

Heterogeneity along the Height in Disc Specimens of Graphite/Tungsten Powder Mixtures with Sub-Stoichiometric Carbon Atom Ratios Heated by Concentrated Solar Beam to 1600°C

Nobumitsu Shohoji¹, Teresa Magalhães¹, Fernando Almeida Costa Oliveira¹, Luís Guerra Rosa², Jorge Cruz Fernandes², José Rodríguez³, Inmaculada Cañadas³ and Diego Martínez³

¹LNEG-Laboratório Nacional de Energia e Geologia, LEN-Laboratório de Energia, 1649-038 Lisboa, Portugal

²IST-Instituto Superior Técnico, Departamento de Engenharia de Materiais, 1049-001 Lisboa, Portugal

³PSA-Plataforma Solar de Almería, CIEMAT-Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Apartado 22, E-04200 Tabernas (Almería), Spain

Compositional heterogeneity along the thickness of compacted disc specimens of graphite/tungsten powder mixtures with sub-stoichiometric carbon atom ratios (0.35, 0.50 and 1.00) heated by concentrated solar beam to 1600°C was characterised by X-ray diffraction. Top surface of any examined test piece was consisted purely of mono-carbide WC while the bottom surface showed different constitution depending on the net initial C/W ratio of the test piece; almost pure metallic W for the C/W = 0.35 specimen, dominant metallic W associated with small proportion of W₂C for the C/W = 0.50 and dominant W₂C with trivial proportion of WC for the C/W = 1.0. In the intermediate zone between the top and the bottom layers, the constitution held virtually constant depending on the nominal C/W ratio of the starting material: co-existing metallic W and W₂C for the C/W = 0.35, pure W₂C for the C/W = 0.50 and predominant WC with trace W₂C for the C/W = 1.00. Unlike for the top surface of the C/W = 0.35 test piece heated in a solar furnace to 1900°C reported earlier, no evidence of formation of nano-meter scale WC whisker was detected for the top surface in any sample heated to 1600°C in the present work. [doi:10.2320/matertrans.M2009313]

(Received September 17, 2009; Accepted November 16, 2009; Published January 7, 2010)

Keywords: tungsten carbides, solar furnace, X-ray diffraction, temperature gradient

1. Introduction

In a preceding publication,¹⁾ growth of nano-meter scale WC whiskers over top surface of compacted pellet of graphite/tungsten powder mixture with C/W atom ratio 0.35 heated to 1900°C in a solar furnace at PROMES-CNRS (Laboratoire Procédés, Matériaux, Energie Solaire) in Odeillo (France) was reported. This WC whisker formation was detected during the course of processing C/W test pieces with sub-stoichiometric C atom ratios by solar radiation heating aiming at synthesising pure sub-carbide W₂C.^{2,3)} Thus, the results were later subjected to further comprehensive analysis in terms of surface singularity in tungsten carbide synthesis by solar radiation heating.⁴⁾

In fact, our recognition on surface singularity in the solar-synthesised W carbide specimens was somewhat accidental. Compared with the C/W powder compacts processed at 1600°C, the counterparts processed at 1900°C were not easy to pulverise for XRD (X-ray diffraction) characterisation probably on account of advanced degree of sintering consolidation at a higher temperature. The degree of difficulty for pulverisation among C/W powder compact specimens after solar-heating to 1900°C tended to rise with the decreasing C/W atom ratio in the range of C/W between 1.00 and 0.35. Thus, aiming at avoiding difficult grinding process for pulverisation for the C/W specimens heated in solar furnace to 1900°C, we tried to characterise the C/W specimens in terms of the XRD patterns taken from the top surface alone. This decision was made after the XRD characterisation of the C/W compacts solar-heated to 1900°C was proceeded from C/W = 1.00 test piece down to C/W = 0.50 test piece in order of descending C/W atom ratio.

Then, as presented in Table 1 (reproduced from Ref. 4)), weak but unmistakable WC peaks besides intense W₂C peaks were detected in the top surface XRD patterns taken for the specimens with C/W = 0.45, 0.40 and 0.35, heated to 1900°C.

Thus, in spite of difficulty, we decided to pulverise the C/W = 0.35 test piece processed at 1900°C to be characterised by XRD for average composition. Then, as seen in Table 1,⁴⁾ XRD peaks identifiable as WC became indiscernible in the pulverised specimen representing the averaged-out composition of the entire test piece implying that WC in the C/W = 0.35 test piece processed at 1900°C must have been localised only in the very thin top surface layer.

Anyway, before destructively pulverising the C/W = 0.35 test piece solar-heated to 1900°C for the XRD characterisation, top surface of this test piece was inspected under SEM (scanning electron microscope). Then, to our surprise, we detected nano-meter scale WC whiskers developed over this test piece as reproduced in Fig. 1.^{1,3)}

As listed in Table 1,⁴⁾ no separate top surface XRD characterisation was made for the test pieces processed at 1600°C due to lacking insight in this aspect when the specimen characterisation was undertaken at that stage and thence the standard XRD characterisation was done for the pulverised specimen representing the entire test piece.

