Influence of Colour Filter on Reaction Products from Mo and W Heated to 2000°C by Concentrated Solar Beam in N₂ Gas Environment in a Solar Furnace at PROMES-CNRS

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In a preceding work, we reported attempts of synthesizing nitride of *d*-group transition metals including Ti, V, Nb and Ta using a solar furnace at PROMES-CNRS. In standard solar furnace experimental setup, graphite crucible is used as the sample holder on account of its resistance against high temperature and thermal shock. Plume of C₂ radical with high chemical activity *a*(C) of C was reported to yield from graphite crucible under irradiation of concentrated solar beam. Thus, synthesis of pure metal nitride MN was not successful in the preceding work done in N₂ gas environment heated by solar beam irradiation under standard experimental setup. To overcome this problem of undesired carburization in solar furnace, insertion of colour filter in the path of solar beam was tried and it was found that the C₂ radical yield from the graphite crucible was effectively suppressed by insertion of Sky blue filter and carbo-nitride M(C,N) with comparatively low C-content was synthesized for Ti, V, Nb and Ta at 2000°C in N₂ gas environment while, without the Sky blue filter, M(C,N) with high C-content and low N-content was synthesized under the otherwise comparable conditions of temperature and nitrogen partial pressure. These evidences appeared to suggest that nitride synthesis might be realized in standard solar furnace experimental setup using standard sample holder made of graphite by insertion of Sky blue filter. In the present work, reaction products from Mo and W in N₂ gas environment under solar heating to 2000°C were characterized and effectiveness of the Sky blue filter for suppression of C₂ radical yield from the graphite crucible was ascertained.

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1. Introduction

In a preceding publication,¹⁾ we reported nitriding performances of *d*-group transition metals including Ti, V, Nb and Ta at a target temperature of 2000°C in a solar furnace at PROMES-CNRS in Odeillo, France. The PROMES-CNRS is located in southern Pyrenees at height about 1500 m from the sea level. In the conventional experimental setup using solar furnace at PROMES-CNRS, sample holder was made of graphite. Under concentrated solar beam radiation, plume of C₂ radicals emitting radiation at 517 nm was reported to yield from graphite.²⁾ As the consequence, the reaction products from Ti, V, Nb and Ta in N₂ gas environment under the solar beam heating were all carbo-nitride MC_{1-x}N_x¹⁾ rather than nitride MN_x on account of presence of C₂ radical with high chemical activity *a*(C) of carbon emitted from the graphite crucible.

Aiming at suppressing the influence of C₂ radical under solar beam heating to synthesize carbo-nitride with reduced C content, insertion of colour filter in the path of solar beam before entering into the parabolic concentrator was tested.¹⁾ Two colour filters, Sky blue filter (Ref.# 068) and Medium yellow filter (Ref.# 010), supplied from Lee Filters (<http://www.leefilters.com/>) that were readily available at PROMES-CNRS were tested for this purpose. The Sky blue filter cuts more than 60% of the light of wavelength between 500 nm and 700 nm while the Medium yellow filter cuts

more than 80% of the light of wavelength below 475 nm (Fig. 1).

As reported in the preceding publication,¹⁾ filtering experimental results revealed intriguing features such as (i) temperature drop by inserting the colour filter in the light path was negligible under otherwise comparable optical setting under absence of colour filter suggesting that the heating effect by the concentrated solar beam must arise mainly from the IR (infra-red) range of waves, (ii) significant retardation of carburizing reaction was realized with the Sky blue filter implying that C₂ radical emission from the graphite crucible was suppressed efficiently by the Sky blue filter.

To look further into the effectiveness of the colour filter insertion for reactions of *d*-group transition elements in N₂ gas environment under concentrated solar beam irradiation, additional experiments were done for VIa-group metals, Mo and W, in this work.

2. Experimental

2.1 Specimen materials

Specifications of the sample materials used for the present work were as follows; Mo: 99% pure supplied from Ventron (Karlsruhe, Germany) with particle size < 50 μm, W: 99.5% pure supplied from Minas e Metalurgia (Albergaria-a-Velha, Portugal) with particle size < 75 μm, C: graphite supplied from E. Merck AG (Darmstadt, Germany) with particle size < 50 μm.

