

Carbide Synthesis from Graphite/molybdenum Powder Mixtures at Sub-Stoichiometric Ratios under Solar Radiation Heating to 1900°C

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A solar furnace at PROMES-CNRS in Odeillo (France) is with very unique capacity of heating the specimen material from ambient temperature to a target temperature exceeding 2000°C within fractions of a second in arbitrary gas environment with pressure no higher than 1 atm. In the preceding work on the Mo-C synthesis using this solar furnace with the set target temperature 1600°C, evidence of formation of η -MoC_{1-x} besides α -Mo₂C (the low temperature phase of Mo₂C) was confirmed under presence of excess free carbon (graphite). The η -MoC_{1-x} is known to be stable at temperatures between 1650°C and 2500°C with range of x between 0.25 and 0.35. Thus, in the present work, carbide synthesis experiments were carried out for compacted powder mixtures between graphite and molybdenum at C/Mo mole ratios, 2/3 and 3/4, as well as the ratios, 1/2 and 1/1, as the references in the solar furnace at Odeillo under application of the ultra-fast heating rate to the set target temperature 1900°C in search of favourable processing condition for η -MoC_{1-x} synthesis. The gained experimental evidences indicated that, at any chosen C/Mo ratio in the starting powder compact, formation of β -Mo₂C (the high temperature phase of Mo₂C) took place preferentially while certain proportion of the η -MoC_{1-x} formed besides the β -Mo₂C from the powder compacts with C/Mo mole ratios, 2/3 and 3/4.

[doi:10.2320/matertrans.MRA2008202]

(Received July 2, 2008; Accepted August 13, 2008; Published October 16, 2008)

Keywords: molybdenum carbides, non-stoichiometry, solar furnace, ultra-fast heating

1. Introduction

Equilibrium phase relationship for binary Mo-C system was thoroughly investigated by Rudy *et al.*¹⁾ in the late 1960s which was largely in accordance with the one compiled by Storms²⁾ except in some designations for the phases. For example, the high temperature phase of hypo-stoichiometric mono-carbide phase designated as β -MoC_{1-x} by Storms was re-designated as α -MoC_{1-x} by Rudy *et al.* and the designation by Rudy *et al.* is now widely accepted by the worldwide refractory carbide research community. Likewise, the low temperature phase of hypo-stoichiometric mono-carbide phase designated initially as α -MoC_{1-x} was later re-designated as η -MoC_{1-x} by Rudy *et al.* and now it is known as η -MoC_{1-x}. There is anyway no such changes in nomenclature for the sub-carbide phase; β -Mo₂C for the high temperature phase and α -Mo₂C for the low temperature phase.

Table 1 lists the peak positions, 2θ , of XRD (X-ray diffraction) with CuK α radiation for all the possible phases in Mo-C binary system between $2\theta = 25^\circ$ and $2\theta = 43^\circ$. In Table 1, 2θ values for the respective phases are taken from the Tables summarised in the monograph by Storms²⁾ but using the phase designations defined by Rudy *et al.*¹⁾

In the recent work of Mo carbide synthesis using the solar furnace at PROMES-CNRS in Odeillo, compacted pellet consisting of Mo powders mixed with excess proportion of graphite powders (C/Mo mole ratio 1.5/1) was used as the starting material.³⁾ The target temperature at the top surface in this earlier experiment was set to be 1600°C by locating the top surface of the pellet by a few cm down from the exact

focal point of the parabolic concentrator mirror. The solar furnace at PROMES-CNRS is characterised by its special capacity of realising ultra-fast heating rate at the onset of heating from ambient temperature to a specified target temperature. On account of this solar beam alignment, certain extent of temperature gradient along the pellet thickness was detected to arise (50–100 K along the 5–10 mm thickness of the pellet from the hotter top to the cooler bottom).

Several intriguing aspects were found in this Mo carbide synthesis work (cf. Fig. 2 in Ref. 3));

(1) In spite of the set target temperature 1600°C where the phase diagram suggests the co-existence β -Mo₂C (high temperature Mo₂C phase stable between 1430°C and 2520°C) under the equilibrium condition, the detected phases by the XRD analysis were α -Mo₂C (low temperature Mo₂C phase stable below 1430°C) and η -MoC_{1-x} (mono-carbide phase with the lower-C range stable between 1655°C and 2550°C) co-existing with residual un-reacted graphite after 90 min holding at 1600°C.