Being intrigued by the observed yield of mono-carbide WC in form of the nano-meter scale WC whiskers over the bulk substrate composed of W₂C/W mixture for the test piece with C/W = 0.35 heated to 1900°C in the solar furnace at PROMES-CNRS in Odeillo,^{1,3,4)} comparative experiment was decided to be done using a solar furnace at PSA (Plataforma Solar de Almería) in Tabernas (Spain) at a

Table 1 Measured $CuK\alpha$ XRD peak positions for the graphite/tungsten powder mixtures processed in the solar furnace to two different levels of target temperatures, 1600°C and 1900°C (reproduced from Ref. 4)) compared with the standard XRD peak positions of the relevant compounds in the binary W-C system compiled by Storms.¹¹⁾

Storms data				Experimental 2θ (degree)											
				1600°C					1900°C						
				powder					powder	top surface	top surface	top surface	powder	powder	
2θ (degree)	(hkl)		G/W ratio		0.35	0.40	0.45	0.50		1.0	0.35	0.35	0.40	0.45	0.50
31.51			001	31.428	31.440	31.404	31.452	31.452		31.416	31.416	31.428			31.420
34.61		100		34.572	34.572	34.572	34.536	34.512	34.620	34.464	34.400	34.488		34.596	34.440
35.64			100	35.604	35.593	35.580	35.603	35.592		35.585	35.568	35.580			35.568
38.10		200		38.051	38.052	38.028	38.016	37.992	38.064	37.968	37.956	37.968		38.064	37.940
39.67		101		39.624	39.636	39.612	39.588	39.552	39.672	39.510	39.440	39.520		39.648	39.500
40.26	110			40.224	40.212	40.212	40.200	40.236	40.224						
										<i>44.436</i>	<i>44.440</i>	<i>44.424</i>			
48.30			101	48.264	48.287	48.228	48.242	48.264		48.240	48.216	48.240			48.220
52.41		102		52.380	52.392	52.380	52.332	52.284	52.248	52.230	52.170	52.250		52.404	52.212
58.25	200			58.224	58.236	58.212			58.236						
62.03		110		62.016	62.004	62.016	61.932	61.872	62.124	61.824	61.692	61.840		62.052	61.770
64.03			110	64.008	63.960		63.996	63.984		64.008	63.970	63.980			63.955
65.78			002					65.736		65.688	65.680	65.690			65.705
69.90		103		69.852	69.864	69.864	69.792	69.744	69.936	69.751	69.620	69.690		69.900	69.675
73.02		200		72.974	72.962	72.890	72.924		73.164	73.080	73.040	73.080		73.056	73.050
73.11			111	73.140		73.092	73.104	73.068							73.050
73.18	211			73.164	73.140	73.198									
75.17		112		75.168	75.156	75.144	75.017	74.988	75.264	74.940	74.800	74.945		75.216	74.860
75.49			200	75.491	75.456		75.481	75.444							75.425
76.18		201		76.200	76.212	76.224	76.080	75.996	76.320	75.960	75.785	75.970		76.200	75.880
77.12			102	77.077	77.111	77.053	77.052	77.088		77.052	77.040	77.052			77.052
81.50		004		81.455	81.528	81.467	81.384		81.552	81.276	81.228	81.255		81.480	81.280
84.08			201	84.049			84.060	84.036		84.090	84.036	84.060			84.020
85.47		202		85.476	85.499	85.524	85.356		85.644	85.188	84.990	85.224		85.480	
86.99	220			87.000	86.976	86.939									
91.67		104		91.704	91.668	91.692	91.548		91.740	91.410	91.320	91.400		91.668	
98.73			112	98.736	98.456	98.677		98.700		98.680	98.680	98.680			98.676
100.63	310			100.680	100.632	100.633	100.696								
100.79		203		100.907	100.824	100.860	101.293	100.572	100.943	100.368	100.296	100.490		100.830	
103.82		210		103.825	103.764	103.704	103.704	103.537	104.076	103.310	103.210	103.475		103.872	
106.98		211		107.088	107.063	107.124	106.848	106.728	107.220	106.356	106.320	106.660		107.060	106.572
108.15			210			108.075		108.096				108.160			108.096
109.08			003					109.032				108.980			109.000
109.82			202					109.788				109.790			109.770
112.53		114		112.488	112.560	112.620	112.368	112.260	112.764	112.070	111.984	112.150		112.596	112.128
114.91	222			114.924	114.949	114.937									
116.86		212		116.868	116.808	116.880	116.712	116.508	117.228	116.465	116.020	116.425		116.952	
117.32			211	117.048	117.084	117.179	117.301	117.288				117.300			117.270
120.56		105		120.588	120.659	120.612	120.372	120.205	120.815	120.020	120.060	120.180		120.600	
120.94			103					120.912		120.864		120.830			120.088
124.06		204		124.080	123.960	123.937	123.876		124.297	123.485	123.375	123.660		124.164	
126.35		300		126.168	126.229	126.264	126.180		126.600	125.892	125.556	125.900		126.528	
131.16	321			131.244	131.208	131.220			131.088						
133.33			300					133.308							133.272
135.90		213		135.924	136.176	136.044	135.672	135.456	136.128	134.904	134.960	135.340		136.068	
143.69		302		143.652	143.832	143.952	143.496	143.113	142.884	142.200	142.320	143.060		143.772	
a (A) =	3.165	2.990	2.906	2.992	2.991	2.990	2.994		2.995	3.003	3.006	2.998		2.991	
c (A) =		4.720	2.837	4.725	4.725	4.724	4.729		4.721	4.736	4.737	4.734		4.724	
c/a		1.579		1.579	1.580	1.580	1.579		1.576	1.577	1.576	1.579		1.579	

note) The peak at $2\theta \approx 44.4^\circ$ is identified to arise from the Al specimen holder.⁴⁾



Fig. 1 Appearances of the nano-meter scale WC whiskers formed over the $C/W = 0.35$ test piece top surface solar-heated to 1900°C in a solar furnace at PROMES-CNRS in Odeillo (France). (a) reproduced from Fig. 3(e) in Ref. 1). (b) reproduced from Fig. 3(c) in Ref. 3). Scale bar in both figures refers to length 500 nm.

slightly lower processing temperature, 1600°C , for C/W powder compacts at specified hypostoichiometric ratios.

