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Nano-Meter Size WC Whiskers Grown over a Compacted Pellet of Graphite/Tungsten Powder Mixture Heated with an Ultra-Fast Heating Rate by a Concentrated Solar Beam

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In equilibrium binary W-C system, mono-carbide WC is acknowledged as the stable phase under presence of excess free carbon up to temperature 2700°C whereas sub-carbide W_2C would form between 1250°C and 2700°C under the carbon-deficiency condition. In unique setup of solar furnace at PROMES-CNRS in Odeillo (France), temperature of specimen is raised from the ambient temperature to target temperature up to 2000°C within fractions of a second. In the recent experimental attempts of W_2C phase synthesis using this unique experimental facility starting from compacted pellet consisted of graphite and tungsten powders at ratios smaller than 0.50, we detected growth of nano-meter size WC whisker at the top surface directly exposed to the concentrated solar beam. The presence of WC was confirmed also by X-ray diffraction (XRD) of the top surface but, when the specimen as a whole was subjected to powder XRD analysis, WC became indiscernible being masked by principal W_2C phase. Mechanism of formation of the detected WC nano-whisker over sub-stoichiometric C/W pellet during ultra-fast heating by concentrated solar beam is discussed. [doi:10.2320/matertrans.48.919]

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1. Introduction

In the binary W-C system, mono-carbide WC is acknowledged as the thermodynamically stable equilibrium phase from ambient temperature up to melting temperature around 2700°C while sub-carbide W_2C might exist as a meta-stable phase over temperature range between 1250 and 2700°C under condition of deficit carbon insufficient to yield stable WC phase.[1)]

During the course of solar carbide synthesis work for W using a solar furnace at PSA (Plataforma Solar de Almería) in Tabernas (Spain), W powders were mixed with powders of excess carbon (graphite or amorphous carbon) to synthesize reaction product WC under condition of co-existence with excess free carbon.[2–5)] In these experiments, the compacted pellet of the C/W powder mixtures was heated in inert Ar gas to a target temperature around 1600°C and held at this temperature for 30 min. Under these conditions, the formed reaction product was consistently WC irrespective of whether the used carbon material was graphite (reference material of C with carbon activity $a(C) = 1$) or amorphous carbon (carbon with $a(C) > 1$). These results were largely compatible with the available phase equilibrium information on the binary W-C system.[1)]

In the early work by Hara and Miyake[6)] on tungsten carbide synthesis from mixed powders of graphite and tungsten at an exact stoichiometric proportion (C/W mole ratio to be set at 1/1) by 20 min heating at a target temperature in the range over 1000°C and 1900°C, it was demonstrated that W_2C formed over the target temperature between 1000°C and 1400°C yielded the peak proportion at 1200°C while WC formation started from the target temperature higher than 1200°C and the proportion of it tended to rise monotonically with the temperature in the range between 1200°C and 1900°C. Residual metallic W remained up to the target temperature 1400°C showing trend of decreasing proportion with the rising target temperature between 1000°C and 1400°C. In their work,[6)] compacted powder mixture pellet was inserted into the hot zone of the horizontal electric tube furnace heated to the target temperature and thence the specimen temperature was risen from ambient temperature to the target temperature within a few minutes. This heating rate was only slightly slower than the one realised in the solar furnace at PSA (about one minute from ambient temperature to the target temperature up to 1600°C) and the reaction period 20 min employed by Hara and Miyake[6)] was quite close to the standard duration 30 min of solar radiation heating experiments[2–5)] and thence their results provide us quite direct reference for the present series of solar heating experiments done at PSA. The results reported by Hara and Miyake[6)] were in fact fully compatible with the evidences obtained through solar carbide synthesis work for W performed at PSA.[2–5)]

However, under the similar WC synthesis experiments undertaken more recently using a solar furnace at PROMES-CNRS in Odeillo (France), we detected unexpected formation of sub-carbide W_2C co-existing with WC in spite of presence of excess free carbon.[6)] This was totally unexpected because, with reference to the available phase equilibrium information,[1)] we anticipated that the stable WC phase alone would yield under the condition of co-presence of excess free carbon. The once formed W_2C resisted to be further converted to the equilibrium WC by heating to higher temperature (estimated to be no less than 2500°C) at the solar beam focal spot in the solar furnace at PROMES-CNRS.[7)]

