Advanced Powder Technology xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Synthesis of ceramics by sol–gel method in molybdenum, silicon and carbon containing systems. Thermogravimetric studies

Anna Biedunkiewicz [a], Marta Krawczyk [b,*], Urszula Gabriel-Polrolniczak [c], Pawel Figiel [a]

[a] West Pomeranian University of Technology, Szczecin, Faculty of Mechanical Engineering and Mechatronics, Institute of Materials Science Engineering, Piastow Av. 19, 70-310 Szczecin, Poland

[b] West Pomeranian University of Technology, Szczecin, Faculty of Mechanical Engineering and Mechatronics, Institute of Mechanical Technology, Piastow Av. 19, 70-310 Szczecin, Poland

[c] Department of Physics and Chemistry, Maritime University of Szczecin, WalyChrobrego 1-2, 70-500 Szczecin, Poland

ARTICLE INFO

Article history:
Received 31 October 2013
Received in revised form 5 August 2014
Accepted 9 August 2014
Available online xxxx

Keywords:
Molybdenum carbide
Silicon carbide
Molybdenum carbosilicide
Sol–gel method
TG-DSC

ABSTRACT

The results of investigations on synthesis of ceramics in nanometric systems containing molybdenum compounds, silicon compounds and active carbon have been presented. As precursors ammonium molybdatetetrahydrate ($(NH_4)_6Mo_7O_{24}\ 4H_2O$) and tetraethyl orthosilicate ($Si(OC_2H_5)_4$) were used. The samples for analysis were obtained by sol–gel method. The course of the process was investigated by thermogravimetric method. The gaseous products were analysed by mass spectrometry. X'ray diffraction (XRD) method was used for identification of solid phases, and morphology of the samples was studied by scanning electron microscopy (SEM). The process proceeded in the following way. At temperature $t \leqslant 673$ K $(NH_4)_6Mo_7O_{24}\ 4H_2O$ decomposes into MoO_3. Then at temperature range of $1046 \leqslant t \leqslant 1065$ K MoO_3 is reduced into MoO_2 (or also into Mo). Synthesis of Mo_2C proceeds at temperature in the order of 1273 K. Before the carbothermal reduction of SiO_2 and synthesis of compounds containing molybdenum and silicon we have the Mo_2C–SiO_2-active carbon mixtures. In one stage, at temperature of 1523 K in argon, the synthesis of SiC and the synthesis of compounds containing molybdenum and silicon takes place. In the wide range of initial compositions of the mixtures $Mo_{4.8}Si_3C_{0.6}$ was obtained as the main phase.

1. Introduction

In our laboratory the research on synthesis of ceramics containing transition metals and silicon is carried out [1–5]. The sol–gel method with precursors is used. It should be added that usually the precursors, at low temperature, are converted to metal oxides or SiO_2 [6,7]. The synthesis of ceramics takes place at high temperatures, usually higher than 1273 K. The application of precursors facilitates preparation of the samples for synthesis of the desired composition and good homogenization of the reactants.

This work relates to the synthesis of ceramics in the systems containing molybdenum, silicon and carbon. The materials obtained in this system have high resistance to oxidation and corrosion, have high melting point and a relatively low specific gravity. They are used as structural materials and as protective coatings. As the substrates Mo, MoO_3, SiO_2 and activated carbon were most commonly used. The synthesis of ceramics was usually carried out by thermal methods. Reactive milling was also used [8,9].

During the development of synthesis methods and analysis of the measurement results phase diagrams are of great importance. Phase diagrams of the investigated systems are given in [10–13]. In [10] the isotherm for 1827 K, and in [11] the isotherm for 1427 K is described. These diagrams are discussed in [12]. In [10] pseudo-two-component MoO_3–C system, and in the work [13] pseudo-two-component Mo_2C–SiC system is also described. It should be added that considering the synthesis of SiC, also Ti–Si–C phase diagram was used [14].

