the simplicity of the process [1, 2]. Many studies on the simultaneous synthesis and sintering of ceramic powders have been conducted by SHS, resulting in the preparation of dense products in a very short time. However, investigations dealing with the preparation of composites by SHS process, starting from the mechanically pre-activated compounds, are scare [3-6]. In the present work, we studied the formation of Si/Al_2O_3 composites by the mechanical activation assisted self-propagating high-temperature synthesis (MA SHS), starting from the SiO_2/Al mixture. For the first time, the SHS process is followed in-situ by X-ray synchrotron radiation technique.

2 Experimental

The SiO_2/Al mixture was mechanically activated in an AGO-2 water-cooled planetary ball mill (product of the Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia). An activation chamber (250 cm^3 in volume) and balls (5 mm in diameter) made of stainless steel were used. The ball-to-powder weight ratio was 20:1. Milling experiments were performed in argon at 1000 rpm. The IR spectra were recorded using Vector 22 and Specord 75 IR spectrometers. The XRD patterns were taken by the time-resolved synchrotron radiation diffractometer using one coordinate detector OD3 at the Siberian Center of Synchrotron Radiation, Novosibirsk [7]. Thermal analysis data were recorded by NETZSCH STA 409 PC/PG analyzer.

3 Results and Discussion

Correspondence to: grig@solid.nsc.ru

The IR spectroscopic studies (fig. 1) revealed that no chemical reduction of SiO_2 by Al takes place within 6 min of mechanical activation of the SiO_2/Al mixture. The IR spectrum of the initial mixture exhibits clear absorption bands with the maxima at 1005 and 480 cm^{-1} (stretching and deformation vibrations of Si-O bonds of SiO_4 tetrahedrons) and two maxima in the region of 900-670 cm^{-1} which are due to the vibrations of Si-O-Si bridges. Only a gradual decrease in the intensity and broadening of the characteristic bands of Si-O bonds are observed in the spectra of the mechanically activated samples. Thus, the mechanical treatment of the mixture leads only to the formation of the SiO_2/Al mechanocomposite. Scanning electron microscopic (SEM) investigations of the SiO_2/Al mechanocomposite, obtained after mechanical activation for 1 min, revealed its ultrafine dispersed state and the homogeneity of the components distribution (fig. 2).

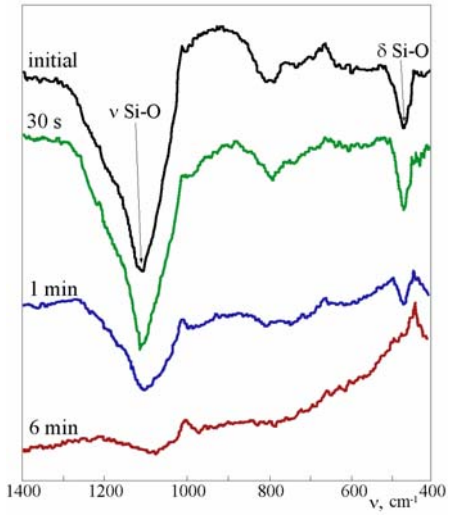

Figure 1. IR spectra of the SiO_2/Al mixture mechanically activated for various times. The milling times are shown in the figure.

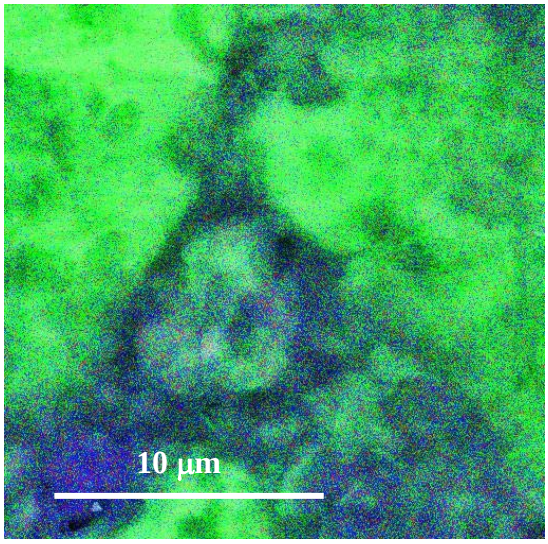

Figure 2. SEM image of the as-prepared SiO_2/Al mechanocomposite. Green and blue colors indicate Al and Si, respectively.