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Fig. 1 Wave transmission performances of the Pyrex Glass and the Lee Colour Filters. (A) Pyrex glass (Corning 7740 with thickness 1 mm); reproduced from <http://www.quartz.com/pxprop.pdf> (B) Sky blue (Ref.# 068) filter; reproduced from <http://www.leefilters.com/lighting/products/finder/act:colourdetails/colourRef:C4630710C4A5A9/> (C) Medium yellow (Ref.# 010) filter; reproduced from <http://www.leefilters.com/lighting/products/finder/act:colourdetails/colourRef:C4630710C3E644/>.

Fig. 2 Graphite crucible setups. (A) with graphite lid, pyrometric temperature measurement done at spot (a), (B) without lid, pyrometric temperature measurement done at spot (b).

N_2 gas was 99.99% pure (Azote U) supplied from Air Liquide (France) with nominal impurities, $H_2 \leq 5$ ppm and $O_2 \leq 5$ ppm.

Each test piece (pure metal M or mixture (M+1.5G) consisting of metal M and excess graphite G with mole ratio 1.5 against M) was a pellet of dimension, 8 mm ϕ and about 4 mm thick, prepared by compacting the powders by applying uniaxial pressure of 400 MPa at ambient temperature.

2.2 Solar irradiation procedure

The solar irradiation experiments in the present work were done using the PROMES solar furnace consisted of a 200 cm ϕ parabolic silver-mirror with the focal length 851 mm and the cone tip angle 120° receiving solar beams reflected by a flat mirror beneath. The flat silver-mirror reflector was mobile along NS (north-south) and EW (east-west) axes driven by a servo electric motor system to track the sun. The effective power of the solar furnace was 2 kW with a peak density at the focal spot 16 MW/m².

As the details of the experimental setup and procedure are referred to elsewhere,¹⁾ only the essential features of the experimental setup and the procedure are described below.

The reaction chamber made of Pyrex glass was with capacity about 3000 mL. Amount of solar beam entering into the parabolic mirror was controlled by extent of opening of

(A)

(B)

Fig. 3 Appearances of the solar heating experiments with colour filters. (A) with Sky blue (068) filter, (B) with Medium yellow (010) filter.

the louvered shutter made of light-weight C/C composite sheet placed horizontally in the solar beam path between the parabolic mirror concentrator and the flat reflector mirror beneath. The louvered shutter was closed (opening angle 0°) at the onset of the solar heating and it was opened to angle 30° at the onset of the solar beam heating. This led to temperature rise of the test piece to about 1000°C. This level of the shutter opening was held for at least 5 min to allow progress of nitriding or carburizing reaction at around this temperature to minimize unfavourable sublimation loss of metallic Mo or W. Then, the shutter opening angle was increased stepwise to 75°.

Table 1 Grouped test runs with measured test piece mass and N₂ gas pressure in the reaction chamber of about 3000 mL.

Group	run	starting material	w_i (g)	w_f	Δw	$\Delta w/w_i$	p_i (Torr)	$p_i(2000^\circ\text{C})$	p_f	Δp	phases in the reaction product (by XRD)
I: setup A: graphite lid no filter	06	Mo	1.1614	1.1567	-0.0047	-0.0041	403.3	618.8	NA	NA	β-Mo₂C
	04	W	1.9067	1.9198	+0.0131	+0.0069	407.6	637.3	NA	NA	W₂C, WC
II: setup B: no lid no filter	13	Mo	1.1704	1.1627	-0.0077	-0.0066	402.1	616.3	410.3	+8.2	β-Mo₂C, (Mo)
	14	W	1.9533	1.9101	-0.0432	-0.0022	402.7	613.0	405.8	+3.1	W, W₂C, (WC)
III: setup B: no lid sky blue filter.068	24	Mo	1.1812	1.1749	-0.0063	-0.0053	403.3	573.5	407.7	+4.4	Mo
	25	W	0.9731	0.9512	-0.0209	-0.0021	408.0	580.5	416.4	+8.4	W
	27	1.5G/Mo	1.0290	1.0018	-0.0272	-0.0264	404.5	571.3	417.4	+12.9	β-Mo₂C
	28	1.5G/W	1.2292	1.2066	-0.0226	-0.0184	406.6	567.1	415.0	+8.4	WC
IV: setup B: no lid medium yellow filter.010	34	1.5G/Mo	1.1994	1.1726	-0.0268	-0.0223	402.0	590.1	406.9	+4.9	η-MoC_{1-x}, (β-Mo₂C)
	35	1.5G/W	1.1766	1.1579	-0.0187	-0.0159	396.7	579.3	401.3	+4.6	WC