As reported in the following text, no whisker formation was detected over any C/W specimen heated to 1600°C in the present work unlike for the $C/W = 0.35$ specimen heated to 1900°C .^{1,3)}

In the present work, XRD patterns were taken for the specimen surfaces at specified height from the bottom surface made available by stepwise polishing to look into transition of constitution of the phases present in the test pieces along the depth for the C/W powder compacts with C/W atom ratios, 0.35, 0.50 and 1.00, heated to 1600°C .

2. Experimental

Experimental procedures in the solar heating experiments at PSA are described only very briefly in the following text as the details might be referred to in our preceding publications.⁵⁻⁸⁾

Present experiments were done using a solar furnace at PSA under flowing inert Ar gas in a so-called Min-Vac reaction chamber like in the preceding series of works on the synthesis of tungsten carbide.⁵⁻⁸⁾ Schematic constitution of the Mini-Vac reaction chamber was displayed elsewhere (Fig. 1 in Ref. 5) and Fig. 2 in Ref. 8)). Solar furnace optical system configuration at PSA was shown schematically in Fig. 1 in Ref. 8).

Figure 2 shows appearance of the specimen discs during cooling in the reaction chamber under flow of inert Ar gas and Fig. 3 the monitored temperature profile together with the degree of opening of the louvered shutter in the solar furnace optical system as well as the measured natural solar power density which was around 850 W/m^2 . Temperature was measured using a thermocouple inserted from the bottom into the alumina sheath at the centre of the graphite crucible (Fig. 2). The tip of the thermocouple was set to be at around the height corresponding to the top surface level of the specimen discs as exhibited in Fig. 3 in Ref. 8).

The test pieces were compacted pellets of graphite/tungsten powder mixtures. Graphite powder ($< 50\ \mu\text{m}$) was supplied from E. Merck A.G., Darmstadt (Germany) and tungsten powder ($> 99.5\%$ purity; $< 75\ \mu\text{m}$) from Minas e

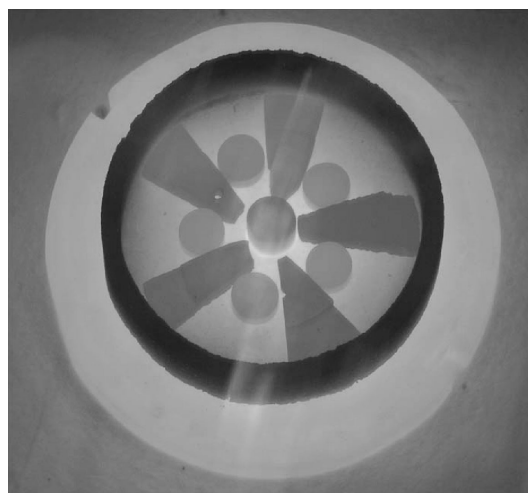


Fig. 2 Appearance of the specimen discs (diameter about 8 mm at this stage of progress of the reaction; total of 5 discs placed inside a graphite crucible with a diameter *ca.* 70 mm; separated by graphite wedges) during cooling in the reaction chamber under flow of inert Ar gas. At the centre of the crucible, alumina sheath containing thermocouple for temperature control is seen. The tip of the thermocouple inserted from the bottom was set to be at around the level corresponding to the top surface of the specimen discs.

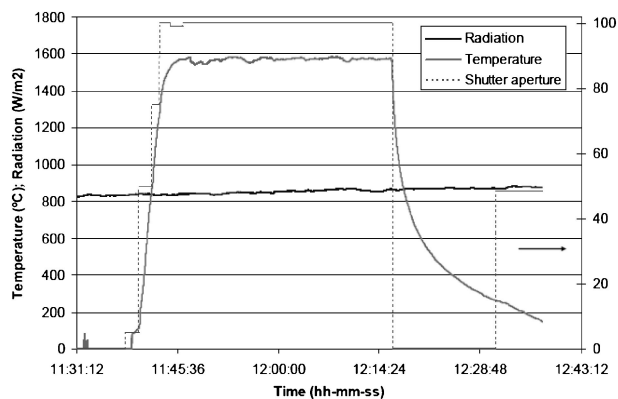


Fig. 3 Temperature profile during the solar-synthesis of tungsten carbides measured using a thermocouple inserted in a hole drilled at the centre bottom of the graphite crucible. Measured natural solar radiation intensity and extent of opening of the louvered shutter in the solar furnace optical system are also plotted.