Table 1. Parameters of exopeaks on DSC-curves of SiO_2 + Al samples after MA

MA time	I peak,		II peak,	
	max temperature, C	Peak area, J/g	max temperature, C	Peak area, J/g
0 (initial mixture)	639.2	-	1083.6	-
20 s	632.7	306.2	1029.2	654.5
40 s	612.6	637.1	1038.1	1203
1 min	604.8	863.8	-	-
1 min 20 s	598.0	914.3	-	-
2 min	595.9	939.2	-	-
4 min	596.9	811.8	-	-
6 min	596.8	798.2		

The differential thermal analysis (DTA) data (table 1) show that even a short-term mechanical activation has a substantial effect on thermal behavior of the mixture. While the real chemical interaction in the initial mixture takes place at temperature above 1000 C (much above the melting point of aluminum), quite a different situation is observed in the case of mechanically activated samples. The DSC curve of the sample treated for 1 min exhibits only one peak (it starts at 593.9 C

and ends at 630.3 C). This provides evidence that mechanical pre-activation decreased the temperature of chemical interaction of SiO_2 with Al from 1100 C to about 600 C.

The time-resolved synchrotron radiation diffraction measurements showed that SiO_2/Al mechanocomposites can be used as precursors for the preparation of Si/Al_2O_3 composites in the subsequent SHS process. It was found that in the case of the SiO_2/Al mechanocomposite, the SHS process leads to the formation of Si and α-Al_2O_3 with the combustion temperature of about 1288 C (burning rate is ~ 1.5 mm/s). Note that in the case of the non-activated SiO_2/Al mixture, SiO_2 cannot be reduced by means of SHS under the same conditions. Kinetics of the phase transformation of the SiO_2/Al mechanocomposite during the SHS process is shown in figure 3. In view of the X-ray amorphous character of SiO_2 used in these experiments, only the diffraction peaks of Al are observed initially. One can clearly see that the sample gets heated while the combustion wave approaches (the peaks shift to the region of smaller angles, i.e., larger interplanar spacings).

