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Synthesis of tungsten sub-carbide W_2C from graphite/tungsten powder mixtures by eruptive heating in a solar furnace

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Abstract

Synthesis of single-phase tungsten sub-carbide phase W_2C was attempted in inert Ar gas atmosphere started from compacted powder mixtures of graphite (G) and tungsten (W) with controlled mole ratios between 0.35 and 0.50 under solar radiation heating for 30 min at two target temperatures T, 1600 °C and 1900 °C, followed by initial eruptive heating from the ambient temperature to the target temperature. Under most of the examined conditions excluding the G/W = 0.50 specimens at both $T = 1600$ °C and 1900 °C, there was discernible proportion of non-reacted metallic W co-existed with the formed W_2C. For the reference test specimen possessing the G/W mole ratio exactly at 1.0, W_2C phase emerged as the trace second phase co-exiting with the principal mono-carbide phase WC. Vickers microhardness Hv was measured using a load of 25 g to be 2785 ± 335 and 2645 ± 210, respectively, for the WC phase in the G/W = 1.0 specimen and for the W_2C phase in the G/W = 0.50 specimen processed at $T = 1900$ °C. Discrete growth of nano-meter scale WC whiskers over the top surface of the specimens heated to 1900 °C was detected by scanning electron microscope inspection.

Keywords: Tungsten sub-carbide W_2C; Nano-meter scale WC whisker; Non-stoichiometry; Vickers microhardness; Solar furnace; Ultra-fast heating

1. Introduction

In our recent carbide synthesis work using a solar furnace at PROMES-CNRS in Odeillo (France) for tungsten (W) started from tap densified powder mixture of W with excess amorphous carbon (aC) with the mole ratio aC/W = 2, we detected sub-carbide phase W_2C co-existing with the principal mono-carbide phase WC in spite of presence of excess free carbon [1].

In our earlier works on similar carbide synthesis for W under presence of excess carbon material (graphite (G) or amorphous carbon (aC)) using a solar furnace at PSA (Plataforma Solar de Almería) in Tabernas (Spain), no formation of W_2C phase was detected [2–5] in spite of the comparable holding temperature $T = 1600$ °C and duration 30 min between the experiments done at PROMES and the ones at PSA.

In the available phase equilibrium information for binary W–C system [6], mono-carbide WC is certainly the equilibrium phase under presence of excess carbon. Thus, the detected yield of W_2C phase in the solar furnace at PROMES was concluded to be the consequence of ultra-fast heating rate of the starting material from the ambient temperature to the target temperature $T = 1600$ °C within fractions of a second [1]. The heating rate of the solar

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furnace at PSA is also very fast compared with that of the conventional industrial or laboratory electric furnaces but it takes about a minute or more to heat the starting material from ambient temperature to the target temperature depending on the rate of opening of the louvered shutter [2–5]. The once-formed W_2C phase besides WC phase under co-presence of excess free aC was not converted readily to WC even by subsequent heating to a temperature exceeding 2500 °C at the focal spot of the PROMES solar furnace for 30 min [1]. Therefore, we speculated that W_2C phase must be a meta-stable phase with considerably high degree of thermodynamic stability.

Being intrigued by this aspect, we decided to try synthesising single-phase W_2C phase starting from the compacted pellet of G/W powder mixtures with specified G/W mole ratios, 0.35, 0.40, 0.45 and 0.50, using the solar furnace at PROMES in Odeillo. As the reference specimen, we also prepared the pellet of G/W with mole ratio 1.0.

Although industrial usage of W_2C is not yet exploited fully compared with that of WC as a refractory hard metal, W_2C possessing crystal structure unlike that of WC might find some other unique industrial application if further experimental verification is made for thermodynamic and chemical stability of W_2C phase. This is one of the reasons why we attempted to synthesise single-phase W_2C phase in this work.

2. Experimental

2.1. Sample materials

Graphite powder (<50 μm) was supplied from E. Merck A.G., Darmstadt (Germany) and tungsten powder (>99.5% purity; <75 μm) from Minas e Metalurgia, S.A., Aveiro (Portugal). They were mixed to G/W mole ratios, 0.35, 0.40, 0.45 and 0.50, and compacted into a pellet of diameter 10 mm and thickness about 3 mm by applying uni-axial pressure 450 MPa. The G/W pellet with the G/W mole ratio 1.0 was also prepared as the reference material.

2.2. Experimental procedure

The PROMES solar furnace used for this work is consisted of a parabolic mirror with focal length 648 mm and diameter 150 cm (the cone tip angle 120°). Its effective power is about 1.5 kW with a peak density at the focal point 15 MW/m^2.

The consolidated pellet specimen was placed in a specially designed crucible (see Figs. 1 and 2 in Ref. [1] and Fig. 1 Ref. [7]) for the exposure to the concentrated solar beam. The reaction chamber (Pyrex glass; 5 l capacity; see Fig. 2 in Ref. [7]) was flushed twice with inert Ar gas (99.7% with nominal O_2 impurity 5 ppm) before being filled with 460 mbar Ar gas at the ambient temperature.

As in the preceding solar carburisation experiments at PROMES-CNRS [1,7,8], reaction chamber with the installed sample stage was brought into the hot spot of the solar furnace by sliding over a pair of guiding rails. Within fractions of a second, the temperature of the specimen rose from the ambient temperature to the target temperature, 1600 °C or 1900 °C. Thus, we call this mode of solar heating "eruptive" or "ultra-fast" heating.

For the standard experiments with the target temperature 1600 °C, the top surface of the pellet was set at the height by a few cm lower than the focal spot while the top surface of the pellet was set exactly at the focal spot height for the high temperature experiment to reach the holding temperature 1900 °C. The test piece was held at the target temperature for 30 min.

It must be noted that the temperature measurement by optical pyrometer was made from the side of the pyrex glass reaction chamber through vertically cut slits in three layers of the crucible set (see Figs. 1 and 2 in Ref. [1] and also Figs. 1 and 2 in Ref. [7]). Across the vertical 25 mm height in the crucible, gradient of the measured radiation temperature was no greater than 100 K [7]. Radiation temperature measurement from the top surface is impractical in the present experimental setup unless solar-blindness condition was somehow arranged to cancel the contribution from the reflected solar radiation overlapping the genuine temperature radiation from the specimen material surface.

After the specified reaction period of 30 min, the reaction chamber was removed away from the hot spot of the solar furnace and it was cooled down naturally to ambient temperature. Then, air was introduced slowly to open the chamber and the prepared specimen materials were characterised by XRD (X-ray diffraction) by CuKα radiation in the Geigerflex D/MAX IIIC diffractometer of RIGAKU. For some specimens heated to 1900 °C, Vickers microhardness measurements were carried out on polished cross section of the sample mounted in an epoxy resin using 25 g load in the HMV-2000 of SHIMADZU.

SEM (scanning electron microscope) inspection was made using XL30 FEG of PHILIPS and optical microscope observation using AXIOVERT 200 MAT of ZEISS.

3. Results and discussion

3.1. XRD characterisation

XRD patterns obtained for the specimens are reproduce in Figs. 1 and 2. From these evidences, following features were noticed.

3.1.1. Synthesis of single-phase W_2C specimen was difficult at either 1600 °C or 1900 °C

This feature was noticed evidently for the powder XRD patterns obtained for the 1600 °C specimens (Fig. 1). Thus, in the following, discussion is made with reference to the data set acquired at the holding temperature 1600 °C unless otherwise stated.