(2) Additional heating to a temperature exceeding 2500°C at the exact focal point for 10 min applied to this test piece promoted conversion of the carbide to η -MoC_{1-x} but with detectable remain of α -Mo₂C showing no evidence of formation of α -MoC_{1-x} (mono-carbide phase with the higher-C range stable between 1960°C and 2550°C) in spite of the presence of excess free carbon (graphite).

These observed deviations of the reaction products in the Mo-C samples synthesised under irradiation with the concentrated solar beam with the initial application of ultra-fast heating rate from the phases anticipated to be synthesised with reference to the equilibrium phase relationship were interpreted in terms of similarity in energy states for Mo carbide phases with different stoichiometry demonstrated by

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Table 1 Possible XRD peak positions with $\text{CuK}\alpha$ radiation for the Mo-C specimens in the range of 2θ between 25° and 43° . Reproduced from Tables summarised by Storms.²⁾ Stability temperature range information for each phase as well as the MoC_{1-x} phase designation was taken from Rudy *et al.*¹⁾

peak	2θ ($^\circ$)	<i>hkl</i>					
		graphite	Mo	$\alpha\text{-MoC}_{1-x}$ ^{*1}	$\eta\text{-MoC}_{1-x}$ ^{*2}	$\beta\text{-Mo}_2\text{C}$ ^{*3}	$\alpha\text{-Mo}_2\text{C}$ ^{*4}
0	26.40	002					
1	34.32						021
2	34.35					100	
3	34.43						002
4	34.93				101		
5	36.32			111			
6	36.56				102		
7	36.83				006		
8	37.90						200
9	37.96					002	
10	39.15				103		
11	39.38						121
12	39.40					101	
13	39.48						102
14	40.51		110				
15	42.18			200			
16	42.55				104		

^{*1} $\beta\text{-MoC}_{1-x}$ according to the designation by Storms. Stability temperature range: $2600 (\pm 5) \sim 1960 (\pm 20)^\circ\text{C}$.

^{*2} $\alpha\text{-MoC}_{1-x}$ according to the designation by Storms. Stability temperature range: $2550 (\pm 5) \sim 1655 (\pm 15)^\circ\text{C}$.

^{*3}Stability temperature range: $2522 (\pm 5) \sim 1190 (\pm 20)^\circ\text{C}$.

^{*4}Stability temperature range: $1430 (\pm 10)^\circ\text{C} \sim \text{ambient temperature}$.

the first-principle electronic calculation by Hugosson and co-workers.⁴⁻⁶⁾ They argue that, on account of this similarity in electronic energy states among different carbide phases of Mo, a certain Mo carbide phase might be prepared by slight modifications of synthesis conditions. For example, Hugosson and his colleagues⁷⁾ at Uppsala University conducted experiment to synthesise mono-carbide phase of Mo at 800°C by CVD (chemical vapour deposition) process using $\text{MoCl}_3/\text{H}_2/\text{C}_2\text{H}_4$ as the reactant gas mixture. They managed to synthesize MoC co-existing with Mo_2C by this experiment whereas MoC was not registered as a stable mono-carbide phase for Mo-C system at temperatures lower than 1200°C .^{1,2)}

Keeping in mind these available evidences, we investigated formability of $\eta\text{-MoC}_{1-x}$ phase under solar heating to the target temperature 1900°C with the initial application of ultra-fast heating rate using compacted powder mixtures of Mo and graphite at C/Mo mole ratios, 1/2, 2/3, 3/4 and 1/1, as the starting materials.