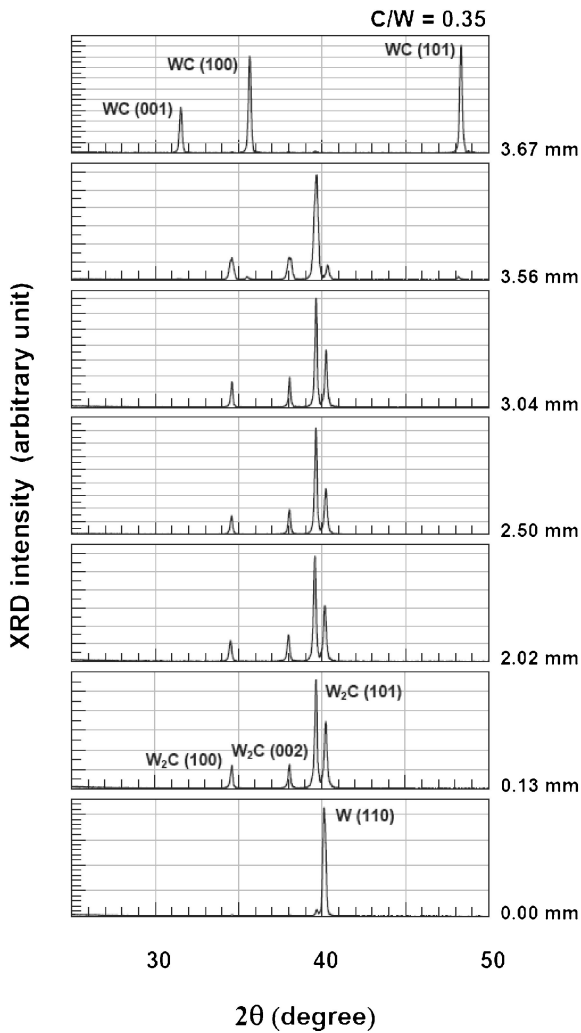


Fig. 4 XRD patterns taken for the $C/W = 0.35$ test piece (thickness 3.67 mm) processed at 1600°C at different heights of the disc from the bottom surface.

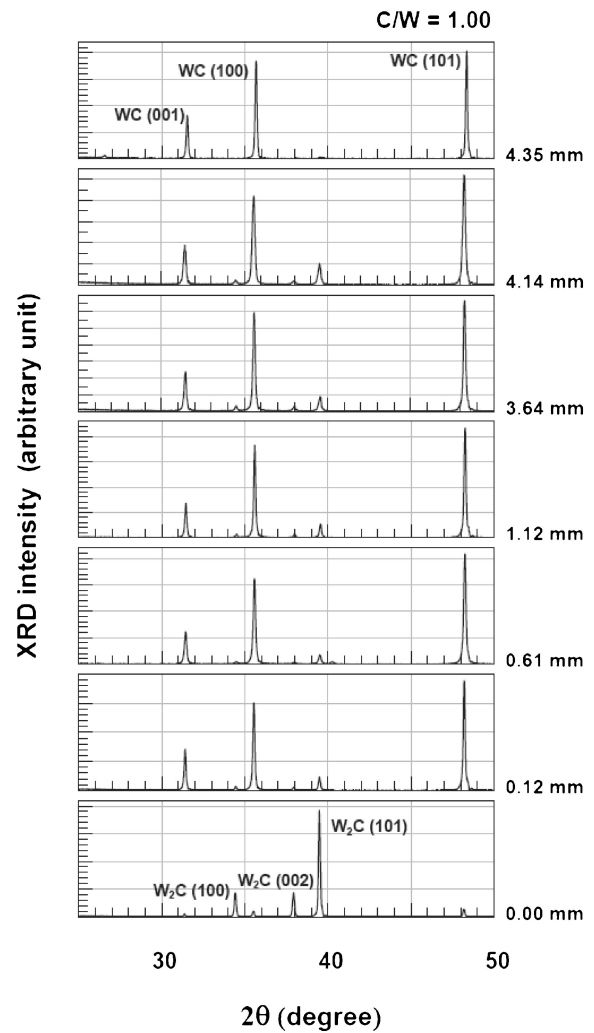


Fig. 5 XRD patterns taken for the $C/W = 1.00$ test piece (thickness 4.35 mm) processed at 1600°C at different heights of the disc from the bottom surface.

Metalurgia, S.A., Aveiro (Portugal). They were mixed to C/W atom ratios, 0.35, 0.50 and 1.00, and compacted into pellets of 10 mm in diameter and about 4 mm thick by uniaxial pressing at 450 MPa. The mixing of the powders was done using Type T2C Turbula mixer of Willy A. Bachofen AG Maschinenfabrik (Basel, Switzerland) for 1 h duration.

The as-prepared top and bottom surfaces as well as the as-polished intermediate surface were inspected by SEM using XL30 FEG of PHILIPS and XRD characterisation was done using Geigerflex D/MAX IIIC diffractometer of RIGAKU with $\text{CuK}\alpha$ radiation for the disc surfaces at different heights from the bottom surface as well as for both the very top and the very bottom surfaces.

3. Results and Discussion

Figures 4–6 summarise the XRD patterns obtained for the disc surfaces at different heights from the bottom for the test pieces with $C/W = 0.35$, 1.00 and 0.50, respectively.

By comparing the top surface XRD patterns among these three test pieces, it is evident that the top surface of the test

piece was consisted of tungsten mono-carbide WC alone irrespective of the bulk C/W atom ratio of the test piece. On the other hand, the bottom surface constitution varied depending on the C/W ratio of the test piece; almost purely metallic W with scarce W_2C (101) peak for the test piece with $C/W = 0.35$ (Fig. 4), mainly W_2C with trace WC for the $C/W = 1.00$ (Fig. 5) and largely metallic W with trace W_2C for the $C/W = 0.50$ (Fig. 6). In the intermediate range excluding the top and the bottom layers, the composition of the test piece appeared to hold constant along the height with the constituents depending on the bulk C/W atom ratio; W_2C associated with metallic W for the $C/W = 0.35$ (Fig. 4), WC associated with trace W_2C for the $C/W = 1.00$ (Fig. 5) and W_2C single-phase for the $C/W = 0.50$ (Fig. 6).

These evidences show following features.

(1) Top surface is always consisted of pure WC phase irrespective of the bulk C/W ratio.