In the Mo–C system molybdenum carbides Mo_2C (stable) and MoC can occur. In the Mo–Si system molybdenum silicides: Mo_3Si, Mo_5Si_3 and $MoSi_2$, and in the Mo–Si–C system also a ternary molybdenum carbosilicidephase $Mo_{4,8}Si_3C_{0,6}$ (Novotny phase) can be formed. For technological applications the synthesis of Mo_2C, Novotny phase and $Mo_{\leqslant 5}Si_3C_{<1}$–SiC composites, as well as and $MoSi_2$ and $MoSi_2$–SiC composites is essential.

* Corresponding author. Tel.: +48 91 449 43 77.
E-mail addresses: anna.biedunkiewicz@zut.edu.pl (A. Biedunkiewicz), mkrawczyk@zut.edu.pl (M. Krawczyk), u.polrolniczak@am.szczecin.pl (U. Gabriel-Polrolniczak), pfigiel@zut.edu.pl (P. Figiel).

http://dx.doi.org/10.1016/j.apt.2014.08.004
0921-8831/

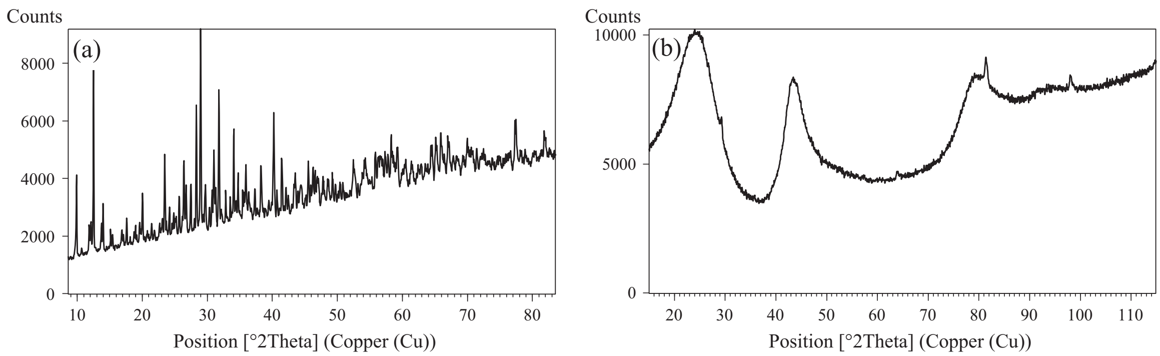

Fig. 1. XRD diffractograms of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (a) and activated carbon (b).

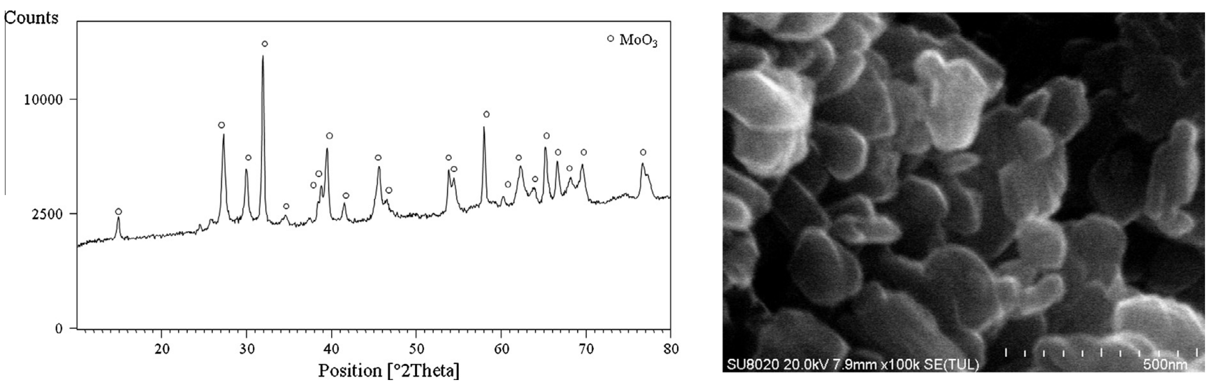

Fig. 2. XRD pattern and SEM image of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ sample after decomposition under argon.