2. Experimental

The experimental setup used to perform the synthesis experiments in the solar furnace at PROMES-CNRS was described in detail elsewhere.^{3,8-11)} The compacted pellets of Mo and graphite powder mixture (C/Mo atom ratio was set to 1/2, 3/4, 2/3 and 1/1 to ensure full coverage of compositional range of interest) with diameter 8 mm and height 5 mm were uni-axially pressed at 400 MPa. Mo powder (99.9% pure, mean grain size: $2\text{ }\mu\text{m}$) was supplied from Goodfellow

(Cambridge, England) and graphite powder ($< 50\text{ }\mu\text{m}$) from E. Merck AG (Darmstadt, Germany). The consolidated pellet specimen was placed in a specially designed crucible for the exposure to the concentrated solar beam. The reaction chamber (Pyrex glass; 5 l capacity) was flushed twice with inert Ar gas with grade U (nominal purity 99.999% with O_2 no higher than 5 ppm and H_2O also no higher than 5 ppm) before being filled with 460 Pa Ar gas at the ambient temperature. It should be noted that the PROMES-CNRS facilities lies about 1500 m from the sea level and the atmospheric pressure is normally *ca.* 850 Pa.

Like in the earlier experimental works performed at PROMES-CNRS,^{3,8-11)} the sample holder was brought into the hot spot of the solar furnace by sliding the reaction chamber over a pair of guiding rails. Within fractions of a second, the specimen temperature rose from the ambient temperature to the target temperature (1900°C).

The radiation temperature of the specimen material was measured through the triple vertical slits of width 1 mm cut in the graphite crucible using an optical pyrometer (Model 95 of Pyrometric Instrument Company, Inc., Bergenfield, N.J., USA) through a view window from the side of the Pyrex glass reaction chamber. Although the surface temperature of the specimen might have reached temperatures slightly in excess of 1900°C by natural fluctuation of solar flux, the temperature across the specimen height was kept within the range $1900 \pm 50^\circ\text{C}$ over the entire exposure period. Therefore, we refer to these results as the ones obtained at the reaction temperature 1900°C for the sake of convenience.

After 30 min holding at 1900°C, the sample holder was taken away from the hot spot of the solar furnace and the specimen material was cooled down under flowing Ar gas. After about 30 min, the Pyrex glass reaction chamber was opened to take out the specimen cooled down near ambient temperature. Then, the specimens were characterized by means of X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).

Phase identification and their relative intensities were ascertained by XRD using a Geigerflex D/MAX IIIC diffractometer (Rigaku Internat. Corp., Japan) and $\text{CuK}\alpha$ radiation. For this purpose, as-synthesized specimens were stuck to a glass sheet surface and scanned over a range 2θ from 5° to 150°, at a scanning speed of $2^\circ 2\theta \cdot \text{min}^{-1}$.

The morphology of the specimens synthesized at 1900°C were observed on a Field Emission Philips XL 30 FEG scanning electron microscope using secondary electron beams at 10 to 15 kV.

The XRD characterization and the SEM surface inspection were made for the top and the bottom surfaces of each specimen.

3. Results and Discussion

The results of the present work are summarised in Figs. 1–3. As pointed out above in the text, both the XRD characterisation and the SEM surface inspection were made for the top and the bottom surfaces of the respective test pieces.

Individual top and bottom surface characterisations of the pellet specimens were carried out noting the acquired evidences during the course of the solar carbide synthesis works for W-C system^{8–10)} indicating clearly that the top surface layer must be treated as the special singular zone being distinguished from the rest of the pellet bulk including the bottom surface. This must be ascribable to the inherent characteristic of the heating with concentrated solar beam. That is, in the experimental setup in the PROMES-CNRS solar furnace at Odeillo, the pellet top surface is exposed to the concentrated solar beam and heated very rapidly and the heat is then transferred downwardly through the compacted C/Mo mixture.

As a matter of fact, in the case of W-C system, formation of nano-meter scale WC whiskers was detected over compacted pellet with C/W mole ratio as low as 0.35 in the solar heating experiment with the target temperature 1900°C while the bulk composition of this specimen was W_2C .^{9,10)}

As the Mo-C pellets heated to 1900°C were tightly sintered together, compared with their counterparts heated to 1600°C, they were difficult to be crushed into powders for characterisation by powder XRD and thence the top and the bottom surfaces of the as-synthesised pellets were analysed individually by XRD. The bottom surface was considered to represent the bulk composition of the specimen excluding the thin top layer.

