Int. Journal of Refractory Metals and Hard Materials 55 (2016) 11–15

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

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

Mechanosynthesis of rhenium carbide at ambient pressure and temperature

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ARTICLE INFO

Article history:
Received 4 June 2015
Received in revised form 30 October 2015
Accepted 1 November 2015
Available online 3 November 2015

Keywords:
Rhenium carbide
Polyhedral shape
Mechanosynthesis
Thermal stability

ABSTRACT

We report the synthesis of Re_2C at ambient pressure and temperature. The formation of rhenium carbide (Re_2C) from the elements was obtained by mechanochemical treatment after 640 min of milling. The microscopy analysis shows polyhedral particle agglomerates with diameters of less than 600 nm. Thermogravimetric analysis results revealed the stability of material at up to 800 °C as well as chemical and surface analysis of polyhedral particles which show oxidative properties and a surface area of 2.0 $m^2\ g^{-1}$, respectively.

1. Introduction

Current research in materials science has been directed towards improving material properties [1]. It is known that the structure and constitution of materials can be better controlled by processing them under non-equilibrium conditions [2] such as rapid solidification, plasma processing, vapor deposition and mechanical alloying (MA) [3–5]. MA is a technique that allows the synthesis of materials starting from elemental powder mixtures; moreover, it improves the chemical and physicochemical properties thereof. Carbides are of considerable interest for industrial applications due to their wear resistance, high temperature oxidation resistance, high hardness, high toughness and resistance to chemical attack. Their current applications are heat engine components, wear components, armor, corrosion resistant and high temperature burners, among others [6]. Among these, rhenium carbide is one of the most incompressible materials, which make it suitable for several industrial applications [7]. Nevertheless, it was established that rhenium does not form any carbide, neither at ambient pressure nor at low temperature. The Re–C phase diagram shows the limited solubility of carbon into rhenium [8]. Maximum solubility is reached at 11.7 at.% C at the eutectic temperature (2500 °C) and it falls sharply with the temperature (4.2 at.% C at 1800 °C). However, rhenium carbide obtained at high pressure and temperature was reported in 1971 by Popova and Boiko [9]; they used 6 GPa and 800 °C in a molar mixture of Re:C = 1:1 and determined the crystal structure of ReC by X-ray diffraction. In 1972, Popova et al. [10] reported the synthesis of ReC with cubic structure, obtained from a powder mixture of rhenium and graphite in a pressure range of 16 to 18 GPa and 1000 °C. In 2008, Juarez-Arellano et al. [11] reported the formation of a hexagonal phase of Re_4C_2 in conditions of 12 GPa and 1400 °C in a mixture of equal parts rhenium and graphite. Moreover, the synthesis of rhenium carbide with a stoichiometry Re:C = 2:1 is reported in 2009 by Juarez-Arellano et al. [12]; they used laser heating in diamond cells at high pressure (10 to 70 GPa) and high temperature (1000 to 3727 °C) from leaves of rhenium (25 μm thick) and graphite as starting materials. The Re_2C phase has been studied by Zhao et al. [13] who in 2010 reported its synthesis under conditions of pressure from 2 to 6 GPa and temperature of 600 to 1600 °C from rhenium powder and carbon black as precursors using a cubic press. Also in 2014, Dyachkova et al. [14] reported the Re_2C phase, obtained from the mechanical blending of rhenium and carbon at high pressure treatment of 6 to 10 GPa and at a high temperature of 1800 °C. In summary, high pressure and moderate temperatures (above 550 °C) are required for the synthesis of Re_2C. Mechanosynthesis rhenium carbide at room-temperature was reported by Matteazzi et al. in 1991 [15], but only they obtained a partial carburization of rhenium. In this study, we report the synthesis of rhenium carbide (Re_2C) at ambient pressure and temperature starting from rhenium powder and graphite through a high energy ball milling process. The synthesized material was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy

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http://dx.doi.org/10.1016/j.ijrmhm.2015.11.002
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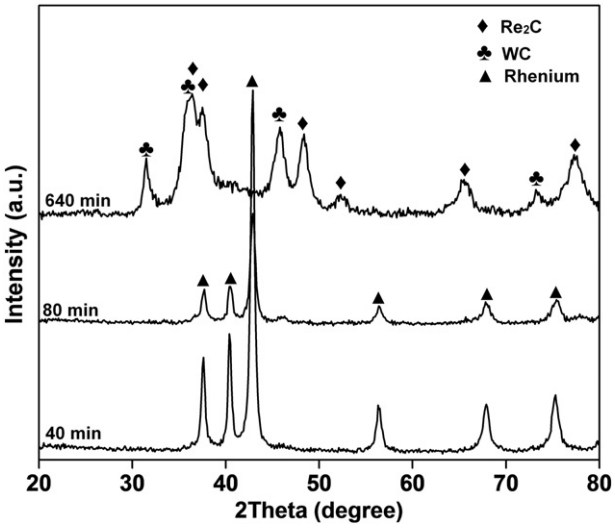

Fig. 1. XRD patterns of the materials obtained at different milling times.

dispersive spectroscopy (EDS), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and surface properties (BET).