w_i : initial test piece mass (g),

w_f : final test piece mass (g),

$\Delta w = w_f - w_i$ (g),

p_i : initial N₂ gas pressure (Torr),

$p(2000^\circ\text{C})$: maximum measured N₂ gas pressure at the reaction temperature (Torr),

p_f : final N₂ gas pressure (Torr),

$\Delta p = p_f - p_i$ (Torr).

Temperature was measured using a single-colour optical pyrometer (KT15 IR Pyrometer manufactured by HEITRONICS; wavelength $\lambda = 5\mu\text{m}$) set at the center of the parabolic concentrator looking down the reaction chamber. The colour filter of dimension $2 \times 2\text{ m}$ was inserted horizontally between the louvered shutter and the parabolic concentrator where desirable.

Figure 2 depicts schematically the graphite crucible setups for the experiments. In the setup A, test piece was held in a graphite crucible being covered with 2 mm thick graphite disc lid. With this configuration, focal spot of the optical pyrometer was placed at the center of the graphite lid top surface. Under typical clear sky condition yielding the natural solar intensity range $900\sim 1000\text{ W/m}^2$, target temperature 2000°C (measured using the optical pyrometer controlled with EasyConfig Software with the calibrated emissivity ε for graphite taken to be 0.70 at $\lambda = 5\mu\text{m}$) was reached with the louvered shutter opening angle at around 75° after typically 10 min from the onset of the heating.

In the experiments with the crucible setup B with no graphite lid, the top surface height of the test piece was arranged to coincide with the graphite lid surface height in the setup A by inserting a thicker graphite spacer beneath the test piece. By so arranging, the energy density of the concentrated solar beam flux at the test piece top surface was considered to be made comparable to that at the graphite lid top surface in the setup A which led to the pyrometric temperature reading 2000°C for the graphite lid.

In the experiments using the crucible setup as depicted in Fig. 2(B), pyrometric temperature monitoring was done at a spot (b) over the edge surface of the graphite crucible. This zone was outside the hot spot of the solar beam ($\sim 1\text{ cm}\phi$) and the measured pyrometric temperature was by about 300 K lower than that at a spot (a) in the setup depicted in Fig. 2(A).

Figure 3 shows typical appearances of the reaction chamber during experiments with the colour filters.

The high purity N₂ gas was introduced into the reaction chamber to a partial pressure $p(\text{N}_2) \approx 400\text{ Torr}$ ($\approx 55\text{ kPa}$) at ambient temperature after at least twice evacuating and flushing with the same high purity N₂ gas.

Each test piece was held at the target temperature 2000°C for 30 min.

3. Results and Discussion

Measured experimental parameter values in the test runs together with the phases identified at the top surface of the test piece by XRD (X-ray diffraction) using $\text{CuK}\alpha$ radiation are listed in Table 1 (see Tables 4 and 5 for XRD peak positions used for the phase identification).

For Mo-N and W-N binary systems, mono-nitride phases, MoN and WN, were reported to form under conditions of extremely high nitrogen chemical activity $a(\text{N})$ realized by flowing NH₃ gas to inhibit dissociation into N₂ and H₂ to equilibrium level in a classical report by Hägg.³⁾ In fact, in the later follow-up experiment,⁴⁾ synthesis of mono-nitride MoN of Mo in NH₃ gas stream took place at 700°C but it dissociated to sub-nitride Mo₂N readily by raising the temperature by mere 25°C to 725°C ensuring validity of the pioneering work of Hägg.³⁾ Soon thereafter, Jehn and Ettmayer⁵⁾ reported that synthesis of MoN was impossible even in autoclave with high pressure N₂ gas up to 300 atm at 700°C . Theoretical validation of extremely high $a(\text{N})$ as well as of modestly high $a(\text{H})$ of NH₃ under suppressed extent of dissociation of NH₃ gas by flowing was presented later by Katsura.⁶⁾ In batch reaction system in which dissociation equilibrium in gas phase is reached among NH₃, N₂ and H₂

no effect of high $a(\text{N})$ and $a(\text{H})$ of “un-cracked” NH₃ in non-equilibrium state is gained and $a(\text{N})$ and $a(\text{H})$, respectively, are represented by the equilibrium partial pressures, $p(\text{N}_2)$ and $p(\text{H}_2)$.^{7,8)}