Among the XRD patterns exhibited in Fig. 1, the simplest one is the XRD pattern for the top surface of the C/Mo = 1/2 specimen which consisted solely of $\beta\text{-Mo}_2\text{C}$ (high-temperature Mo_2C phase) yielding 3 peaks, (100) at $2\theta = 34.4^\circ$, (002) at $2\theta = 38.0^\circ$ and (101) at $2\theta = 39.4^\circ$,

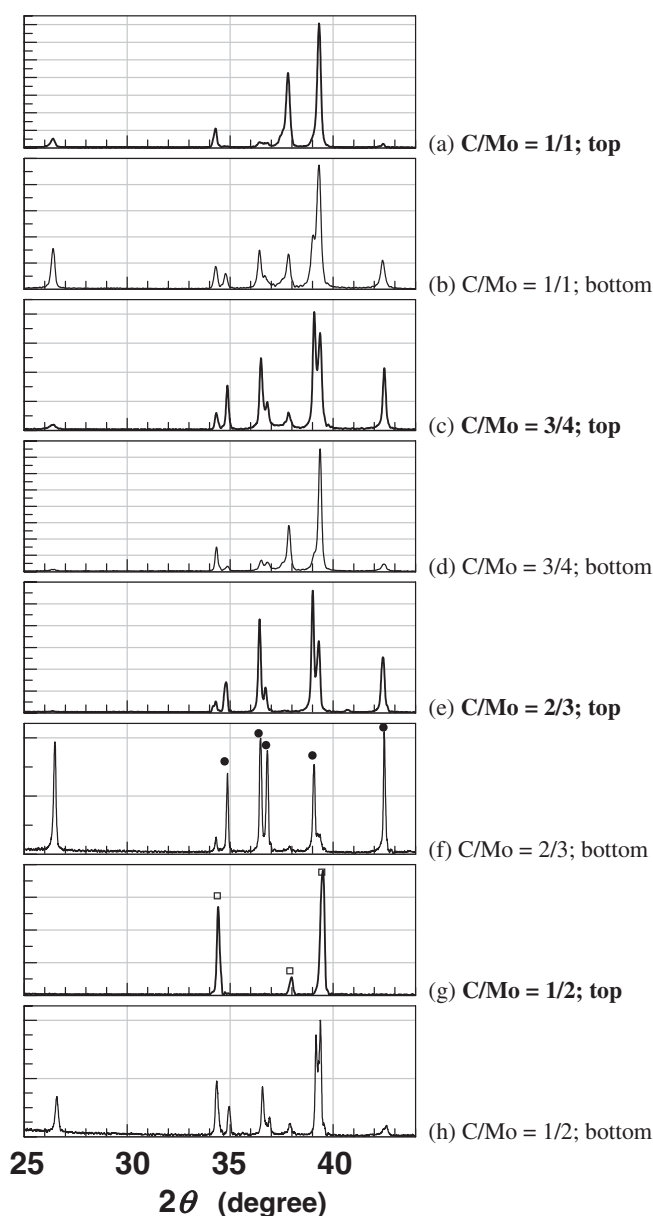


Fig. 1 The XRD patterns ($\text{Cu K}\alpha$) of the top and the bottom surfaces of the pellets of graphite/molybdenum powder mixtures with C/Mo mole ratios, 1/1, 3/4, 2/3 and 1/2, heated to 1900°C in the solar furnace with the initial ultra-fast heating rate. (●) $\eta\text{-MoC}_{1-x}$ (□) $\beta\text{-Mo}_2\text{C}$.

in the presented range of $2\theta = 25\text{--}43^\circ$. Even graphite peak at $2\theta = 26.4^\circ$ is not detected for the top surface of this C/Mo = 1/2 specimen implying the full consumption of graphite mixed with Mo powders for the conversion of Mo to Mo_2C at the top surface layer.