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One of differences between the solar furnace in PSA and that in PROMES-CNRS is the heating rate at the onset of the experiment. In the former, heating rate is by far faster than the normal industrial or laboratory electric furnace but it takes about one minute to heat the specimen from ambient temperature to the target reaction temperature of around 1600°C depending on the rate of opening of louvered shutters.[2–5)]

On the other hand, in the solar furnace at PROMES-CNRS, the specimen was heated from ambient temperature to the target temperature within fractions of a second because the specimen to be heated was held in a pyrex glass reaction chamber and it was brought to the hot spot of the solar furnace optical system by sliding over the rail. Thus, we refer the realized ultra-fast heating rate in the PROMES-CNRS solar furnace as "eruptive heating" in the preceding publications.[7,8)] Then, we tentatively appreciate the detected unexpected formation of W_2C phase besides the thermodynamically stable phase WC under presence of excess free carbon in terms of the realized ultra-fast heating condition in the solar furnace at PROMES-CNRS.

In the experiments undertaken at PROMES-CNRS,[7–9)] temperature was measured by optical pyrometer (Model 95 of Pyrometric Instrument Company, Inc., Bergenfield, N.J., USA) from the side of the crucible through 3 aligned layers of slits of 1 mm width cut vertically and thence we believe the near-black body radiation condition was achieved for the temperature measurement. The temperature measurement along the height of about 25 mm ensured that the temperature gradient from the top to the bottom of the crucible was no greater than 100 K.

Being intrigued by these experimental evidences implying high degree of meta-stability of W_2C phase, we decided to try synthesis of single-phase W_2C phase using the solar furnace at PROMES-CNRS started from the controlled C/W mole ratios in the range between 0.35 and 0.50.[10)] In this work, the hot spot position for the standard experiment to reach measured temperature by optical pyrometer 1600°C was by a few cm lower than the focal point of the concentrated solar beam 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 objective of undertaking the high temperature experiment to reach 1900°C was to enhance densification of the sintered pellet because one of the aims of the work was to measure Vickers microhardness Hv for the prepared compact specimen.

In fact, the sintered pellet specimen at 1900°C was clearly with enhanced degree of densification compared with that of the counterpart sintered at 1600°C and it was quite difficult to be pulverized for characterization by powder XRD (X-ray diffraction) analysis. Thus, we undertook the XRD analysis for the top surface of the pellet without pulverizing the pellet. To our surprise, we detected XRD peaks identifiable as WC besides W_2C for the pellet top surface heated to 1900°C in spite of the net C/W mole ratio to be set lower than 0.50, as reported in detail in the preceding publication.[10)] Anyway, when we undertook the XRD analysis for the same specimen as a whole by pulverizing it, WC peak became indiscernible below detection threshold and, instead, metallic W co-existing with W_2C became detectable as shown in Fig. 1. Thus, we concluded that the surface of the C/W pellet specimen subjected to ultra-fast heating at the focal spot of the PROMES-CNRS solar furnace must be with certain singularity distinguishable from the lower part of the pellet.

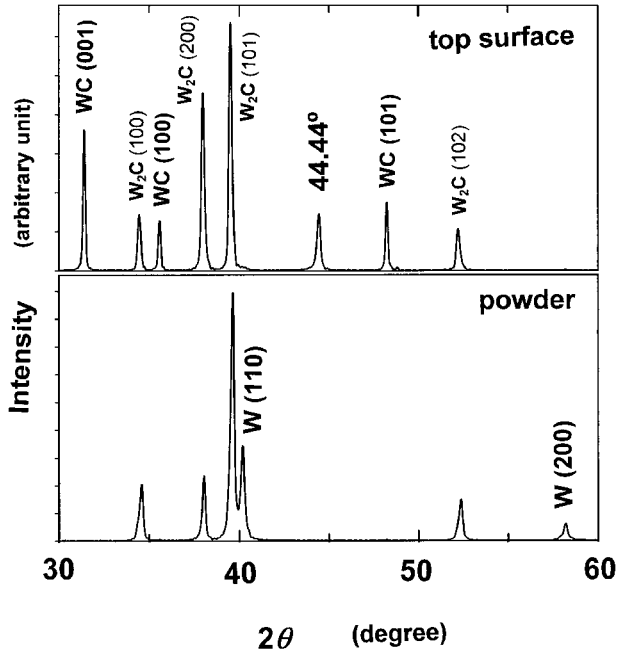

Fig. 1 XRD patterns of the G/W = 0.35 specimen held at 1900°C for 30 min after the initial eruptive heating (reproduced from Fig. 2 in Ref. 10). <top> XRD pattern of the top surface of the as-synthesised pellet showing peak from the aluminium specimen holder at $2\theta = 44.44°$. <bottom> XRD pattern of the pulverised pellet.