2. Experimental procedure

A 2:1 M ratio mixture of rhenium (Sigma-Aldrich, 99.995%) and carbon (graphite, Sigma-Aldrich, <20 μm) was placed in a mortar. The staring materials were mechanically treated with mortar and pestle until a homogeneous powder was obtained. The high-energy ball milling process was carried out in a Pulverisette 7 premium line mill (Fritsch) using tungsten carbide grinding jars (volume 80 mL) and balls (15 of 10 mm). The ball milling was carried out in air in hermetically closed jars with a rotation rate of 600 rpm, cycles of 5 min milling and 12 min of pause (to reduce overheating). Samples of 1 g were removed from the milling jars at the following time intervals: 40, 80, 160, 320 and 640 min to study the reaction progress.

X-ray powder diffraction patterns were obtained using a Bruker D8 Advance diffractometer with CuK_α ($\lambda = 1.5406$ Å) radiation source operated at 40 kV and 30 mA. Scanning electron microscopy observations were made using a FEI Quanta 200 ESEM and a Dual Beam (FIB/SEM) FEI Helios Nanolab-600. The samples were lightly coated with gold to avoid the accumulation of charge on the surface. The thermogram of the reacted sample was obtained in a Perkin Elmer STA6000 thermal analyzer from 50 to 800 °C, 5 °C min^{-1} and 20 mL min^{-1} of N_2 flow. Infrared spectra were obtained using a Perkin Elmer spectrometer, Spectrum One model 59081. The samples were mixed with KBr in a 1:100 ratio and the resulting mixtures were pressed until transparent plates were obtained. The specific surface area was obtained by the BET method (N_2 adsorption at −197 °C) using a porosity measuring system in Micromeritics model ASAP 2020 surface area equipment.

3. Results and discussion

3.1. X-ray diffraction analysis

The formation of rhenium carbide was monitored by X-ray diffraction. The X-ray diffraction patterns of samples at different milling times are shown in Fig. 1. Below 640 min of milling, the powder diffraction patterns were indexed entirely by assigning peaks to rhenium (▲) (01-087-0599). No diffraction peak from graphite was seen due to the loss of its structure by the milling treatment. The effect of the milling process on graphite's morphology and particle size distribution depends, mainly on the milling

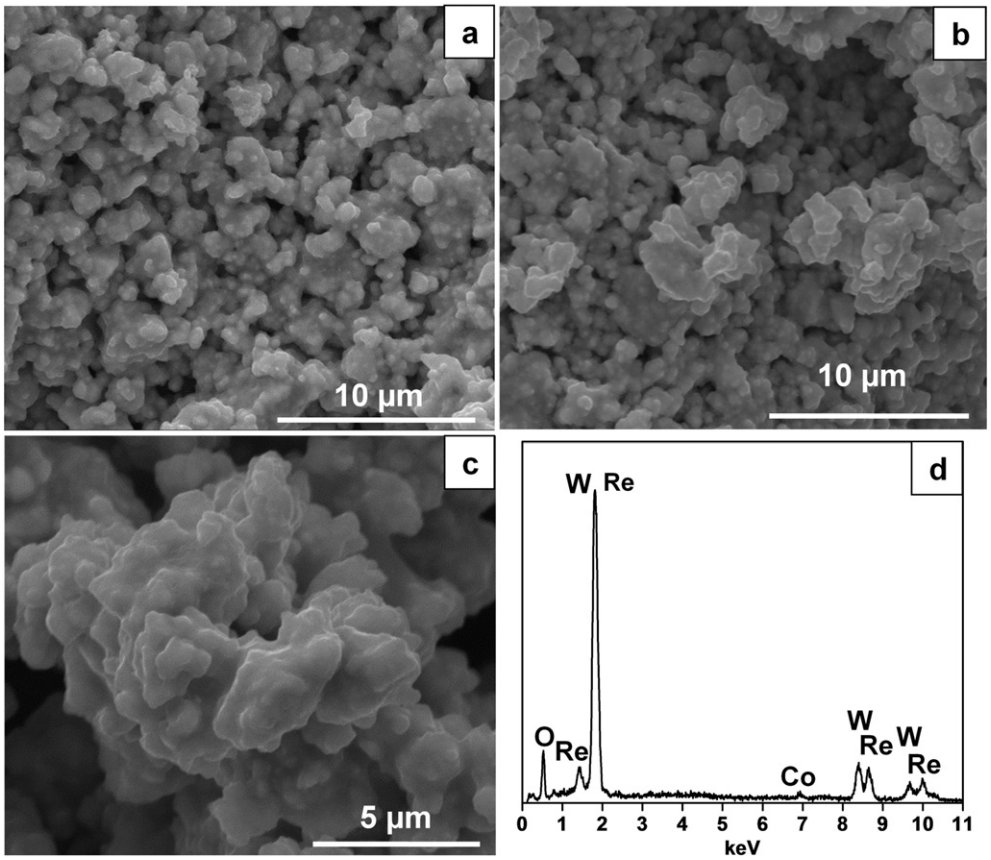

Fig. 2. SEM images of Re_2C sample obtained at 640 min of milling. a), b), and c) are secondary electron images and d) is an EDS spectrum from image a).