Correspondingly, SEM top surface appearances of the C/Mo = 1/2 specimen (Fig. 2(g)–(l)) are quite homogeneous. The Figure 2(g) (C/Mo = 1/2 top surface image) shows surface cracks while the right-most image shows the dendrite-like surface pattern. Both these evidences are considered to represent that the surface layer was once melted during the heating and cooled very rapidly after ceasing the solar beam radiation. The target temperature 1900°C was definitely too low to yield any type of liquid phase for the Mo-C binary mixture but, judging from these top surface appearances of the C/Mo = 1/2 specimen, the

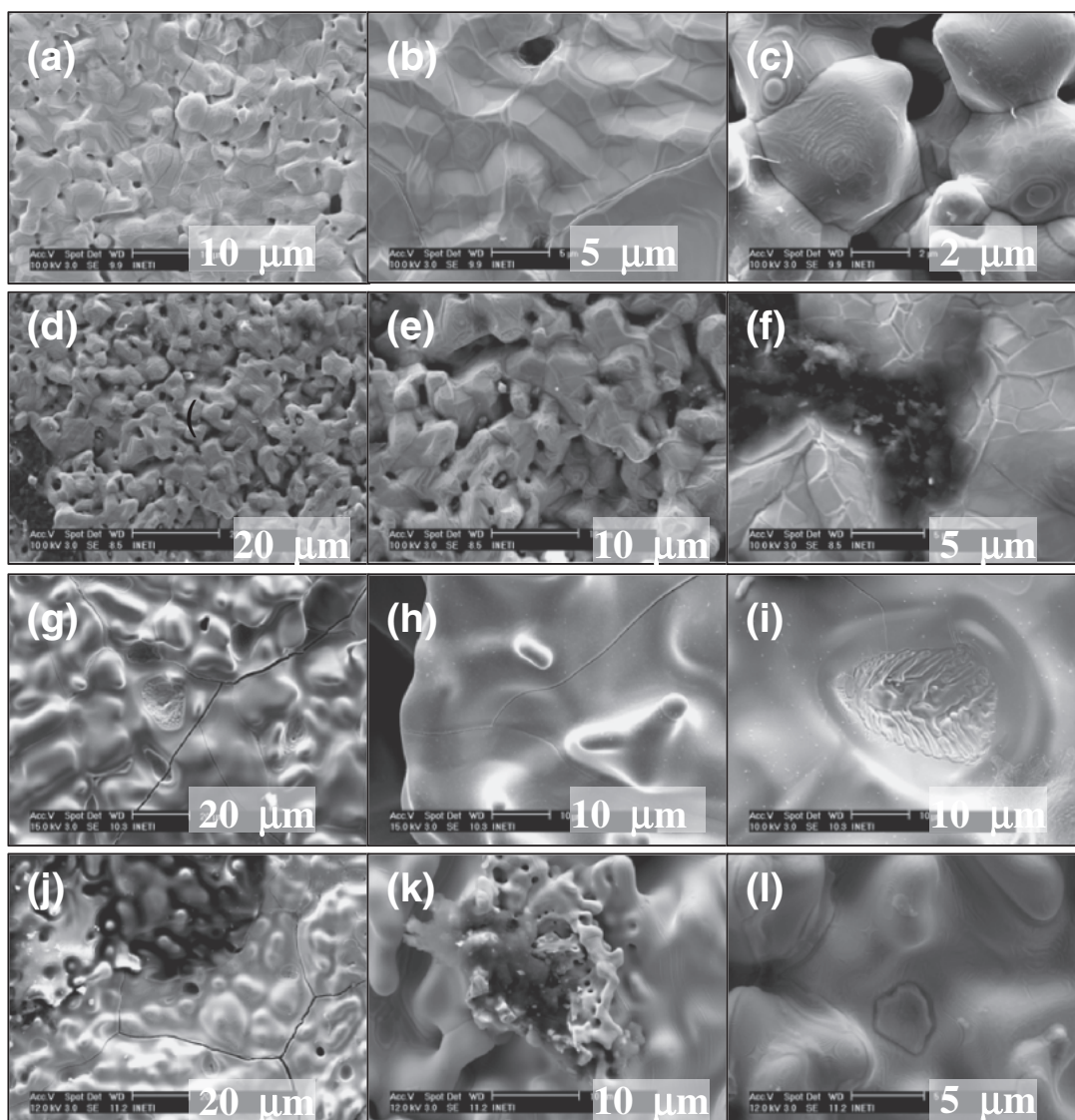


Fig. 2 SEM appearances of the top and the bottom surfaces of the C/Mo = 1/1 and 1/2 specimens. (a)–(c): C/Mo = 1/1 top, (d)–(f): C/Mo = 1/1 bottom, (g)–(i): C/Mo = 1/2 top, (j)–(l): C/Mo = 1/2 bottom.

surface layer must have been melted without doubt as the consequence of large reaction heat evolved on formation of Mo_2C from Mo and graphite at the onset of the reaction.