This curiosity led us to examine in detail the specimen surface by SEM (scanning electron microscopy). The other aspects of this work was reviewed in detail in the preceding publication[10)] and thence, in the following, the aspect of nano-meter size WC whisker growth detected over the W_2C surface alone is discussed exclusively because this aspect was a bit outside the scope of the preceding publication[10)] and was not discussed in detail therein.

2. Experimental Setup in the Solar Furnace at PROMES-CNRS in Odeillo (France)

As the solar furnace is not yet widely employed for materials synthesis experiments, setup of the solar furnace at PROMES-CNRS in Odeillo is exhibited as Fig. 2 to help readers' understanding for the used experimental system.

Figure 2(a) shows the components of the crucible. The specimen pellet was held in the innermost graphite crucible. Slit cut vertically over the second inner graphite crucible holding the innermost graphite crucible was aligned to the vertically cut slits over the two layers of alumina crucible casings. This configuration was designed to ensure the realisation of near-black body condition for the pyrometric temperature measurement from the side view-port as well as to minimise the dissipation heat loss from the sample material heated by the concentrated solar beam from above.

Figure 2(b) shows the composed set of crucible elements.

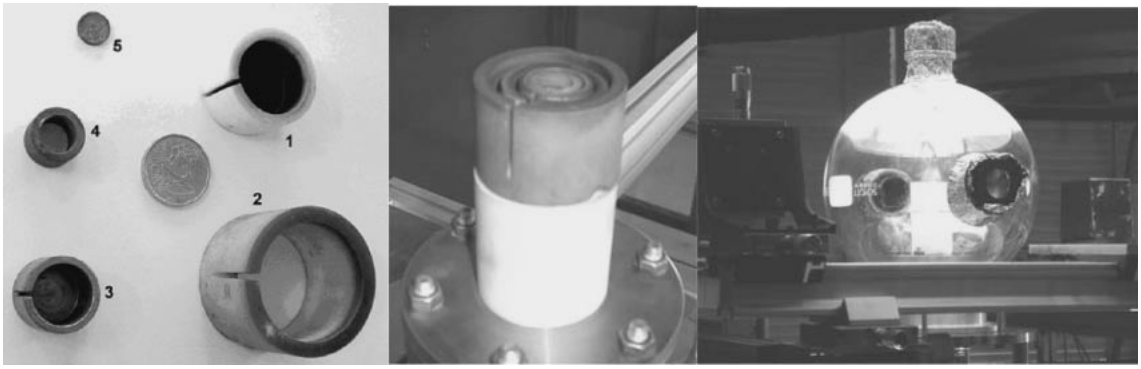

Fig. 2 Appearances of the crucible elements (a), the composed set of the crucible (b) and the reaction chamber during a solar carbide synthesis (c). ((a) and (b) reproduced from Fig. 1 in Ref. 7 and (c) from Fig. 2 in Ref. 8). In (a), following crucible elements are exhibited from the right hand side top, in clockwise direction, around a 20 cent Euro coin placed at the center for the sake of the reference of the dimension. (1) inner alumina holder with vertical slit of width 1 mm, (2) outer alumina holder with vertical slit of width 1 mm, (3) graphite holder with vertical slit of width 1 mm, (4) graphite crucible of inner diameter 10 mm holding specimen materials, (5) graphite disk separator of diameter 10 mm and thickness 3 mm.

In order to realise the experiments in controlled gas environment as well as in dynamic vacuum, transparent pyrex glass reactor of about 5 L capacity was placed over it.

Figure 2(c) shows the appearance of the reaction chamber during a solar carbide synthesis experiment. Orange plume emerged over the crucible must be SIF (solar-induced fluorescence) of C_2 radicals at 517 nm as reported earlier by Badie *et al.*[11]

3. Results and Discussion

As presented in Fig. 3, we detected nano-meter size hexagonal columnar WC whiskers growing over the W_2C surface. From this set of pictures, we can draw the following conclusions.