Table 2 Values of XRD angle $2\theta_{\text{Cu}}$ with $\text{CuK}\alpha$ radiation converted from observed values of $\sin^2(\Theta/2)_{\text{Cr}}$ with $\text{CrK}\alpha$ radiation for sub-nitride Mo_2N (β - and γ -phases; Tables 2 and 4) and mono-nitride MoN (δ -phase; Table 5) reported by Hägg.³⁾ $2\theta_{\text{Cu}}$ values aligned in ascending order from the top towards the bottom in the columns.

<i>hkl</i>	Mo₂N		MoN					
	γ -single phase		$(\beta + \gamma)$ -two-phase				δ -phase	
	$\sin^2(\Theta/2)_{\text{Cr}}$	$2\theta_{\text{Cu}}$	γ -phase		β -phase		$\sin^2(\Theta/2)_{\text{Cr}}$	$2\theta_{\text{Cu}}$
			$\sin^2(\Theta/2)_{\text{Cr}}$	$2\theta_{\text{Cu}}$	$\sin^2(\Theta/2)_{\text{Cr}}$	$2\theta_{\text{Cu}}$		
001	—	—	—	—	—	—	0.166	31.83
100	—	—	—	—	—	—	0.212	36.10
111	0.226	37.32	0.230	37.66	0.230	37.66	—	—
200	0.302	43.41	0.306	43.71	0.299	43.18	—	—
002	—	—	—	—	0.323	44.98	—	—
—	—	—	—	—	—	—	0.335	45.85
101	—	—	—	—	—	—	0.378	48.88
—	—	—	—	—	—	—	0.408	50.92
—	—	—	—	—	—	—	0.413	51.25
—	—	—	—	—	—	—	0.519	58.00
220	0.605	63.13	0.614	63.65	0.598	62.72	—	—
202	—	—	—	—	0.623	64.17	—	—
110	—	—	—	—	—	—	0.637	64.98
002	—	—	—	—	—	—	0.666	66.63
111	—	—	—	—	—	—	0.805	74.29
311	0.832	75.74	0.842	76.27	0.830	75.63	—	—
200	—	—	—	—	—	—	0.851	76.76
102	—	—	—	—	—	—	0.877	78.14
113	—	—	—	—	0.879	78.24	—	—
222	0.908	79.78	0.921	80.46	0.921	80.46	—	—

Conversion was made using following values of characteristic X-ray wave length λ cited by Cullity.⁹⁾

$\lambda(\text{CuK}\alpha) = 0.1541838 \text{ nm}$,

$\lambda(\text{CrK}\alpha) = 0.229100 \text{ nm}$,

whereas Hägg³⁾ referred to $\lambda(\text{CrK})$ values to be

$\lambda(\text{CrK}\alpha_1) = 0.22848 \text{ nm}$,

$\lambda(\text{CrK}\alpha_2) = 0.22890 \text{ nm}$,

$\lambda(\text{CrK}\beta) = 0.20895 \text{ nm}$.

Θ defined by Hägg³⁾ corresponds to 2θ in the current conventional definition of the XRD angle.

XRD peaks for δ - MoN phase with unidentified hkl index value were speculated by Hägg³⁾ as representing the super-structure lines on account of the ordered N atom configuration over the interstitial sites in the Mo lattice.

For example, by suppressing dissociation of NH_3 gas molecules by flowing condition, $a(\text{N})$ as high as 10^4 might be gained at the extent α of the dissociation 0.2 or 10^3 at $\alpha = 0.5$ at 700°C (the upper threshold temperature for formation of MoN by Hägg³⁾) under normal pressure environment according to the theoretical estimate presented as Fig. 1 in Ref. 6). Such high $a(\text{N})$ could not be realized with any available autoclave using N_2 gas.