Consistent yield of WC phase over the top surface of the C/W powder mixture specimen irrespective of the initial bulk composition is the most intriguing aspect to note in the carbide synthesis experiments using a solar furnace and was discussed as the surface singularity in a preceding work.⁴⁾

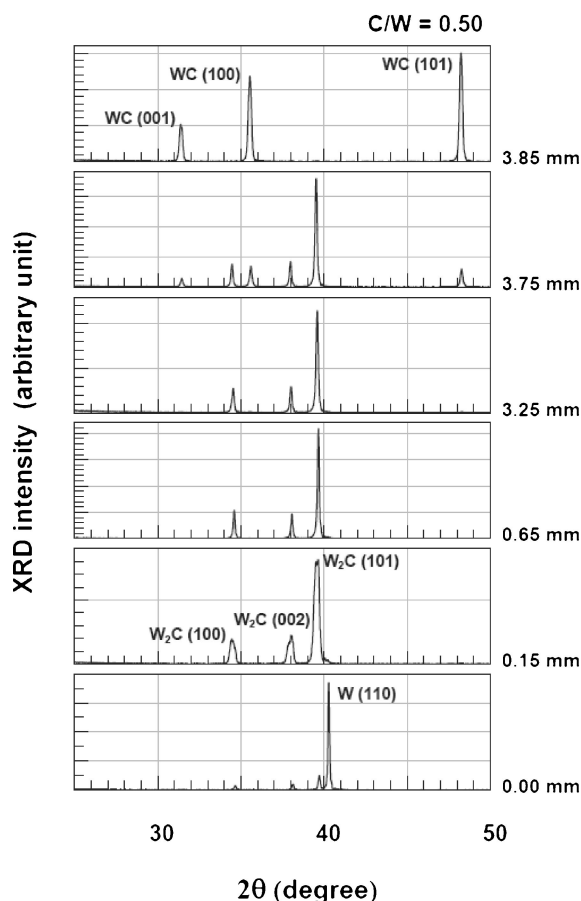


Fig. 6 XRD patterns taken for the $C/W = 0.50$ test piece (thickness 3.85 mm) processed at 1600°C at different heights of the disc from the bottom surface.

Anyway, in the present work undertaken at a set processing temperature 1600°C , no evidence of formation of nano-meter scale WC whiskers was detected unlike for the $C/W = 0.35$ test piece processed at 1900°C .^{1,3)} The detected formation of the nano-meter scale WC whiskers at 1900°C was appreciated in terms of the VLS mechanism proposed by Milewski *et al.*⁹⁾ where V stands for “vapour feed gas”, L for “liquid catalyst” and S for “solid crystalline whisker growth” by assuming the low melting point impurities like Al and Fe contained in the W acted as the liquid catalyst to realise the VLS process. Under the present experimental condition at the target processing temperature 1600°C , the VLS mechanism did not seem to prevail and thence there was no yield of nano-meter scale WC whiskers over any test piece top surface although the top surface was consistently covered with WC no matter what the bulk C/W ratio in the starting material was.

Figure 7 compares typical top surface appearances of the test pieces synthesised in the present work at 1600°C . Unlike the top surface of the $C/W = 0.35$ test piece processed at 1900°C (cf. Fig. 1^{1,3)}), we do not find any evidence of formation of WC whisker over the top surface of the present test pieces. It is also noticed in Fig. 7 that the extent of partial melting of the test piece top surface processed at 1600°C was evidently less than that processed at 1900°C (Fig. 1^{1,3)}) judging from smoother continuous appearance of grains of the latter than those of the former.

Partial melting of the top surface is speculated to be the consequence of instantaneous massive heat evolution from exothermic reaction taken place at the onset of solar heating to turn the specimen top surface temperature by far higher than the target processing temperature 1600°C . For example, we noticed such temporary temperature overshoot in measured temperature profile using a thermocouple reproduced in Fig. 4(a) in Ref. 8) although no clear temperature overshoot is noticed in temperature profile obtained during the present test run (Fig. 3).

In contrast to the top surface, the bottom surface did not seem to demonstrate any evidence of partial melting as represented in Fig. 8 (a; $C/W = 1.00$), (c; $C/W = 0.50$) and (e; $C/W = 0.35$) judging from the feature that individual grains in Fig. 8(a), (c) and (e) were by far smaller than those in Fig. 7 (top surface pictures).

In Fig. 8 (b; $C/W = 1.00$; $h = 3.64$ mm), (d; $C/W = 0.50$; $h = 3.25$ mm) and (f; $C/W = 0.35$; $h = 2.02$ mm), representative as-polished intermediate surface SEM appearances at the height h from the bottom surface are compared. These as-polished intermediate surface appearances look almost comparable to the appearances of the bottom surface (Fig. 8(a), (c) and (e)) rather than those of the top surface (Fig. 7) showing the brittle nature of the specimens allowing detachment of agglutinated grains as individual units revealing no intra-granular surface of grains. Anyway, unlike the as-prepared top (Fig. 7) and bottom (Fig. 8(a), (c) and (e)) surfaces, cracks induced during polishing are visible in the as-polished intermediate surface (Fig. 8(b), (d) and (f)).

Yield of WC, although not in form of nano-meter scale whisker, detected over the present test piece top surface irrespective of the bulk C/W ratio might be appreciated in terms of the presence of gaseous C_2 radical over the test piece. Badie *et al.*¹⁰⁾ reported detection of C_2 radical plume during heating of graphite target by concentrated solar beam in an experiment aiming at synthesising fullerene C_{60} in a solar furnace at PROMES-CNRS. During the course of our solar tungsten carbide synthesis work undertaken at PROMES-CNRS,¹⁻⁴⁾ we certainly saw orange-colour plume of the C_2 radical over the crucible (see Fig. 9 reproduced from Fig. 2(c) in Ref. 1)).