3.1 The top surface was subjected to melting at least temporarily

It is certain noting the seamless network of grains ((a), (c) and (d) in Fig. 3) and occasional presence of spherical nodules like (b) in Fig. 3 as well as nano-meter size WC whisker growth. If there were no molten phase of W and W vapour in equilibrium with the molten W present, WC whisker formation would not take place. It might sound a bit strange to claim the presence of molten W even temporarily noting the melting point of W metal is around 3410°C and the measured temperature was 1900°C. However, noting that the carbide formation reaction from raw materials, mixture of W and C, is highly exothermic, it must have been quite probable that the top layer temperature was at least locally and instantaneously reached to such high temperature as to yield temporary melting pool of W.

Yield of gaseous carbon and tungsten appears to be quite feasible noting early publications by Badie *et al.* reporting SIF (solar-induced fluorescence) of C_2 radical[11] or YO[12] in the same solar furnace at PROMES-CNRS. Thus, the solid-liquid-gas three-phase condition at the solid/gas interface desirable to lead to the WC whisker growth must have been realised in the present experiment with the target temperature 1900°C.

As such, details of the mechanism of formation of the detected WC whiskers are still not very clear at this stage and they must be elucidated by further investigation. However, the VLS mechanism proposed by Milewski *et al.*[13] to explain the SiC whisker growth might provide us a valuable hint for this concern. In the VLS process, V is claimed to stand for "vapour feed gas", L for "liquid catalyst" and S for "solid crystalline whisker growth". Milewski *et al.*[13] claimed that the presence of a liquid catalyst is the key factor for the VLS process to allow the concerned crystalline whisker growth at the liquid-vapour interface. Trace impurity of low melting temperature metals like Al and Fe appear to function as the liquid catalyst in the VLS process by allowing super-saturation of carbon in it. It is quite likely that raw W powders used for the present experiment contained such low melting metal impurities.

3.2 WC whisker growth site preference

As can be seen in Fig. 3, nano-meter size WC whiskers grew over W_2C grain (e) as well as along grain boundary (f) but it appears that the grain boundary provided as the preferential WC whiskers growth sites. This aspect must be made clear by further systematic experimental elaboration.

Anyway, grain boundary is generally acknowledged as the location with surface energy lower than that over the crystal grain surface and further the impurity elements are readily to be segregated to the grain boundary from the W metal matrix. Thus, it is not quite surprising that the detected WC whiskers grew preferentially over the grain boundary by the VLS mechanism,[13] although conclusive mechanism must be decided by further systematic investigation.

As reported in the preceding publication,[10] synthesis of single-phase W_2C was not easy under any examined condition. From the pellets with initial C/W ratio over 0.35–0.50, reaction products after 30 min solar heating to either 1600°C or 1900°C contained free metallic W phase besides W_2C (and trace WC as nano-meter size whiskers grown over the top surface of the pellet) and the proportion of the unreacted metallic W phase tended to rise with the decreasing C/W ratio as might be easily anticipated with