Under heating using concentrated solar beam as the heat source, highly reactive C_2 radical plume with high $a(\text{C})$ was reported to yield from graphite.²⁾ Likewise, highly reactive N^+ or N^- with high $a(\text{N})$ might yield from N_2 gas under irradiation with concentrated solar beam to promote nitride formation from Mo and W. To see whether nitride from Mo and W formed or not under the present solar heating test runs undertaken in N_2 gas environment, we calculated XRD peak positions $2\theta_{\text{Cu}}$ with $\text{CuK}\alpha$ radiation for possible nitrides of Mo and W from the reported XRD peak positions Θ_{Cr} with $\text{CrK}\alpha$ radiation in the classical work of Hägg.³⁾ Tables 2 and 3 reproduce the calculation results using wavelength values cited in a classical textbook authored by Cullity.⁹⁾

Table 3 Values of XRD angle $2\theta_{\text{Cu}}$ with $\text{CuK}\alpha$ radiation converted from observed values of $\sin^2(\Theta/2)_{\text{Cr}}$ with $\text{CrK}\alpha$ radiation for mono-nitride WN reported by Hägg.³⁾

<i>hkl</i>	WN	
	$\sin^2(\Theta/2)_{\text{Cr}}$	$2\theta_{\text{Cu}}$
111	0.231	37.74
200	0.310	44.01
220	0.6175	63.86
311	0.847	76.54
222	0.924	80.62

The acquired XRD patterns for the present test pieces showed no evidence of formation of nitride phases from Mo nor W under any condition examined as reviewed in Tables 4 for $\text{M} = \text{Mo}$ and 5 for $\text{M} = \text{W}$. In these two tables, $2\theta_{\text{Cu}}$ values for carbide phase as well as for metals were taken from the monograph compiled by Storms¹⁰⁾ while those for nitride phases were calculated from Hägg's paper³⁾ as summarized in Tables 2 and 3.

Table 4 Detected positions of XRD peak angle $2\theta_{Cu}$ in the range between 30° and 70° for the test pieces with Mo in the runs 06, 13, 24, 27 and 34 compared with literature values of $2\theta_{Cu}$ for binary compounds in Mo-X (X = C or N) systems.

$2\theta_{Cu}$ (degree)	<i>hkl</i>			Run						
	Mo	β -Mo ₂ C	η -MoC _{1-x}	β -Mo ₂ N	δ -MoN	06	13	24	27	34
31.83					001					
34.35		100				34.3	34.5		34.3	34.3
34.93			101							34.8
36.10					100					
36.56			102							36.3
36.83			006							36.8
37.66				111						
37.96		002				37.9	37.9		37.9	
39.15			103							39.0
39.40		101				39.3	39.4			
40.51	110						40.4	40.4		
42.55			104							42.4
43.18				200						
44.98				002						
46.62			105							46.6
48.88					101					
52.12		102				52.0	52.2		52.0	
56.38			107							56.2
58.62	200							58.5		
61.52		110				61.5	61.8		61.6	
61.57			110							61.3
61.93			108							
62.72				220						
64.17				202						
64.98					110					
66.63					002					
67.89			109							
69.54		103				69.4			69.4	
phases identified						β -Mo ₂ C	β -Mo ₂ C (Mo)	Mo	β -Mo ₂ C	η -MoC _{1-x} (β -Mo ₂ C)

Run 13: In phase identification for this test run, Mo was indicated with parentheses to represent that Mo content was trivial in the reaction product because Mo peak $2\theta_{Cu}(110)$ was detectable at around 40.4° but $2\theta_{Cu}(200)$ peak was not detected at around 58.6°.

Run 34: In phase identification for this test run, XRD peaks identifiable as β -Mo₂C were detected for indices, (100) and (110), alone not for indices, (002), (101), (102) and (103), and thence β -Mo₂C content in the reaction product was judged to be very low.

The most remarkable aspect noticed in Table 1 is the results obtained in runs 24 (for Mo) and 25 (for W) under the condition with the inserted Sky blue filter (Group III experiments) showing that the test piece remained as metallic Mo and W, respectively, yielding no carbide in contrast to the carbide formation detected under the absence of the Sky blue filter in the experimental runs started from metallic Mo and W (Group I and Group II experiments).