In the present experimental setup at PSA, we could not observe the reaction chamber interior from the side during the solar heating experiment session but it was quite likely that plume of C_2 radical was emitted from the graphite contained in the specimen pellets as well as from the graphite crucible.

Thus, consistent WC formation at the top of compacted C/W powder mixture at any C/W atom ratio as observed in this work was concluded to be ascribable to the presence of C_2 radical plume formed over the test piece containing graphite placed over the graphite crucible.¹⁰⁾ It is quite likely that carbon activity $a(\text{C})$ of C_2 radical is considerably higher than $a(\text{C})$ of graphite ($= 1$; reference state of C) and accordingly W at the top of the pellet being in contact with the plume of C_2 radical might be carburised to the highest form of tungsten carbide, WC.

(2) Certain extent of carbon deficiency at the bottom surface of the test piece.

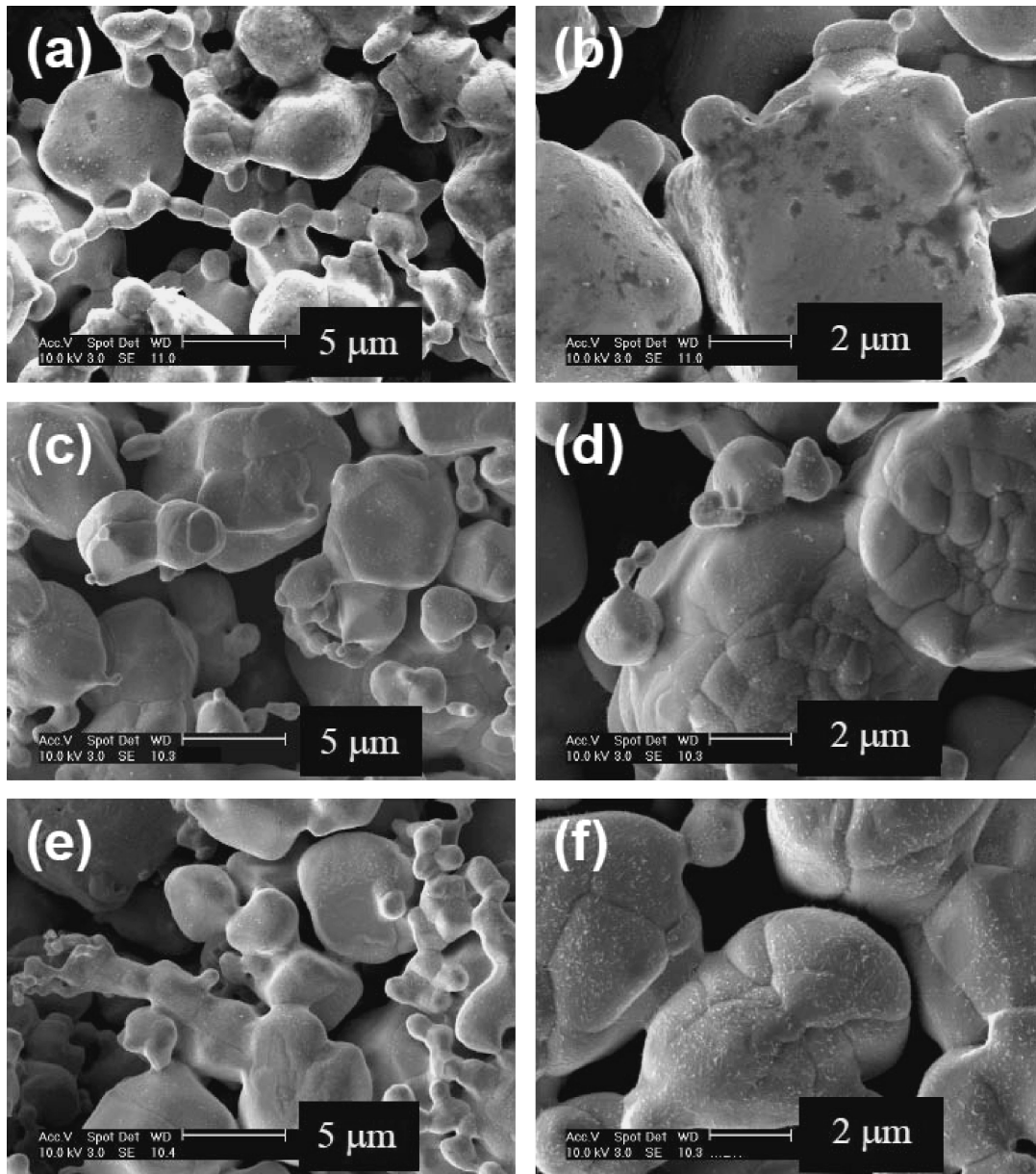


Fig. 7 SEM appearances of the as-obtained top surface of the test pieces at different C/W atom ratios. (a) & (b): C/W = 1.00, (c) & (d): C/W = 0.50, (e) & (f): C/W = 0.35.

In any examined test piece in the present work, bottom surface was consisted of phases with diminished C content compared with the ones anticipated from the initial bulk C/W atom ratio.