Among XRD patterns summarised in Fig. 1, the one for the top surface of the C/Mo = 1/1 specimen looks the most alike to the one for the top surface of the C/Mo = 1/2 specimen showing evidence of formation of small proportion of the $\eta\text{-MoC}_{1-x}$ phase besides the principal phase $\beta\text{-Mo}_2\text{C}$. The residual XRD peak at $2\theta = 26.4^\circ$ referring to the presence of graphite at the top surface is understandable noting that principal phase formed from the C/Mo = 1/1 pellet was $\beta\text{-Mo}_2\text{C}$ rather than $\eta\text{-MoC}_{1-x}$ at the top surface. Anyway, the appearance of the top surface of the C/Mo = 1/1 specimen was quite different from that of the top surface of the C/Mo = 1/2 specimen probably on account of the additional formation of $\eta\text{-MoC}_{1-x}$ besides $\beta\text{-Mo}_2\text{C}$ over the C/Mo = 1/1 specimen top surface. The central image (Fig. 2(b)) among the 3 SEM micrographs of the top surface of the C/Mo = 1/1 specimen shows rather edgy contour unlike smooth wavy surface profile of the C/Mo = 1/2 specimen (Fig. 2(g)–(l)).

It is interesting to note that the higher proportion of the $\eta\text{-MoC}_{1-x}$ phase was present beside $\beta\text{-Mo}_2\text{C}$ at the bottom surface of the specimens with C/Mo ratios, 1/2 and 1/1, than at the top surface of these specimens. The similar situation was detected for the W-C system under condition of presence of excess free carbon in the solar processing to the target temperature 1600°C (holding at this temperature for 30 min).⁸⁾ As shown in Fig. 3 in Ref. 8), the bottom surface of the C/W = 2/1 specimen (in this earlier experiment, carbon source was amorphous carbon rather than graphite) was fully converted to mono-carbide WC whereas the top surface was consisted of WC and of co-existed W_2C . It was also shown in the earlier work⁸⁾ that the once-formed W_2C resisted to be converted to WC even by heating to a temperature exceeding 2500°C under presence of excess free carbon.

For the test pieces with the C/Mo ratios, 2/3 and 3/4, formation of $\eta\text{-MoC}_{1-x}$ phase appeared to be promoted besides the $\beta\text{-Mo}_2\text{C}$ phase. No evidence of formation of $\alpha\text{-MoC}_{1-x}$ (high temperature MoC_{1-x} phase reported to be stable between 1960°C and 2600°C) was detected for any

