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Synthesis of nanocrystalline molybdenum carbide (Mo_2C) by solution route

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Abstract

Nanocrystalline molybdenum carbide (Mo_2C) of less than 10 nm size was synthesized by solution route. The process temperature and composition of raw materials were optimized by thermodynamic equilibrium calculation. The raw materials as well as synthesized nanocrystalline molybdenum carbide were characterized by X-ray diffraction (XRD) and thermogravimetric analysis/differential thermal analysis (TGA/DTA).
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1. Introduction

Molybdenum carbide is well-known refractory material. Conventional molybdenum carbide is very brittle and difficult to machine. Nanocrystalline materials offer the advantage of giving new properties like higher fracture toughness. Due to increasing use of molybdenum carbide as catalyst, processing of molybdenum carbide in powder form is gaining importance. Molybdenum carbide can also be used as starting materials for the synthesis of $MoSi_2$–SiC composites. Molybdenum carbide is conventionally produced by powder metallurgy route, which is expensive. Chemical methods are now widely used for production of molybdenum carbide. Many chemical methods are reported for synthesis of molybdenum carbide including sono-chemical synthesis [1], alkalide reduction [2], carbothermal hydrogen reduction [3], and temperature-programmed reduction of oxide by gas [4] and solution derived precursor method [5]. The solution route ensures an intimate mixing of the starting materials at molecular level [6,7]. Nanomaterials are cutting edge materials due to their exceptional properties. In the present work, nanocrystalline molybdenum carbide is synthesized using solution route. In the solution route, initial raw materials are taken though a solution phase enabling the precipitation of new phases in the required nano-structured form. The process temperature and composition of raw materials were optimized by thermodynamic equilibrium calculation.

2. Experimental details

The chemicals used in experiments were ammonium molybdate tetra hydrate and sucrose supplied by Qualigens. The chemical formula of ammonium molybdate and sucrose are $(NH_4)_6Mo_7O_{24}{\cdot}4(H_2O)$ and $C_{12}H_{22}O_{11}$, respectively.

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Water was used as solvent. Required quantities of these chemicals are dissolved in water medium and the solution was dried in air for 4–5 days. Air-dried solution was further dried in vacuum oven at 70–80 °C. The completely dried cake was crushed into powder and heated at 230–240 °C in a vacuum oven. The resultant black powder was pyrolysed at 800 °C and 1200 °C to get Mo_2C powder.

TGA–DTA analysis of the raw materials was carried out with a Setsys TG-24 thermal analyzer in argon atmosphere to check the decomposed product. Derivative of thermogravimetric analysis (DTG) curve was obtained from TG curve. X-ray investigation of the products was performed using Philips X-ray diffractometer with copper radiation as the X-ray source. The crystallite size was measured by calculating full width at half maximum (FWHM) of the peaks. The FWHM was calculated by fitting of pseudo-Voigt profile function. The fitting of pseudo-Voigt profile function is done by using X-ray Line Profile Fitting Program (XFIT). This program was developed by Dr. A.A. Coelho and Prof. R.W. Cheary of School of Physical Sciences, University of Technology, Sydney [8]. The breadths corresponding to the FWHM ($1/D$) were calculated by using Scherrer formula. The Scherrer formula is given as

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is wavelength of Cu source, β is the FWHM and θ is the Bragg's angle corresponding to the peak of FWHM. The strain independent crystallite size was calculated by extrapolating the plot between breadths corresponding to the FWHM ($1/D$) and sin θ for sin θ equal to zero. The inverse of intercept at sin θ equal to zero is the strain independent crystallite size [9].

The pseudo-binary phase diagram of the system MoO_3–C is calculated by global minimization of free energy by using Thermocalc software along with STGE solution and pure substance databases [10].

3. Results and discussion

Pure ammonium molybdate decomposes to molybdenum oxide during heating. The TG–DTA curve for pure ammonium molybdate is given in Fig. 1. This graph shows that ammonium molybdate decomposes in steps with intermediate products. Shaheen et al. [11] showed that final product of decomposition is molybdenum oxide, MoO_3. The decomposed intermediate products are $(NH_4)_4Mo_5O_{17}$, $(NH_4)_2Mo_4O_{13}$, $(NH_4)_2Mo_{14}O_{43}$ and $(NH_4)_2Mo_{22}O_{67}$. The decomposition of ammonium molybdate is completed at about 390 °C. Detail thermal analysis was reported by other authors [11–13].

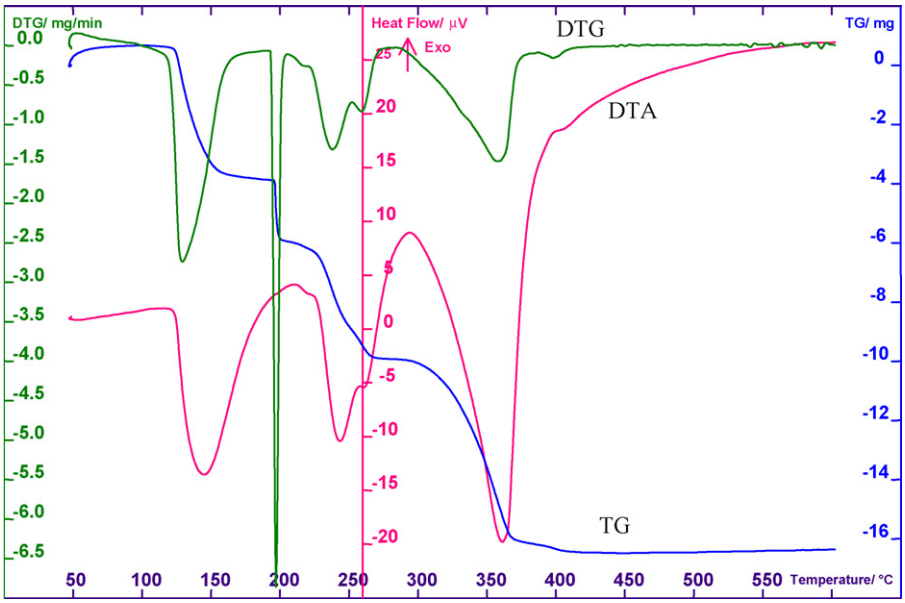

Fig. 1. TG, DTG and DTA curves for pure ammonium molybdate in argon atmosphere.

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