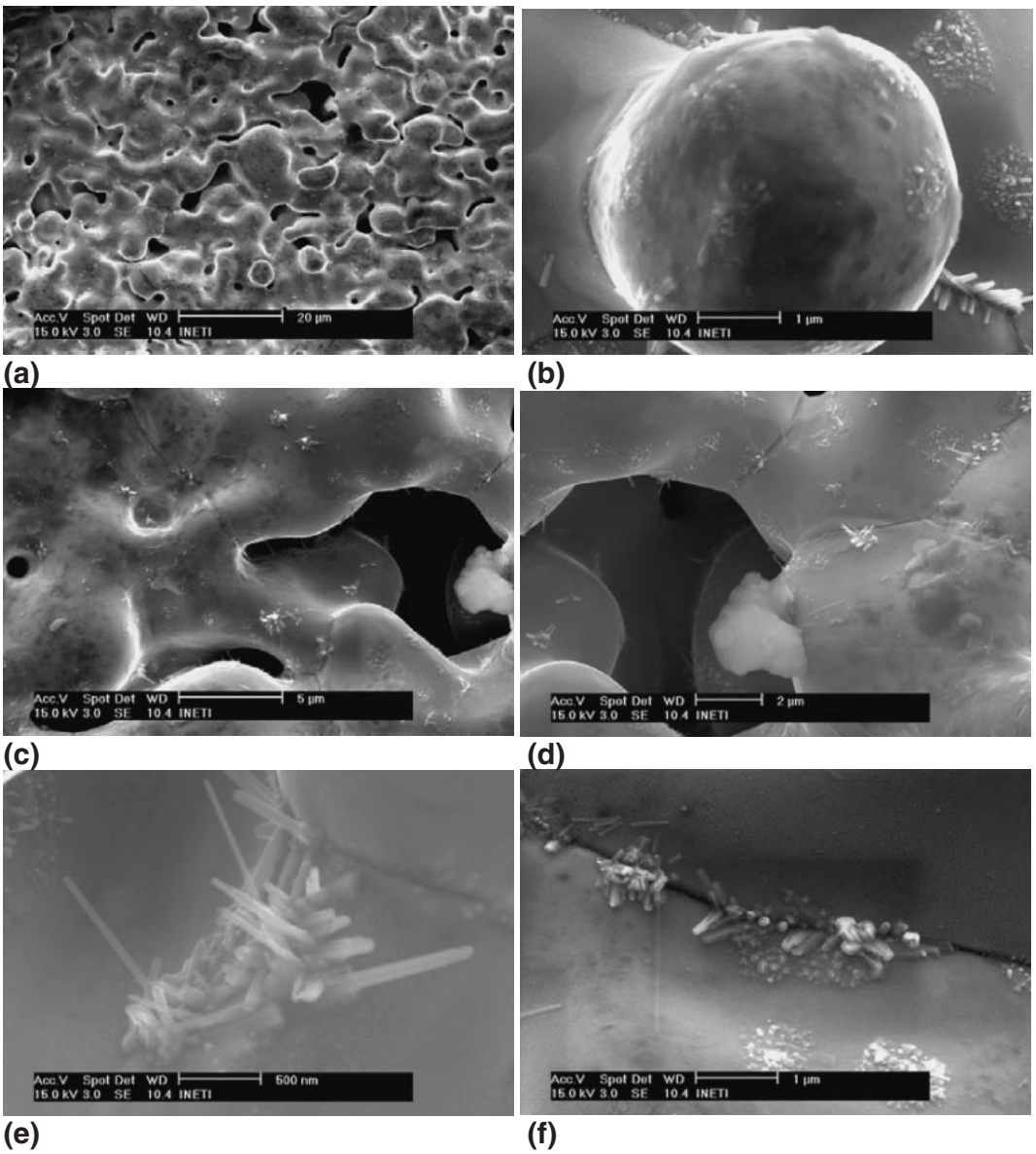

Fig. 3 SEM surface appearances of the C/W = 0.35 pellet subjected to heating by concentrated solar beam up to 1900°C showing evidences of growth of WC whiskers. (a) general appearance showing progressed extent of sintering. (b) spherical particle suggesting occurrence of instantaneous surface melting; growing nano-meter size WC whiskers along a grain boundary are seen at the right hand side bottom corner. (c) magnified surface appearance showing smoothly joined grains of W_2C phase formed from W particles through reaction with graphite decorated partially with growing nano-meter size WC whiskers. (d) magnified view around the right hand side edge of the picture (c). (e) appearance of nano-meter size WC whiskers grown over the W_2C grain surface. (f) appearance of nano-meter size WC whiskers grown along the grain boundary.

reference to the equilibrium phase relationship for the W-C binary system.[1)]

Parallel formation of the meta-stable W_2C and the stable WC might be appreciated in terms of the small difference in phase stability among these phases as demonstrated by a series of *ab initio* molecular orbital calculation works presented by Hugosson and co-workers for W-C system[14)] as well as for Mo-C system.[15–18)]

4. Concluding Remarks

The present results obtained using a solar furnace at PROMES-CNRS in Odeillo (France) exhibited unique possibility of synthesising WC whiskers by heating C/W mixture of arbitrary mole ratio with ultra-fast heating rate to a target temperature at which the additional heat evolved by exothermic carbide-forming reaction would realize the instantaneous formation of melt pool of W metal. This particular evidence of WC whisker formation was detected for the target temperature 1900°C but not in the case of the target temperature 1600°C.

The similar synthesis of MC whiskers for metals other than W might be made using the solar furnace at PROMES-CNRS by taking advantage of its unique capacity of ultra-fast heating rate at the onset of the processing. For the metals with lower melting point, the target temperature for the MC whisker synthesis might be set at lower level than 1900°C used for the WC whisker formation.

Nano-meter size MC whiskers synthesised by such procedure might be collected to be used as acicular reinforcer for MMC (metal matrix composite) or some other hard tool manufacturing applications.

In fact, usage of acicular mono-crystalline hard material including MC whiskers as the reinforcer for composite material was described in some available patents.[19,20)]

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