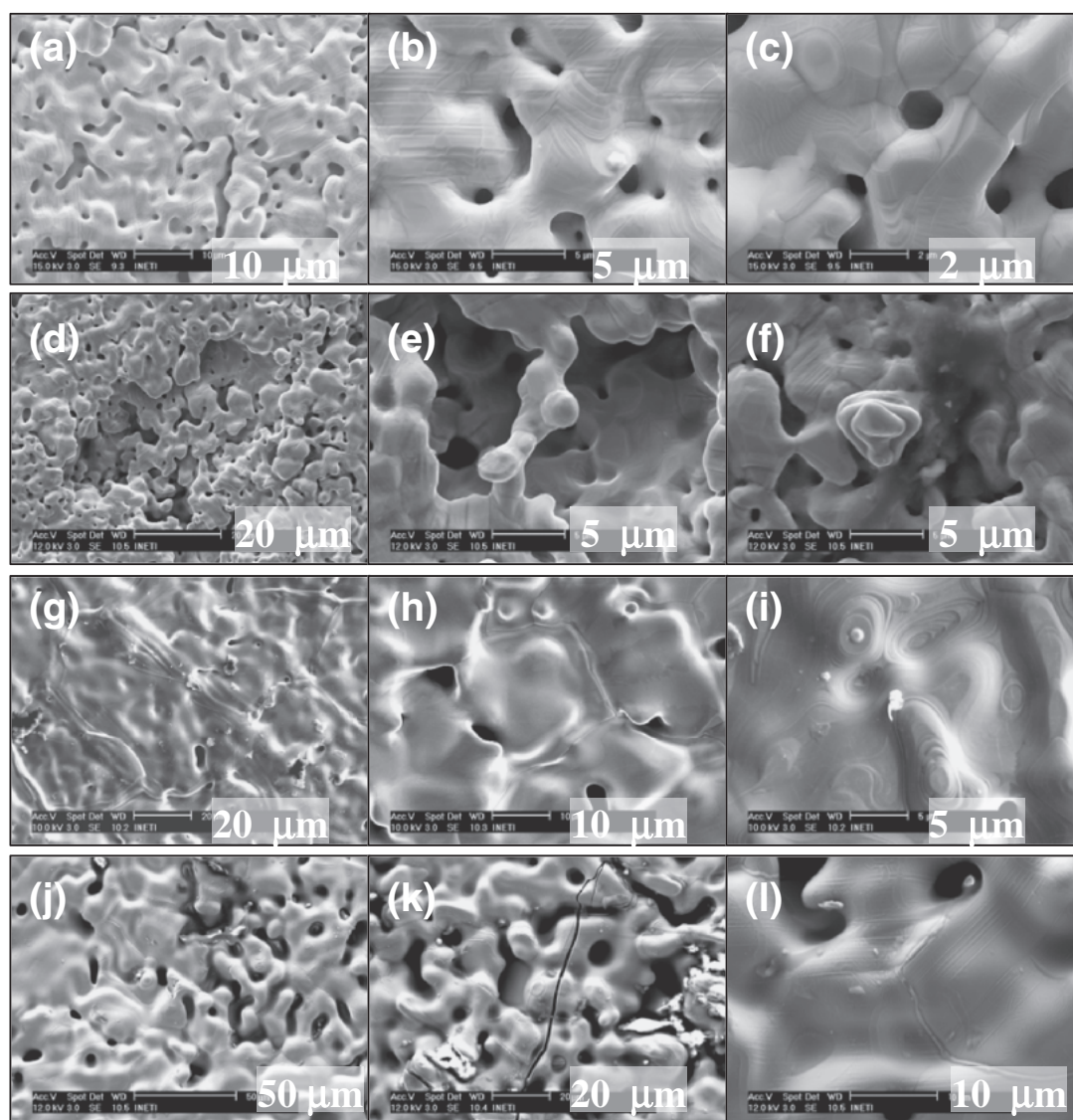


Fig. 3 SEM appearances of the top and the bottom surfaces of the C/Mo = 3/4 and 2/3 specimens. (a)–(c): C/Mo = 3/4 top, (d)–(f): C/Mo = 3/4 bottom, (g)–(i): C/Mo = 2/3 top, (j)–(l): C/Mo = 2/3 bottom.

examined specimen in this work while there was a bit of hope that α - MoC_{1-x} would form from the test piece with C/Mo = 3/4 while η - MoC_{1-x} would yield from the test piece with C/Mo = 2/3 by the solar processing experiment with the target temperature 1900°C.

Anyway, it is intriguing to note that the top and the bottom surface appearances of the C/Mo = 3/4 specimen (Fig. 3(a)–(f)) were similar to those of the C/Mo = 1/1 specimen (Fig. 2(a)–(f)) while those of the C/Mo = 2/3 specimen (Fig. 3(g)–(l)) to those of the C/Mo = 1/2 specimen (Fig. 2(g)–(l)) in spite of distinction in XRD patterns between the respective pairs.