This aspect does not seem to be interpreted solely in terms of inevitable temperature gradient arisen along the test piece height during heating of the test piece by concentrated solar beam. In any solar beam heating experiment for carbide synthesis,¹⁻⁸⁾ test piece top surface was set at a hot spot deviating downwardly from the exact focal spot of the beam-concentrating optical system (cf. bottom left insert in Fig. 1 in Ref. 10) in which the position (a) represents schematically the used hot spot). The extent of the downward deviation of the test piece top surface position from the exact focal spot was chosen according to the target processing temperature. Thus, the bottom surface temperature of the test piece of thickness about 5 mm might be by 50–100 K lower than the top surface temperature.¹⁻⁴⁾

This extent of temperature gradient along the test piece height does not seem to justify the detected degree of the C depletion at the test piece bottom surface. Instead, probable cause for the C deficiency at the bottom surface might be the yield of C₂ radical plume from the top surface which might have induced the forced upward C diffusion through the compacted pellet of the C/W powder mixture.

The bottom surface of the C/W = 0.35 test piece yielded XRD peak identifiable as almost pure metallic W with scarce W₂C. It would mean that no C feed took place from the graphite holder beneath although the test piece bottom surface was in loose physical contact with the block of solid graphite which might have acted as a massive source of C.

(3) Existence of the steady state composition range in the pellet excluding the top and the bottom surface layers.

As seen in the XRD patterns reproduced in Figs. 4–6, each test piece was with intermediate zone in which the compo-

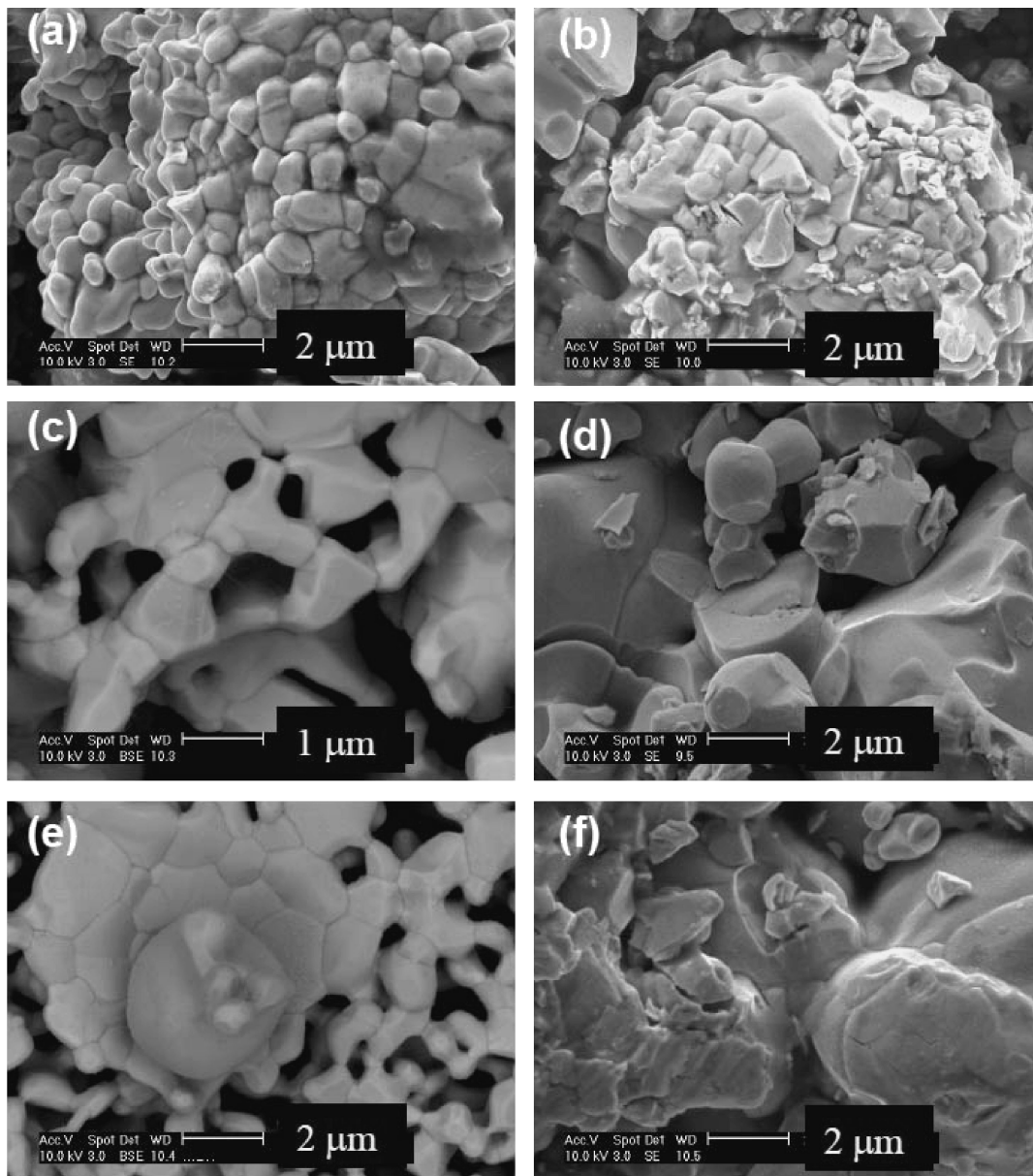


Fig. 8 SEM appearances of the as-obtained bottom surface and as-polished surface at height h from the bottom surface of the test pieces at different C/W atom ratios. (a) C/W = 1.00 bottom surface ($h = 0$ mm), (b) C/W = 1.00 at $h = 3.64$ mm, (c) C/W = 0.50 bottom surface ($h = 0$ mm), (d) C/W = 0.50 at $h = 3.25$ mm, (e) C/W = 0.35 bottom surface ($h = 0$ mm), (f) C/W = 0.35 at $h = 2.02$ mm.