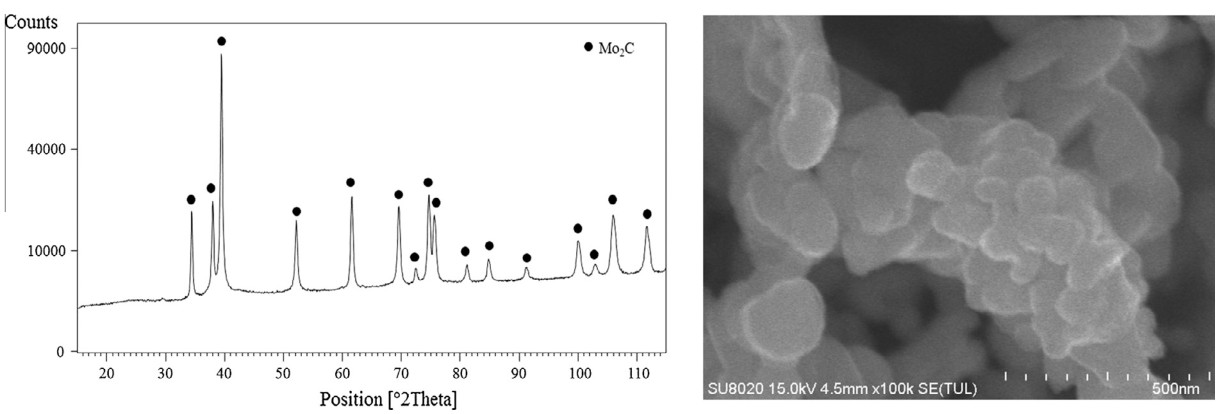

Fig. 3. XRD pattern and SEM image of the sample after carbothermal reduction of the MoO_3-activated carbon mixture.

In [15] physical and mechanical properties of Mo_5Si_3C phase is described. In [16] microstructure and mechanical properties of thin films obtained in Mo–Si–C and Zr–Si–C system have been investigated. In [17] the synthesis and properties of composites containing $Mo_{\leqslant 5}Si_3C_{<1}$ is described. In [18] the properties of $Mo_{\leqslant 5}Si_3C_{<1}$ ceramics obtained under high pressure have been studied. The works [19–21] describe the preparation and properties of $Mo_{\leqslant 5}Si_3C_{<1}$–SiC composites. In [22] instead, the results of research on $Mo_{\leqslant 5}Si_3C_{<1}$–SiC composites are presented. The issues related to the synthesis and properties of $MoSi_2$–SiC composites are presented on the examples of [12,23–25].

Pure $MoSi_2$ is resistant to oxidation and corrosion and has high melting temperature (2293 K). However, it has low resistance to the dynamic load and low strength at elevated temperatures [12]. This limits its use as a structural material or as a protective coating.

The worse properties at elevated temperature, are in part attributed to SiO_2 admixtures. Therefore, the reduction of oxygen content in the $MoSi_2$ is necessary. A deoxidizer, similarly to the other processes, may be carbon, provided the atmosphere in this process is properly controlled. The carbon can also play an important role in improving the mechanical properties of $MoSi_2$. As an auxiliary phase SiC is used. It should be added that $MoSi_2$ and SiC form the pseudo-two-component system. However, the deviations from stoichiometry are almost always present. As an admixture Si usually occurs. The presence of free Si in the material is undesirable.

The issues related to the application of $MoSi_2$ in the form of coatings are also presented on the example of [12]. After application of the molybdenum on the metal and siliconization a protective layer in the form of $MoSi_2$, separated from the metal by molybdenum, is obtained. From this layer Si gets to the free Mo