For any test piece with a given C/Mo ratio, relative intensity of XRD peak for graphite (002) at $2\theta = 26.4^\circ$ for the bottom was higher than that for the top surface. This might be largely due to the fact that the extent of the carburisation reaction was more advanced for the top surface at the higher temperature than for the bottom surface at the slightly lower temperature. Anyway, we cannot rule out the possibility that this difference in XRD peak intensity for the

graphite (002) peak between the top and the bottom surfaces for some given specimen might arise from pick-up of graphite from the graphite crucible in contact with the specimen bottom surface.

For the synthesis of carbide starting from compacted powder mixture of carbon (either graphite or amorphous carbon) and metal M by solar beam heating with the very high initial heating rate, it appears that the lower carbide tends to form preferentially in the M-C system in which more than one carbide phases are known to exist.

For example, during the course of the earlier solar synthesis experiment for TaC under presence of excess free carbon with the set target temperature 1600°C, formation of sub-carbide Ta_2C preceded the eventual formation of mono-carbide TaC.¹¹⁾ For the Va-group metals including V, Nb and Ta, sub-carbide M_2C is known to exist besides mono-carbide MC.²⁾ In case of Ta-C system, thermodynamic stability of Ta_2C must have been appreciably lower than that of TaC and thence, with the extended reaction duration from 30 min to 90 min under co-presence of free carbon, once-formed Ta_2C

was fully converted to TaC whereas once-formed W_2C insisted to remain even after prolonged solar heating duration under presence of excess free carbon.⁸⁾

As demonstrated in the first-principle electronic calculation results presented by Hugosson and co-workers,⁴⁻⁶⁾ electronic states of different carbide phases of VIa-group metals, Mo and W, are comparable to one another and thence, when one type of lower carbide is formed preferentially in the initial stage of the solar carbide synthesis, it would not be converted easily to the genuine stable phase in the later stage of the reaction. On the other hand, thermodynamic stability of sub-carbide M_2C phase of Va-group metal (V, Nb and Ta) must be by far lower than that of mono-carbide MC and accordingly M_2C was readily converted fully to MC.

It is also interesting to note that, in the present experiment with the target temperature 1900°C, the formed sub-carbide phase was β - Mo_2C (the high temperature phase reported to be stable in the range between 1430°C and 2510°C¹⁾) whereas the α - Mo_2C phase (the Mo_2C phase reported to be stable up to 1430°C¹⁾) formed in the earlier work with the target temperature 1600°C. These evidences appeared to indicate that the Mo_2C formation reaction in the earlier solar irradiation experiment with the target temperature 1600°C took place at a temperature lower than 1430°C while, in the present work with the target temperature 1900°C, the Mo_2C formation reaction took place at a temperature higher than 1430°C. As such, these evidences seem to imply significance of rate of heating for C/M mixture to a certain temperature level in forming some target reaction product for a M-C system in which a number of lower carbide phases exist.

4. Conclusions

Solar carbide synthesis with the target temperature 1900°C was undertaken in the solar furnace at PROMES-CRNS in Odeillo for compacted powder mixtures consisting of graphite and Mo powders at four different C/Mo mole ratios, 1/2, 2/3, 3/4 and 1/1 and following conclusions were drawn.

(1) Constitution of the top and that of the bottom surface of any given pellet were distinguishable reflecting differences in the initial heating rate at the onset of the solar beam radiation and also in the steady state temperature during 30 min holding between the top and the bottom surface.

(2) The top surface of the C/Mo = 1/2 specimen alone was identified to be single-phase β - Mo_2C (high temperature Mo_2C phase) while all the other specimen surfaces were with co-existent η - MoC_{1-x} phase besides the β - Mo_2C .

(3) The yield of η - MoC_{1-x} appeared to be stimulated for the specimens with the C/Mo mole ratios set at 2/3 (close to the composition of the η - MoC_{1-x}) as well at 3/4 (close to the composition of the α - MoC_{1-x}) while yield of the β - Mo_2C_{1-x} was comparatively high for the specimen with the C/Mo mole ratio set at 1/1 as well for the specimen with the C/Mo = 1/2.

Acknowledgement

The authors would like to thank Mrs. Teresa Marcelo in INETI for her dedicated assistance in acquiring SEM surface pictures.

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