sition appeared to hold constant along the height. For example, in the C/W = 0.35 test piece with thickness 3.67 mm (Fig. 4), XRD patterns taken between 3.04 mm and 0.13 mm showed peaks identifiable as W_2C and metallic W with comparable intensity ratios among them. The XRD pattern taken at the height 3.56 mm from the bottom (that is, by 0.11 mm away from the top surface), relative intensity of W (110) peak was weaker than the intensity of the W_2C peaks and the W_2C peaks were comparatively broad compared with those in the range between 3.04 mm and 0.13 mm. Such range of intermediate steady state composition for the C/W = 1.00 specimen with thickness 4.35 mm extended between 4.14 mm and 0.12 mm showing dominant WC peaks with trace W_2C peaks (Fig. 5). As reviewed elsewhere,²⁻⁴⁾ W_2C appears to be quite stable (rigorously speaking, meta-stable under certain experimental conditions) and, once it is formed, it would be difficult to convert to WC

even when the condition is established in which WC rather than W_2C is the genuine stable phase in thermodynamic term. In the C/W = 0.50 test piece with thickness 3.85 mm (Fig. 6), such range of intermediate steady state composition extending between 3.25 mm and 0.15 mm was solely composed of W_2C . The XRD peaks identifiable as W_2C phase emerged at 0.15 mm look appreciably broader than those in the range between 3.25 mm and 0.65 mm implying that the extent of progress of the W_2C formation reaction at the height 0.15 mm from the bottom surface was slightly less advanced than that in the range between 3.25 mm and 0.65 mm probably on account of slightly lower temperature at the height 0.15 mm than at the upper part of the test piece.

4. Concluding Remarks

XRD characterization of C/W specimens with C/W atom



Fig. 9 Appearance of orange-colour C_2 radical plume (being highlighted with three arrows) yielded over the graphite crucible during solar radiation heating experiment for the C/W powder mixture compact undertaken at PROMES-CNRS in Odeillo (France) (reproduced from Fig. 2(c) in Ref. 1)).

ratios, 0.35, 0.50 and 1.00, heated to 1600°C under concentrated solar beam in a solar furnace at PSA was done at arbitrary distances from the bottom surface of the test pieces of thickness around 4 mm. In the present work, the lowest threshold C/W ratio in the test piece 0.35 was chosen with reference to the phase diagram for binary W-C system (e.g., Fig. 50 in page 144 in Ref. 11)) in which the lowest threshold composition of the non-stoichiometric W_2C phase extends to 0.35 at 2710°C from around 0.45 at temperatures lower than 2000°C . As seen in Fig. 4, the test piece started from C/W = 0.35 was not free from metallic W in accordance with the phase equilibrium information. Anyway, even for this specimen with C/W = 0.35, the top surface was purely composed of WC.

Single-phase W_2C sample was prepared only in the intermediate zone of the C/W = 0.50 test piece. All the other specimens yielded mixed phases even in this intermediate zone.

As such, synthesis of fully homogenised tungsten carbide specimen (either dual-phase specimen or single-phase specimen) from compacted C/W powder specimen under heating with concentrated solar beam appeared to be difficult. If homogeneous tungsten carbide specimen is desired to be prepared in solar furnace, certain extent of top layer and bottom layer had to be removed away after the solar-carburisation process was completed.

REFERENCES

- 1) S. Dias, F. Almeida Costa Oliveira, B. Granier, J.-M. Badie, J. Cruz Fernandes, L. Guerra Rosa and N. Shohoji: *Mater. Trans.* **48** (2007) 919–923.
- 2) F. Almeida Costa Oliveira, J. Cruz Fernandes, J.-M. Badie, B. Granier, L. Guerra Rosa and N. Shohoji: *Internat. J. Refractory Met. Hard Mater.* **25** (2007) 101–106.
- 3) F. Almeida Costa Oliveira, B. Granier, J.-M. Badie, J. Cruz Fernandes, L. Guerra Rosa and N. Shohoji: *Internat. J. Refractory Met. Hard Mater.* **25** (2007) 351–357.
- 4) F. Almeida Costa Oliveira, B. Granier, J.-M. Badie, J. Cruz Fernandes, L. Guerra Rosa and N. Shohoji: *Mater. Sci. Forum* **587–588** (2008) 993–997.
- 5) D. Martínez, J. Rodríguez, L. Guerra Rosa, J. Cruz Fernandes and N. Shohoji: *J. Physique IV (Symposium Series)* **9** (Proceedings 3) (1999) pp. 405–410.
- 6) N. Shohoji, L. Guerra Rosa, J. Cruz Fernandes, D. Martínez and J. Rodríguez: *Mater. Chem. Phys.* **58** (1999) 172–176.
- 7) N. Shohoji, P. M. Amaral, J. Cruz Fernandes, L. Guerra Rosa, D. Martínez and J. Rodríguez: *Mater. Trans. JIM* **41** (2000) 246–249.
- 8) J. Rodríguez, D. Martínez, L. Guerra Rosa, J. Cruz Fernandes, P. M. Amaral and N. Shohoji: *J. Solar Energy Engineering (Trans. ASME)* **123** (2001) 109–116.
- 9) J. V. Milewski, F. D. Gac, J. J. Petrovic and S. R. Skaggs: *J. Mater. Sci.* **20** (1985) 1160–1166.
- 10) J.-M. Badie, G. Flamant, T. Guillard and D. Laplaze: *Chem. Phys. Lett.* **358** (2002) 199–206.
- 11) E. K. Storms: *The Refractory Carbides*, New York, (Academic Press) p. 1967.