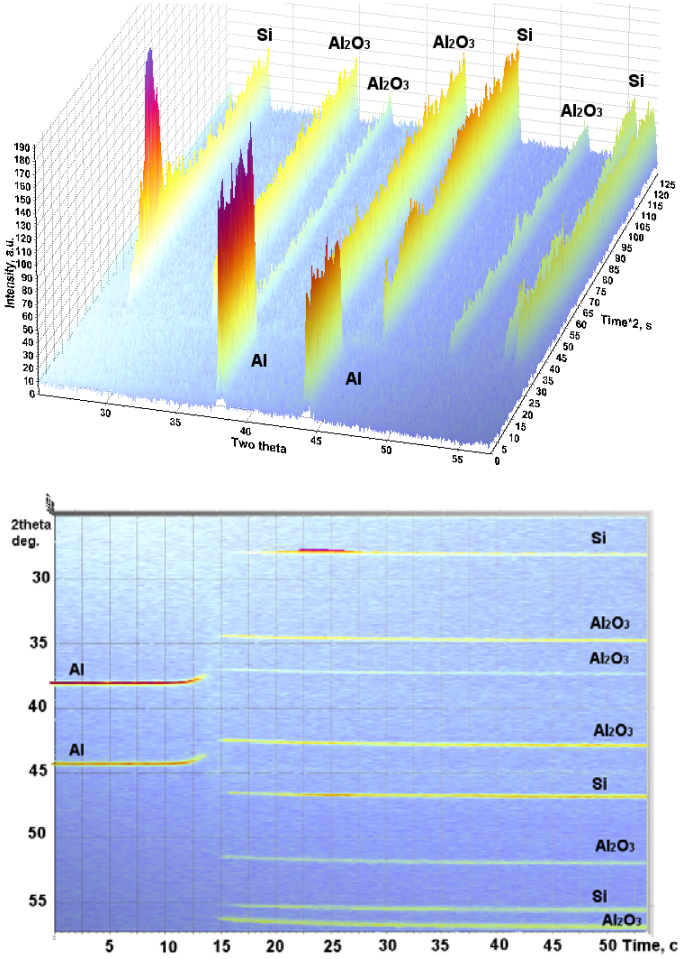

Figure 3. Kinetics of the phase transformation of the SiO_2/Al mechanocomposite during the SHS process followed by the time-resolved diffraction (top). Projection of the XRD patterns on the angle-time plane (bottom).

Then the intensity of the XRD peaks sharply drops, which is likely connected with the melting of Al. In two frames (in the time interval of 14-15 s), no crystalline phase is observed. It should be emphasized that new peaks corresponding to Si and α-Al_2O_3 appear in 1 s (see figure 3, bottom), indicating a very fast kinetics of the formation of Si/α-Al_2O_3 composite. Note that the peaks of α-Al_2O_3 start to appear somewhat earlier than the peaks of Si. It may be due to the lower melting point of Si (1410 □) in comparison with that of α-Al_2O_3 (2050 □). SEM examinations of the product of the SHS process showed rather uniform distribution and a high degree of dispersity of all the chemical

elements present in the system. The particle size of silicon in the formed composite was estimated to be smaller than 1 μm (figure 4).

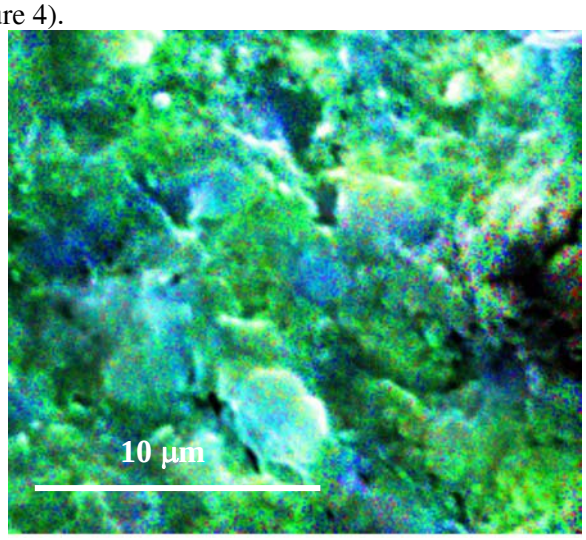

Figure 4. SEM image of the product (Si/Al_2O_3 composite) of the SHS process. Green and blue colors indicate Al and Si, respectively

4 Conclusions

The SiO_2/Al mixture was mechanically activated in an AGO-2 water-cooled planetary ball mill, resulting in the formation of the SiO_2/Al mechanocomposite. Mechanical activation decreased the temperature of chemical interaction of SiO_2 with Al from 1100 C to about 600 C. The as-prepared SiO_2/Al mechanocomposite is in an ultrafine dispersed state with the homogeneous distribution of the components. In contrast to the initial non-activated SiO_2/Al mixture, the as-prepared mechanocomposite can serve as a precursor for Si/Al_2O_3 composites formed by subsequent SHS process. The in-situ time-resolved synchrotron radiation diffraction measurements revealed a very fast kinetics of the formation of the Si/Al_2O_3 composite (1 s). The product of the SHS process shows rather uniform distribution and a high degree of dispersity of all the chemical elements present in the system.

Acknowledgements
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