The evidence obtained in the test runs 24 and 25 suggested that neither carbide nor nitride was synthesized from Mo nor W under the chosen condition. The failed conversion of Mo and W to carbide appeared to ensure that yield of C₂ radical plume with high $a(C)$ was efficiently suppressed by the insertion of the Sky blue filter. On the other hand, failed formation of nitride from Mo or W implied the absence of N-containing species with high $a(N)$ in the gas environment. It is not surprising knowing that the silver-mirror reflector in the solar furnace optical system cuts the UV (ultra-violet) component and the Pyrex glass is opaque to UV. For example, dissociation energy of N₂ gas to yield monatomic N

gas is reported to be $78715 \pm 50 \text{ cm}^{-1}$ ($\approx 130 \text{ nm}$) (page 1600 in Ref. 11)). Indeed, as reproduced in Fig. 1(A), the standard Pyrex glass (Ref.# 7740) cuts considerably the transmission of UV light spectra with the wavelengths shorter than 350 nm. Hence, it was considered unlikely that monatomic N with high $a(N)$ was generated in the present experimental setup.

The reproduced transmittance vs. wavelength curve from the CORNING Catalog made available in the web (<http://www.quartz.com/pxprop.pdf>) is for the Pyrex glass 7440 with thickness 1 mm. Thickness of the Pyrex glass reaction chamber used in the present work was 3 mm and the light transmittance performance of it was anticipated to be not very much different from the one reproduced in Fig. 1(A) for the comparable Pyrex glass of the same quality with 1 mm thickness.

According to information presented by Teixeira,¹²⁾ transmittance of the fluorine glass window used in the present experimental setup was between 90% at the wavelength 250 nm (UV range) and 92% at the wavelength 7000 nm (IR

Table 5 Detected positions of XRD peak angle $2\theta_{Cu}$ in the range between 30° and 70° for the test pieces with W in the runs 04, 14, 25, 28 and 35 compared with literature values of $2\theta_{Cu}$ for binary compounds in W-X (X = C or N) systems.

$2\theta_{Cu}$ (degree)	<i>hkl</i>				Run				
	W	W ₂ C	WC	WN	04	14	25	28	35
31.51			001		31.5	31.6		31.5	31.3
34.61		100			34.4	34.4			
35.64			100		35.6	36.2		35.5	35.3
37.74				111					
38.10		200				37.9			
39.67		101			39.3	39.5			
40.26	110					40.0	40.1		
44.01				200					
48.30			101		48.3			48.3	48.2
52.41		102			52.2	52.2			
58.25	200					58.1	58.2		
62.03		110							
63.86				220					
64.03			110					64.1	64.0
65.78			002					65.6	65.6
69.90		103			69.6				
phases identified					W ₂ C	W, W ₂ C	W	WC	WC
					WC	(WC)			

Run 14: In phase identification for this test run, XRD peaks identifiable as WC were detected for indices, (001) and (100), alone at around $2\theta_{Cu} = 31.6^\circ$ and 36.3° , respectively, but not for indices, (101), (110) and (002), and thence WC content in the reaction product was judged to be very low and thus WC was presented in the parentheses.

range) and, outside this transparency range, transmittance would drop rapidly towards zero. At one of the pyrometer monitoring wavelengths, $5\ \mu\text{m}$ ($= 5000\ \text{nm}$), transmittance of the light through the fluorine glass window under the present setting was determined to be 92% in the preliminary experiment.

Thus, if we manage to arrange reaction chamber made of a material transparent to UV light (e.g. quartz glass) and reflector material with diminished UV component loss allowing yield of N radical species with high $a(\text{N})$, nitriding of *d*-group transition metals might be feasible in a solar furnace even at comparatively high temperatures exceeding 700°C .

Looking at Table 1, there are other features noticeable in the solar furnace experiments for Mo and W.

For instance, even in cases of carbide formation from M, $\Delta w/w_i$ was negative (except in the run 04) implying the mass loss during the solar heating. This mass loss must have arisen from sublimation loss of M during the solar heating process. In fact, deposition of pale blue powder substance was detected over cooler component surface in the reactor after the run 25. It is interesting to note that the detected specific mass loss $\Delta w/w_i$ was less than a single digit % order in the test runs started from M while that in the test runs started from 1.5G/M was a single digit % order.

Regarding Δp ($= p_f - p_i$), the measured values for Δp was all positive suggesting that release of some adsorbed gaseous species over M or G in the starting material was inevitable during the solar heating experiments.

In the Group I (with the graphite lid) and the Group II (without the graphite lid) experiments started from M, sub-carbides, $\beta\text{-Mo}_2\text{C}$ and W_2C , were synthesized from Mo and

W, respectively. Mono-carbide WC was co-existed with W_2C in the reaction product synthesized in the Group I experiment (Run 04). In the Group II experiments, metallic Mo and W coexisted with the sub-carbide phases while M was fully consumed for the carbide synthesis in the Group I experiments. These evidences appear to suggest that carburizing power of the C_2 radical was higher in the Group I experiments than in the Group II experiments because the test piece in the Group I experiment was exposed to saturated C_2 radical environment because the crucible space was loosely sealed with graphite lid whereas C_2 radicals generated from the crucible dissipated to greater volume of the Pyrex glass reactor in the Group II experiment.

In the Group III experiments undertaken with the Sky blue filter, conversion to carbide was perfectly inhibited for M but mono-carbide WC was synthesized from 1.5G/W while the carbide synthesized from 1.5G/Mo was sub-carbide (Tables 1, 4 and 5).

In the present set of experiments, $\eta\text{-MoC}_{1-x}$ was synthesized only from 1.5G/Mo in the Group IV experiment with the Medium yellow filter. For the moment, we have no clear-cut explanation for this.

To compare surface morphologies of the synthesized phases in the present work, Fig. 4 summarizes typical SEM (scanning electron microscope) appearances at the same magnification.

Figure 4(a) shows the metallic Mo surface obtained after the run 24 while Fig. 4(e) the metallic W surface after the run 25. They both show that the initial smooth grain morphology of the metallic starting materials were retained.

On the other hand, certain extent of morphological modifications was detected in Fig. 4(b) for Mo and Fig. 4(f)

Fig. 4 Typical SEM appearances of the test piece top surface. (a) Mo/run 24/Sky blue filter, (b) Mo+1.5G/run 27/Sky blue filter, (c) Mo/run 13/no filter, (d) Mo+1.5G/run 34/Medium yellow filter; (e) W/run 25/Sky blue filter, (f) W+1.5G/run 28/Sky blue filter, (g) W/run 14/no filter, (h) W+1.5G/run 35/Medium yellow filter.

for W representing the conversion of M to single-phase carbide products started from 1.5G/M. Both showed dramatic morphological alteration on account of conversion of M to carbide phases under presence of solid G in tight contact.

Figures 4(c) and (g) show the M_2C -M dual-phase specimens obtained in the Group II experiments started from Mo or W, respectively, whose appearances look clearly distinguishable from single-phase specimens, Figs. 4(b) and (f).

Figures 4(d) and (h) show the morphologies of the 1.5G/M specimens after the Group IV experiments with Medium yellow filter for M = Mo and W, respectively. Appearance of WC single-phase specimen synthesized with the Medium yellow filter (Fig. 4(h)) looks comparable to that synthesized

with the Sky blue filter (Fig. 4(f)). On the other hand, that of β - Mo_2C - η - MoC_{1-x} dual-phase specimen synthesized with the Medium yellow filter (Fig. 4(d)) looks different from that of β - Mo_2C single-phase specimen synthesized with the Sky blue filter (Fig. 4(b)) implying that the $a(C)$ in the environment did indeed play a significant role in the concerned process.

4. Conclusions

Phases synthesized from M or 1.5G/M starting material in N_2 gas environment heated to 2000°C by concentrated solar beam with or without colour filter were characterized by XRD and by supplemental SEM inspection and following conclusions were drawn:

(1) Insertion of Sky blue filter in the solar beam path was effective to suppress yield of C_2 radical plume from the graphite crucible to result in inhibition of carbide formation from Mo and W in the standard experimental setting of solar furnace using graphite crucible as the sample holder.

(2) Synthesis of nitride was not achieved for neither Mo nor W under the present condition using Pyrex glass reaction chamber and silver-mirror reflector because both cut considerably the UV range wave.

(3) Effect of inserting Medium yellow filter was not very clear but η - MoC_{1-x} formation was detected only under the solar irradiation with the Medium yellow filter (Run 34; Table 1) and thence it might be favourable to insert Medium yellow filter for promotion of synthesis of higher carbide of *d*-group transition element although this aspect must be confirmed by further experimental verification.

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